Method For Identification And Quantitation Of Sub-Parts-Per Billion Levels Of Semi-Volatile Organic Contaminants In UPW

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Abstract

A new method was developed for identification and quantitation of parts-per-billion or less levels of semivolatile organic compounds (e.g., dioctyl phthalate, siloxanes, and hydrocarbons) in ultrapure water (UPW). The technique used was thermal desorption - gas chromatography - mass spectrometry (TD-GC-MS). This is a unique technique and does not use organic solvent for extraction of organic compounds from UPW, making it more environmentally friendly. The UPW at selected semiconductor and disk-drive locations was tested and the most common contaminant was found to be dioctyl or higher alkyl phthalates at 0.1 ppbw or less levels.

Introduction

Organic contamination on wafer surfaces can seriously deteriorate wafer cleaning efficiency.[1-4] This leads to non-uniform etching and cleaning of wafer surfaces. The carbon-rich hydrophobic surfaces are known to affect gate oxide growth rates and reliability.[5-7] One source of these contaminants is believed to be ultrapure water (UPW). Organic contamination in UPW is usually monitored as total oxidizable carbon (TOC) which provides excellent sensitivity, but cannot identify the organic contaminants.[8] EPA 502.2 and 524.2 purge & trap methods can identify volatile organic contaminants only (e.g., chloroform and other trihalomethanes, low-boiling organic solvents, etc.).[9,10] EPA method 525.2 provides a

procedure for determination of a variety of organic compounds in water using liquid-solid extraction and then elution with organic solvents.[11] But these methods do not identify and quantitate <1 part-per-billion by weight (ppbw) levels of some semi-volatile organic compounds in UPW, e.g., siloxanes and plasticizers such as dioctyl phthalate & TXIB (2,2,4-trimethyl-1,3-pentanediol diisobutryate).

This paper discusses the results of a method which can provide sub-ppbw level detection, identification and quantitation of semi-volatile organic contamination in UPW. The technique used was TD-GC-MS (Thermal Desorption - Gas Chromatography - Mass Spectrometry). At 0.2 ppbw levels, C16-C28 n-alkanes (hydrocarbons) had >80% recovery, plasticizers (e.g., dioctyl phthalate and TXIB) had > 50% recovery, a siloxane (cyclo(Me$_2$SiO)$_5$) had >70% recovery. Contaminants found in water at disk-drive and semiconductor manufacturing facilities are presented. Some locations had detectable amounts of dioctyl or higher phthalates in final filter water. This method may help the process engineer find the sources of contaminants and improve product yield.

Experimental

The UPW was collected in organic-free glass bottles cleaned to EPA specifications. Typically, one liter UPW was passed through a stainless steel sampling tube containing adsorbent. This adsorbent traps semi-volatile organic contaminants such as phthalates from plasticizers, silicones from lubricants or sealants, hydrocarbons from oils, etc. The sampling tubes were analyzed by a TD-GC-MS method. A Perkin-Elmer ATD-400 automated thermal desorption system connected to a HP 6890 GC (Gas Chromatograph) with a HP 5972 or 5973 quadrapole MSD (Mass Selective Detector) was used for the analysis. The sampling tubes were heated in the ATD-400. As organic compounds were thermally desorbed from the sampling tube, they were swept by the helium carrier gas onto a cold trap containing a proprietary adsorbent. The organic compounds were desorbed from the trap and then passed onto the GC-MS system. Each compound passed down the GC column at a characteristic rate. As each compound exited the gas chromatograph, it entered the MSD where it was ionized using electron impact ionization (70 eV). The MSD collected a full mass spectrum

(10-700 amu) approximately once per second. Identification of each compound detected was first attempted by searching a Wiley library of 275,000 mass spectra. In cases where no matches were found, mass spectra were interpreted by the analyst to give our best estimate of the most probable compound or class of compounds.

The amounts of organic contaminants in UPW 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.

Results And Discussion

Method Development:

Effect of flow rate on the recovery of C7-C28 n-alkane (hydrocarbon):

A stock solution of selected n-alkanes (with number of carbons = 7, 8, 9, 10, 11, 12, 13, 14, 16, 18, 20, 24 or 28) was prepared in pentane. A portion of this solution was used to spike 1000 nanograms of each of the C7-C28 n-alkanes hydrocarbons into one liter of UPW contained in a glass bottle, yielding a 1 ppbw aqueous standard. The bottle had approximately 2 mL of headspace to facilitate mixing. The contents were thoroughly mixed, then 250-mL portions were passed through four sampling tubes at variable pump speeds of 10, 21, 30 and 43 mL per minute. The results are summarized in Table 1 and are plotted in Figure 1. The recovery was affected only slightly by the pump speed at flow rates of 20 - 43 mL per minute. The pump speed of 10 mL per minute gave the poorest recovery. We decided to use 30 mL per minute flow rate for all other experiments reported in this paper.

Table 1: Effect of flow rate on the % recoveries of 1 ppbw of C7-C28 n-alkanes. The amounts of alkanes were estimated using the responses of the individual C7-C28 alkane external standards.

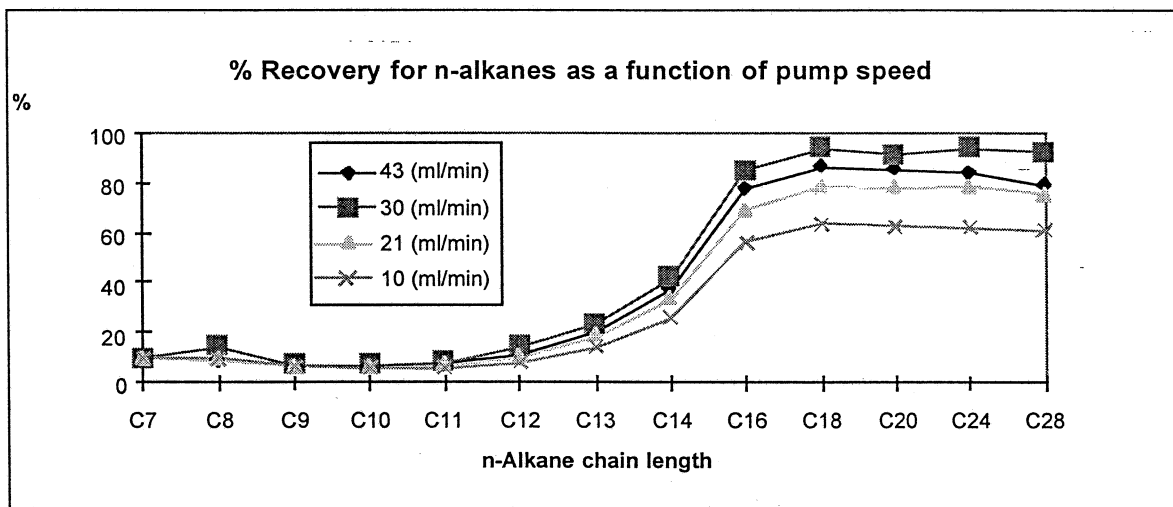| Pump speed	43 (ml/min)	30 (ml/min)	21 (ml/min)	10 (ml/min)
C7-alkane	10	10	10	10
C8-alkane	8	14	9	10
C9-alkane	7	7	6	6
C10-alkane	6	7	6	6
C11-alkane	7	8	7	6
C12-alkane	11	14	10	8
C13-alkane	20	23	18	14
C14-alkane	37	42	33	26
C16-alkane	77	85	69	56
C18-alkane	86	94	78	64
C20-alkane	85	91	78	62
C24-alkane	84	94	78	62
C28-alkane	79	92	75	61

Figure 1. Effect of pump speed (flow rate) on the % recoveries of 1 ppbw of C7-C28 n-alkane standards spiked in one liter of UPW.

Stability Of n-Alkanes In UPW Stored In Glass Bottles:

Three different glass bottles were each filled with one liter UPW. Each bottle was spiked with 200 ng of C6-C28 n-alkane standards and mixed thoroughly. The stock solutions of n-alkane standards were prepared in pentane. This gave 0.2 ppbw (parts-per-billion by weight) of each standard in UPW. One sample was analyzed on the same day. The other samples were left on

the bench and analyzed on the 4th and 7th day after the spike. The resulting chromatogram for the first day spike is shown in Figure 2. The amount of each n-alkane was calculated using the response factor of the corresponding external n-alkane standard. The data are summarized in Table 2 and the % recovery data are plotted in Figure 3.
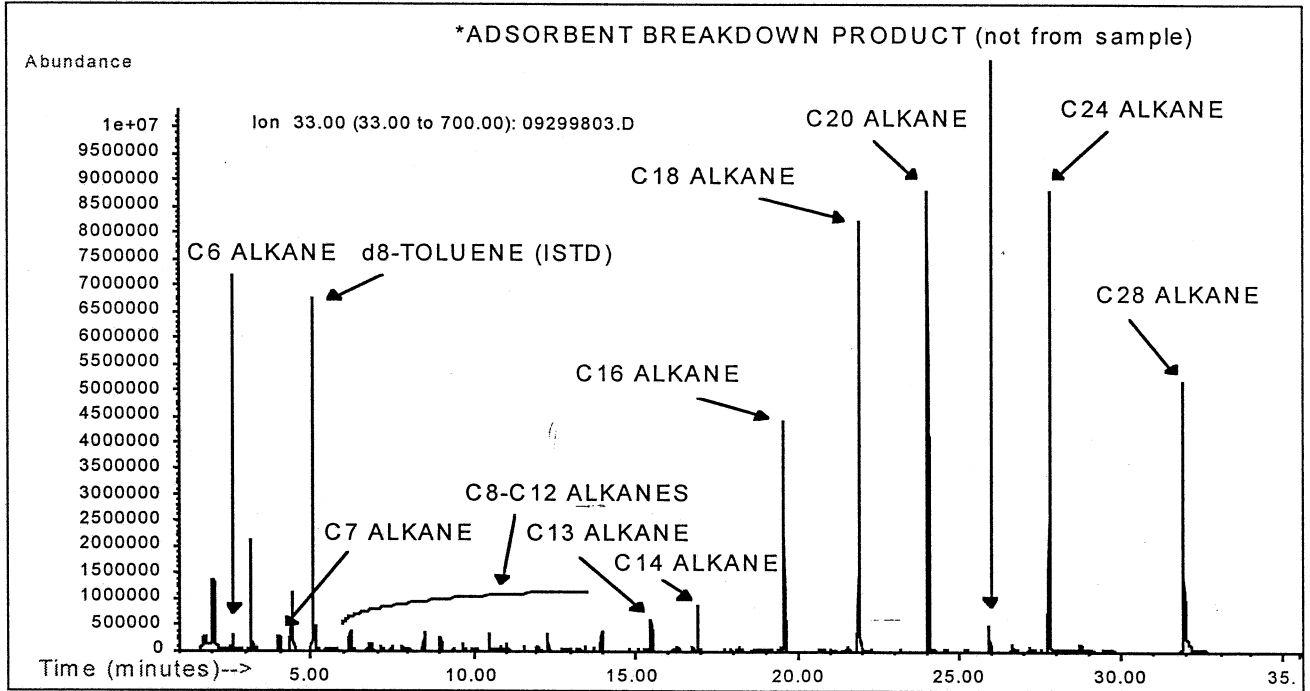

Figure 2: GC-MS chromatogram of C6-C28 n-alkanes (hydrocarbons) recovered UPW. The concentrations of n-alkanes were 0.2 ppbw. This sample was analyzed on same day of spike. The stock solutions were prepared inpentame.
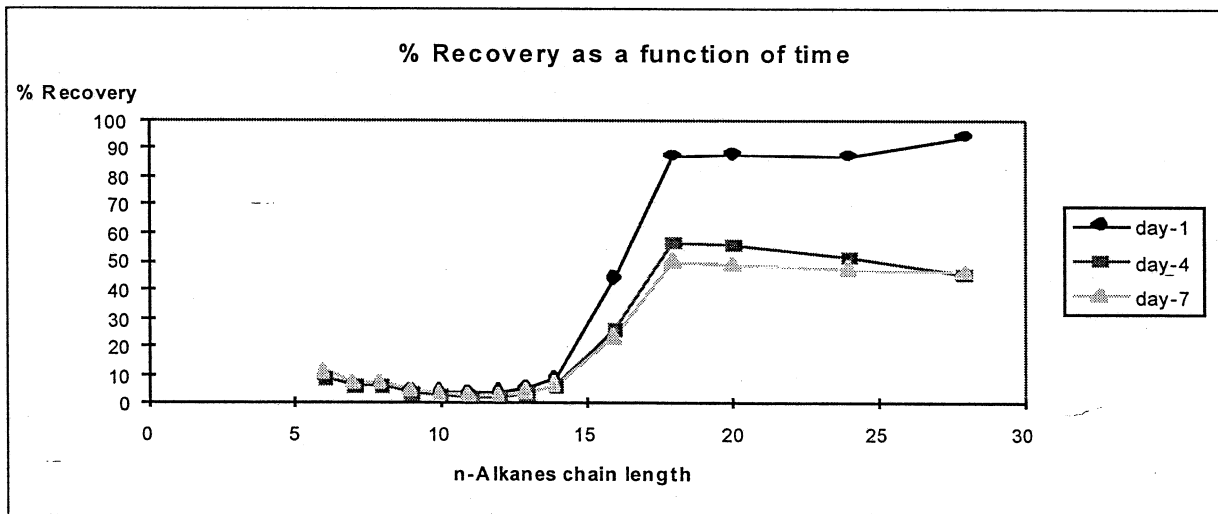

Figure 3: Plots of % recoveries of 0.2 ppbw C6-C28 n-alkanes vs. n-alkane chain length for samples analyzed on days 1, 4 and 7

TABLE 2. % Recoveries of 0.2 ppbw C6-C28 n-alkanes from UPW samples analyzed on different days of storage.

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

The results for day-1 (Table 2, Figure 3) shows that the recoveries of C6-C14 n-alkanes were 2-10%, C16-n-alkane was 44%, and C18-C28 n-alkanes were >85%. For 4th and 7th day samples, the % recoveries of C6-C10 n-alkanes remained the same as the day-1 sample (2-10%). The C16 n-alkane recovery reduced from 44% on day one to approximately 25%, but remained the same for 4th and 7th day samples. The C18-C28 n-alkanes recoveries also reduced to approximately 45% for 4th and 7th day samples.

Storage for 4-7 days reduced the recoveries of ≥C16-n-alkanes. This is most likely due to adsorption of high-boiling n-alkanes to the wall of glass bottle. It means that the samples should be analyzed as soon as possible after collection. The alternative to this is collecting organic contaminants from UPW samples directly onto adsorbent-containing sampling tubes. Online sampling is currently being evaluated in our laboratory. The solubility of hexadecane in water in approximately 1 ppb, and the larger n-alkanes should be less soluble.[12]

At this point, the question is where C6-C14 n-alkanes are lost. Figures 4 shows the chromatogram for 200 ng of each C6-C28 n-alkane spiked directly onto the adsorbent tube, which corresponds to 0.2 ppbw if added to 1 liter of UPW. Comparison of Figures 2 & 4

clearly shows that the dry adsorbent material retains all the n-alkanes (C6-C28) very well, including C6-C14. It's possible that smaller than C16 n-alkanes are lost during the sampling procedure. One possibility could be the evaporation of low boiling alkanes to ambient atmosphere during passage of UPW through the adsorbent containing sampling tube or higher solubility in water.[12] We plan to dynamically spike water with the n-alkanes with no headspace to assess why these are lost. Note that smaller n-alkanes are well below their saturation limits in water, so phase out is not expected to occur. E.g. the solubility of n-octane is about 400 ppb at 25°C.[12]
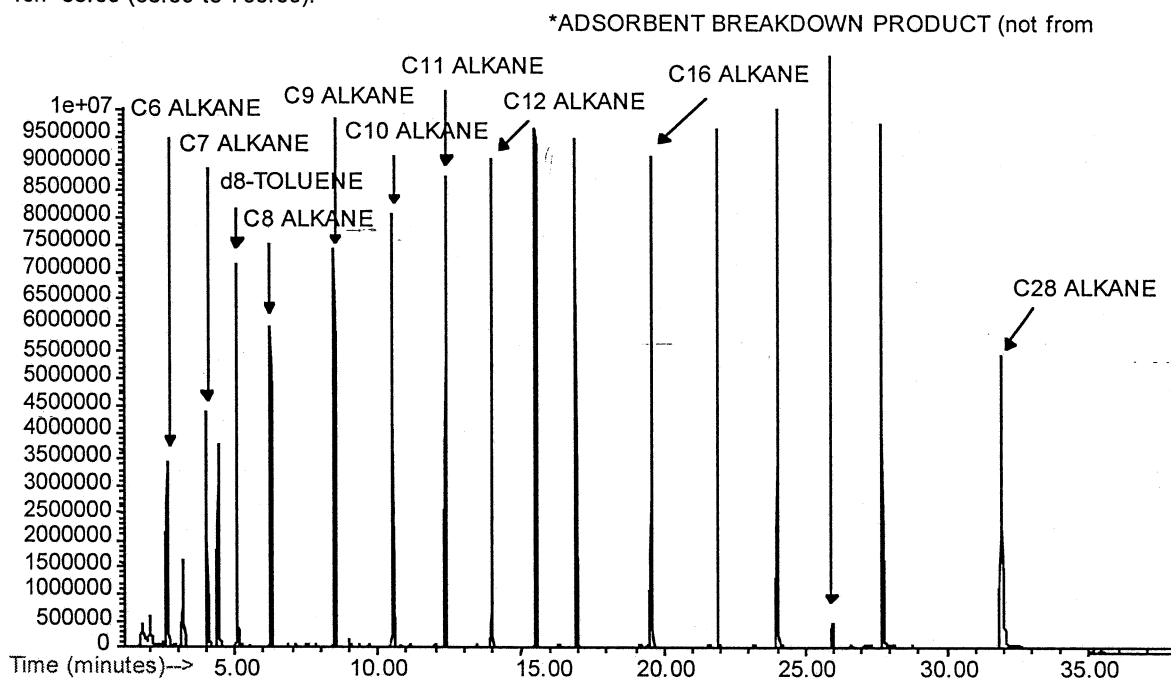

FIGURE 4. GC-MS chromatogram of 200 ng of C6-C28 n-alkanes (hydrocarbons) spiked directly onto dry adsorbent tube. This corresponds to 0.2 ppbw if added to 1 liter

Recovery Of Test Compounds:

A number of target compounds (listed in Table 3) were spiked in UPW at 0.2 ppbw levels (200 ng per liter). The resulting chromatogram is given in Figure 5 and the % recoveries are reported in Table 3.

Two major classes of organic compounds which have detrimental effects on wafer processing are plasticizers and siloxanes. As shown in Table 3, 0.2 ppbw levels of a variety of

plasticizers and siloxanes could be detected by this method. Most of the low boiling polar compounds such as ethyl lactate, PGMEA, NMP, caprolactam, 2-butoxyethanol, and benzyl alcohol had poor or no recovery. Most likely, low-boiling polar compounds are not trapped by the adsorbent since these are very water soluble.
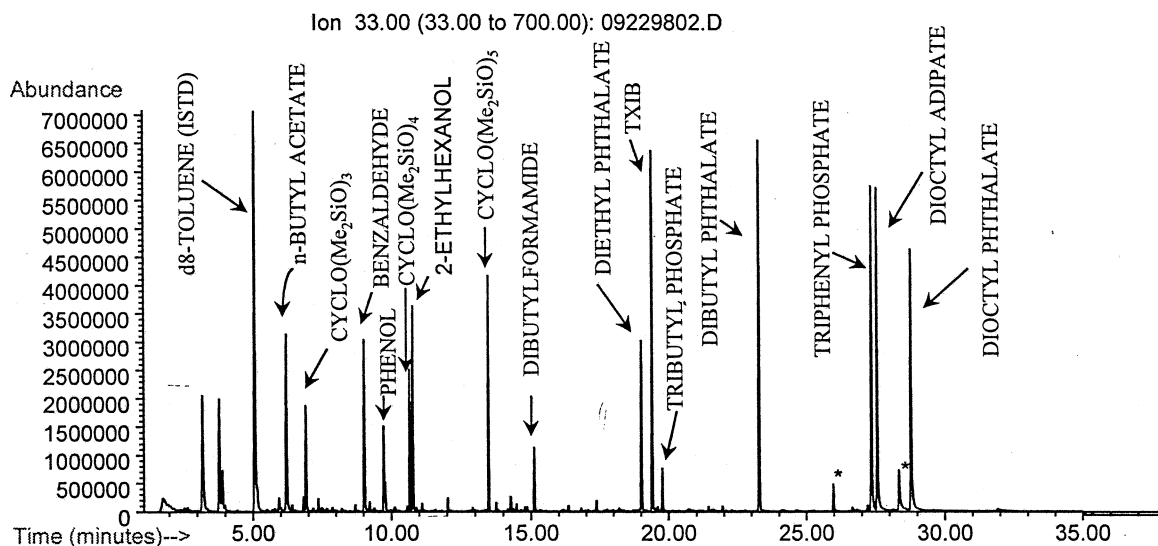

FIGURE 5: GC-MS chromatogram of 0.2 ppbw of test compounds recovered from UPW.

TABLE 3: Recovery of a variety of organic compounds from UPW. The UPW samples contained 0.2 ppbw of each organic compound. The stock solutions of standards were prepared in acetone.

COMPOUNDS	% Recovery	COMPOUNDS	% Recovery
PLASTICIZERS		AMIDES	
Diethyl phthalate	43	Dibutyl formamide	18
TXIB	74	NMP	0
Dibutyl phthalate	97	Caprolactam	0
Dioctyl adipate	56	ALCOHOL / ALDEHYDE	
Dioctyl phthalate (DOP)	54	2-Ethylhexanol	54
SILOXANES		Benzaldehyde	59
$Cyclo(Me_2SiO)_5$	73	2-Butoxyethanol	0
$Cyclo(Me_2SiO)_4$	44	Benzyl alcohol	2
$Cyclo(Me_2SiO)_3$	21	PHOSPHATES	
Hexamethyldisiloxane	16	Triphenyl phosphate	116
ESTERS (low boiling)		Triethyl phosphate	0
Ethyl acetate	0	Tributyl phosphate	10
Butyl acetate	81	Tris(chloropropyl) phosphate	2
PGMEA	6		

The poor recoveries of alkyl phosphates (triethyl, tributyl, and tris(chloropropyl)) may be due to their hydrolysis, poor partitioning from water onto the adsorbent, or decomposition during thermal desorption. The aromatic phosphates (e.g., triphenyl phosphate) are least likely to hydrolyze in water and the recovery was good.

EPA method 525.2 describes the analysis of a number of organic compounds including plasticizers by liquid-solid extraction and capillary column GC-MS.[11] In this method, the organic compounds are extracted from water samples by passing 1 liter of sample water through a cartridge or disk containing a solid matrix with a chemically bonded C_{18} organic phase (liquid-solid extraction, LSE). The organic compounds are eluted from the LSE cartridge or disk with small quantities of ethyl acetate followed by methylene chloride, and this extract is concentrated further by evaporation of some of the solvent. The detection limits for diethyl phthalate and dioctyl adipate were approximately 0.1 to 0.2 ppbw. Our TD-GC-MS method has the following two main advantages over EPA 525.2 method:

(I) Dioctyl and dibutyl phthalates, TXIB, and siloxanes could be analyzed to < 0.2 ppbw levels. EPA 525.2 does not provide recovery data for these compounds by GC-MS.[11]

(II) TD-GC-MS method does not use organic solvents to elute the organic compounds from the adsorbent, because compounds are thermally desorbed from the adsorbent directly into the instrument. Thus the TD-GC-MS method is more environmentally friendly.

Contaminants In Upw Systems:

Two UPW systems were tested. At one facility, the samples were taken from RO (reverse osmosis) reject and final filter sites; and at another location the samples were taken from final filter and return sites. All sites had detectable organic contaminants. The results are summarized below.

The chromatograms of RO reject and final filter UPW samples are given in Figures 6 and 7. The RO reject water sample (Figure 6) had significant amounts of a variety of organic compounds, such as halomethanes, ethyl p-ethoxybenzoate, alkylphenoxyethanol isomers, oleic acid, nonylphenylamine isomers, and squalene. All of these compounds were absent in

the final filter water (Figure 7). This clearly indicates that the RO was working efficiently to remove organic contaminants. A few compounds such as dioctyl adipate (0.01 ppbw) and didecyl phthalate (0.12 ppbw) were detected in the final filter water, but were absent in RO reject sample. This means that didecyl phthalate and dioctyl adipate were added somewhere in the UPW system after the RO.
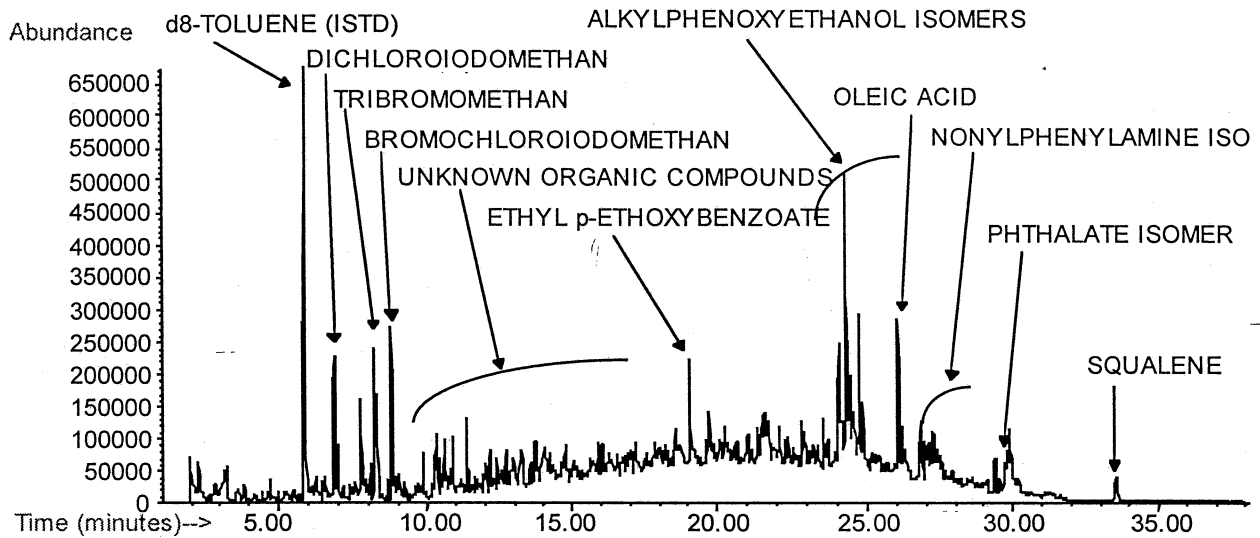
Ion 33.00 (33.00 to 700.00):

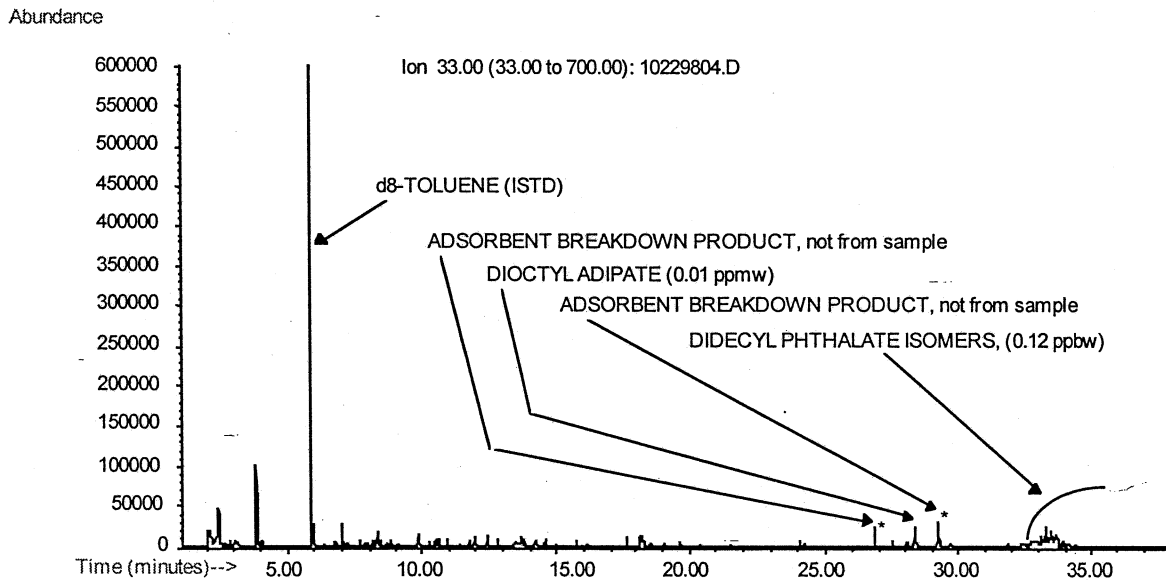FIGURE 6. GC-MS chromatogram of RO reject water sample collected at Sampling volume was 1 liter.

FIGURE 7. GC-MS chromatogram of final filter UPW sample collected at manufacturer-A, showing 0.12 ppbw of didecylphthalate isomers and 0.01 ppbw of dioctyladipate. sampling volume was 1 liter.

At another manufacturing facility, final filter and return UPW samples were collected. The results for the final filter water are shown in Figure 8. The final filter water shows the presence of BHT, acetophenone, 2-ethylhexanol and benzaldehyde. All these compounds were also detected in the return water at similar levels (chromatogram not given).
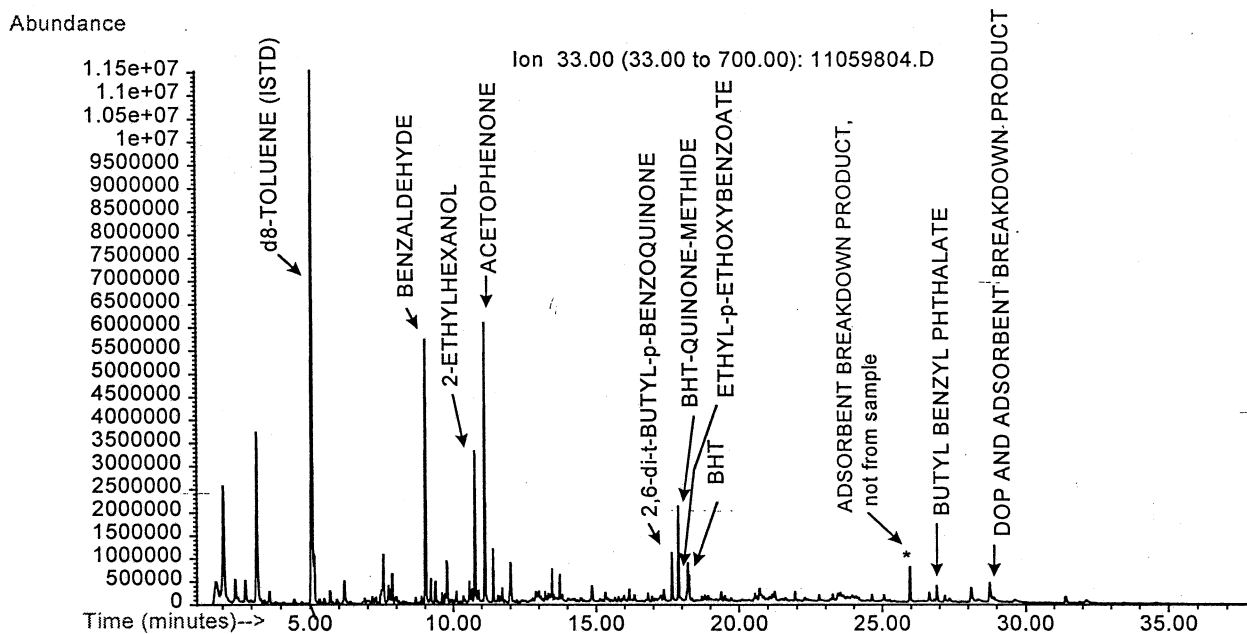

FIGURE 8. GC-MS chromatogram of final filter UPW sample collected at manufacturer-B, showing BHT and DOP. Sampling volume was 1 liter.

Case study

A semiconductor grade ultrapure water system incurred a TOC excursion of 3900 ppb from a baseline of <5ppb after some system modifications were made. One modification included welding in a new segment of PVDF pipe by heat-sealing. The edges of PVDF pipe were wiped with IPA (isopropanol) prior to welding. Seeing a dramatic increase in TOC after the pipe modification, the UPW was analyzed by TD-GC-MS method to identify the contaminant. A huge peak identified as 3-hexanone was detected (Figure 9). In addition to 3-hexanone, 3-hexanol and a variety of other ketones, alkyl esters and n-alkanes were also detected. The PVDF pipe was tested for organic outgassing, but nothing was detected. The

UPW sample was analyzed again after a few weeks and all these contaminants including 3-hexanone disappeared (Figure 10). Examination of several potential sources of the contaminant were negative. The bottle of organic solvent labeled IPA was no longer available, but the maintenance personnel declared it smelled like IPA. However, two operators stated that odor off the system smelled like paint. No painting had been done. Unfortunately the source of contaminant in unknown. The system TOC level came back to normal (<5 ppb) in about a week presumably due to use, dilution and action of TOC removal UV lamps. UPW systems might get contaminated during modifications or system failures. It will help the process engineer to have a baseline established for semivolatile organics in UPW. During baseline shifts, the contaminant in UPW could be identified by TD-GC-MS method and the source could be sought.

For comparison, the 3900 ppb TOC level sample was also analyzed by EPA 502.2 purge and trap gas chromatography method using electrolytic conductivity (ELCD) and photoionization detectors (PID). The resulting chromatograms are given in Figure 11, which shows an unknown peak at 27 minutes on the PID chromatogram. The unknown peak was not identified by purge and trap method using ELCD and PID detectors. The sample was analyzed again when the TOC level was normal (<5 ppb). The unknown peak was gone from the sample (Figure 12).
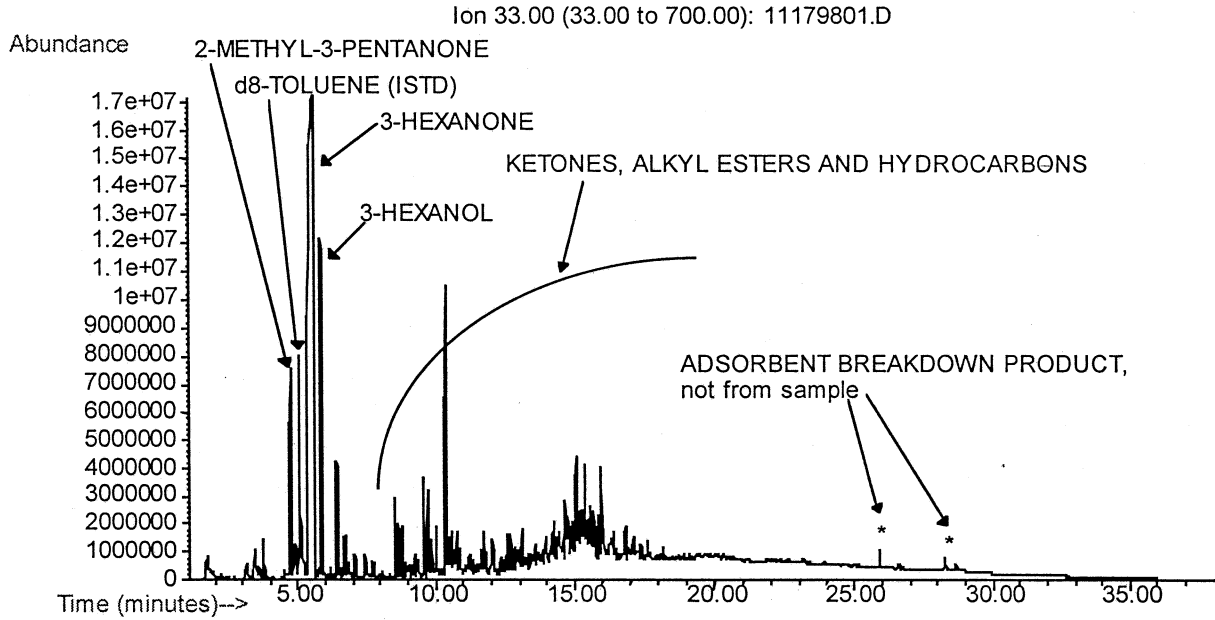
FIGURE 9. GC-MS chromatogram of the UPW semiconductor grade sample collected at final filter. The sample was collected when TOC level was 3900 ppb. Sampling volume was 1 liter.
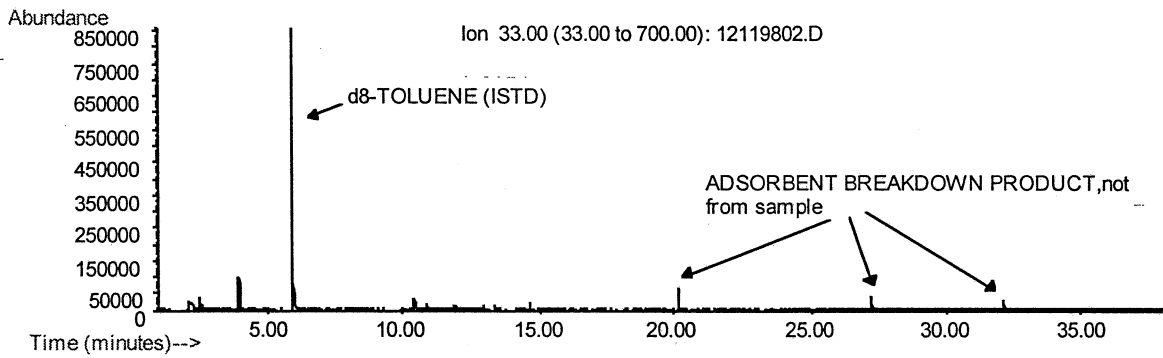

FIGURE 10. GC-MS chromatogram of semiconductor grade UPW sample. The sample was collected when the TOC level was <5 ppb. Sampling volume was 1 liter

PID

98067454.D\ADC1A

UNKNOWN   1-CHLORO-2-FLUOROBENZENE (ISTD)

Response_

```
2500000
2450000
2400000
2350000         27.10    31.27
2300000
2250000      25.81
```

Time (minutes)-->   20.00   25.00   30.00   35.00   40.00   45.00   50.00

ELCD

Response_

98067454.D\ADC1B   31.32   1-CHLORO-2-FLUOROBENZENE (ISTD)

```
4000000
3800000
3600000
3400000
3200000
3000000
2800000
2600000
```

Time (minutes)-->   20.00   25.00   30.00   35.00   40.00   45.00   50.00
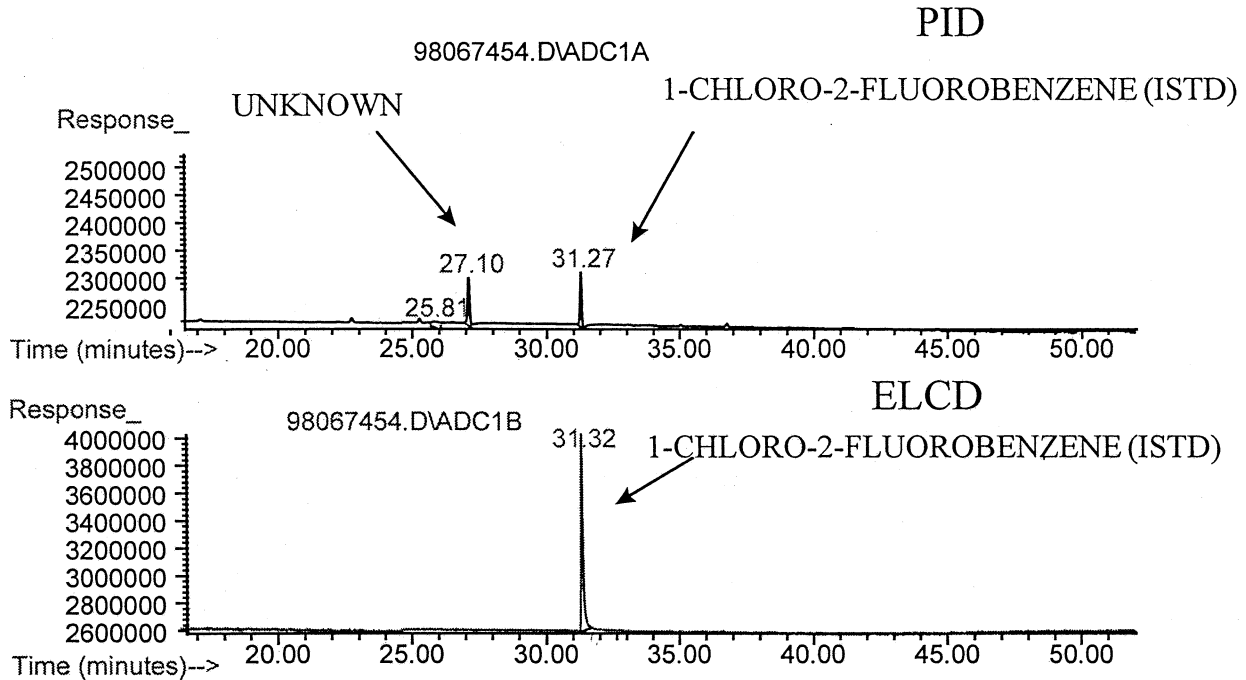
FIGURE 11. Gas chromatograph of UPW sample (TOC 3900 ppb) analyzed by EPA 502.2 purge and trap method using electrolytic conductivity detector (ELCD) and photoionization detector (PID). The PID chromatogram shows a peak at 27.10 minutes which was not identified by purge & trap method.

PID

1-CHLORO-2-FLUOROBENZENE (ISTD)

Response_

```
2550000
2500000         98067631.D\ADC1A
2450000
2400000                            32.11
2350000
2300000
2250000
```

Time (minutes)-->   20.00   25.00   30.00   35.00   40.00   45.00   50.00

ELCD

Response_

```
4200000         98067631.D\ADC1B      32.16   1-CHLORO-2-FLUOROBENZENE (ISTD)
4000000
3800000
3600000
3400000
3200000
3000000
2800000
2600000
```

Time (minutes)-->   20.00   25.00   30.00   35.00   40.00   45.00   50.00
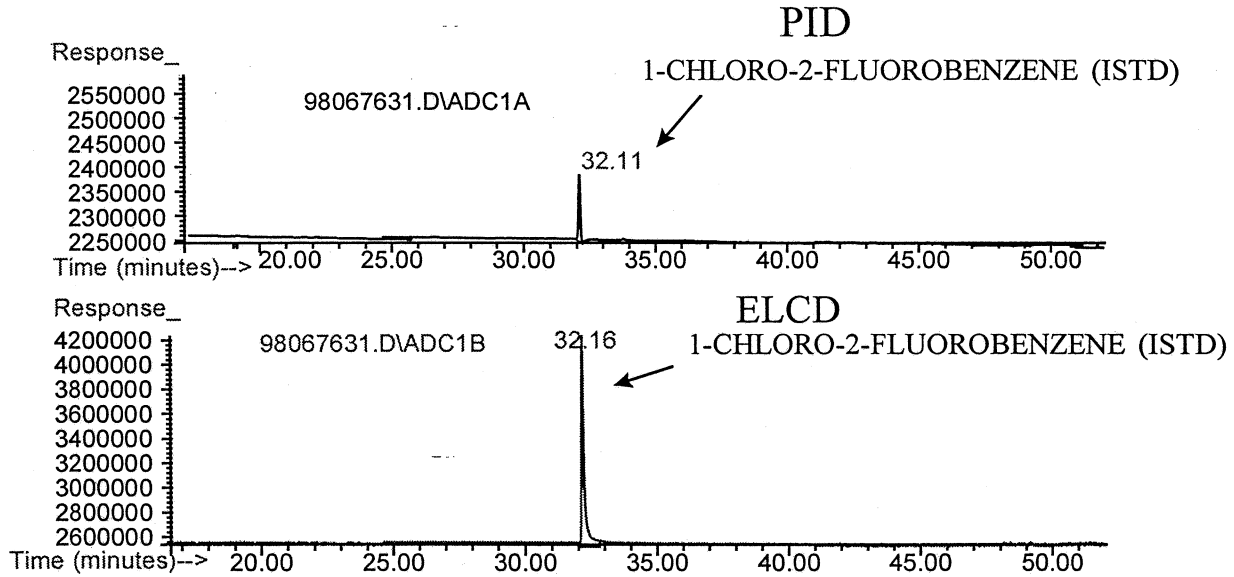
FIGURE 12. Gas chromatograph of UPW sample (TOC <5 ppb) analyzed by EPA 502.2 purge and trap method using electrolytic conductivity detector (ELCD) and photoionization detector (PID). The unknown peak at 27.1 minute disappeared.

Semiconductor Manufacturing Facilities

The final filter and return UPW samples were tested at five more semiconductor plants. Out of five final filter UPW samples, three were relatively clean. A representative chromatogram (Figure 13) shows the absence of peaks due to semi-volatile organic compounds. A fourth site had 0.08 ppbw of dioctyl phthalate (Figure 14). This compound is a plasticizer added to plastics or elastomers. The fifth site had lower levels of 2-methylthio-benzothiazole, styrene and benzaldehyde (chromatogram not shown). The return water samples were tested for three sites only. In all cases, the types and levels of organic compounds in return water were similar to the final filter water.
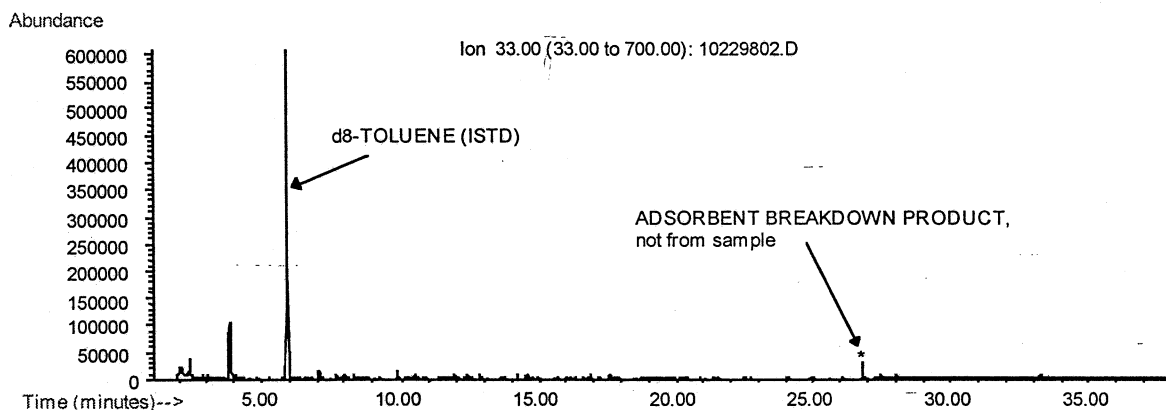

FIGURE 13. GC-MS chromatogram of final filter UPW sample collected from a semiconductor manufacturing facility-A. Sampling volume was 1 liter.
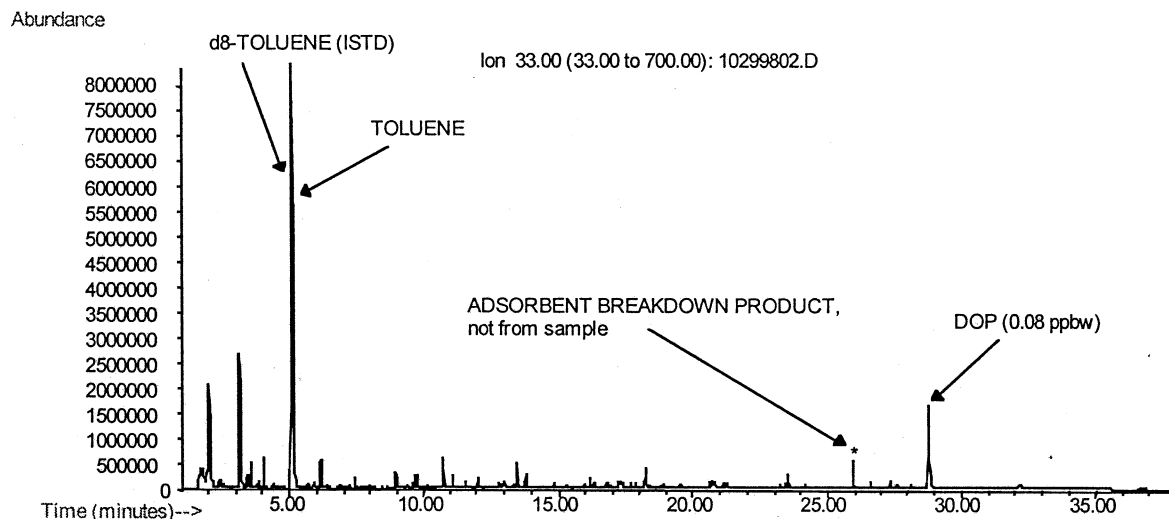
FIGURE 14. GC-MS chromatogram of UPW sample collected at final filter at a semiconductor manufacturing facility-B, showing 0.08 ppbw of DOP. Sampling volume was 1 liter.

Above results indicate that the TD-GC-MS method works very well to trap <0.2 ppbw levels of semi-volatile organic compounds (e.g., >C14 n-alkanes, plasticizers and siloxanes, etc.) from UPW, and sub-ppb level of some of these contaminants are found at some fabs.

Limitations Of Method

Polar organic compounds with lower boiling points are not trapped effectively by this method. The n-alkanes with boiling points significantly lower than C14 n-alkane, or other low-boiling compounds may not be recovered well. Thermally unstable compounds may decompose to other compounds, and some reactive compounds can interact to give new compounds or low recoveries. Amines may react with acidic components to give poor recovery.

Summary

Typically, levels of organic contaminants in UPW are monitored using on-line TOC. This provides information on real-time changes in water quality, and is effective in early detection of trouble in UPW production systems. There are a number of organic compounds which

might not be detected by TOC, but still cause problems. When a problem occurs which correlates to high TOC, the identification of contaminant will be useful to trace the source of contamination. In such cases, the TD-GC-MS method may identify the unknown compounds. The TD-GC-MS technique could also be used for finger printing, e.g., if a contaminant is detected in UPW, the possible sources could be determined by outgassing the materials used in the UPW system. A correlation could be made between what was detected in UPW and what outgassed from the materials used. Since TOC levels at semiconductor plants are often <5 ppb, and few methods identify compounds in UPW at trace levels, this method should prove valuable for baselining what contaminants are in UPW systems and troubleshooting contaminant sources when failures occur.

Acknowledgments

Author Biographies

Mark Camenzind is a senior research chemist at Balazs Analytical Laboratory. He received his Ph.D. in Chemistry from University of California at Berkeley. For over 11 years, he has been developing methods and solving contamination problems for semiconductor and disk drive industries. He actively participates in working groups of SEMI, IDEMA, IEST and ASTM.

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Anurag Kumar received his Ph.D. from University of Roorkee, India, and did postdoctoral research at University of California, Santa Barbara. He is currently the organic laboratory

manager at Balazs Analytical Laboratory. He has been developing methods for solving organic contamination problems for semiconductor and disk drive industries.

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