Thermal Desorption Technical Support

Note 14: Monitoring labile, high-boiling organic vapours such as those found in “clean room air” in semi-conductor fabrication plants

Keywords:

Silicon wafer crystals, particulates, contamination

Introduction

The presence of volatile and semi-volatile organic vapours can adversely affect the growth of silicon wafer crystals and the resultant performance of microprocessors, data storage devices and other key electronic components. The atmospheric concentration of these contaminants in clean room fabrication facilities is thus a critical issue.

The purity of clean room atmospheres must be controlled with respect to both particulates and vapours. Volatile organic components are predominantly present in the atmosphere in the vapour phase and range in volatility up to around n-C_{16}. Concentrations are typically low (low- to sub-ppb) but nevertheless, some of the higher boiling of these compounds (species less volatile than toluene) can condense onto the surface of the silicon wafer crystals causing a reduction in yield. Semi-volatile components (less volatile than n-C_{16}) are present in the atmosphere in both vapour and particulate form. It is the vapour fraction of the semi-volatile compounds that are most liable to condense and cause problems during semi-conductor production. Some of the semi-volatiles are also chemically reactive and prone to oxidative degradation making them difficult to analyse. Examples of key compounds of interest are listed in Table 1.

This technical support note demonstrates the compatibility of Markes TD technology with these challenging semi-volatile components. For details concerning sampling methods and examples of relevant applications see TDTS 62.

Method of Analysis

0.5 µL of a cleanroom/semi-conductor check standard was injected onto a small bed of pre-heated, conditioned quartz wool which was placed inside a Silcosteel® coated stainless steel thermal desorption tube. Silcosteel tubes have an extremely thin (Ångstroms) layer of quartz bonded to the surface of the stainless steel tube and primary (front) sorbent retaining gauze, to make the sampler inert. This makes the tubes suitable for sampling reactive species.

Compound	Formula	Molecular Weight
Palmitic Acid	$C_{16}H_{32}O_2$	256
Butylated Hydroxytoluene	$C_{15}H_{24}O$	220
Triphenyl phosphate	$C_{18}H_{15}O_4P$	326
Oxybenzone	$C_{14}H_{12}O_3$	228
Caprolactam	$C_6H_{11}NO$	113
Hexadecane	$C_{16}H_{34}$	226
DC704 (phenyl silicone)	$[(C_6H_5)_2SiO]_n$	$[198]_n$
Diethylhexyl adipate	$C_{22}H_{42}O_4$	371
Oleamide	$C_{18}H_{35}NO$	281
Diethylhexyl phthalate	$C_{24}H_{38}O_4$	391
Triethyl phosphate	$C_6H_{15}O_4P$	182
D10 anthracene - internal standard	$C_{14}H_{10}$	178

Table 1. Standard solution of key compounds of interest

Analytical conditions

GC column:	30 m x 0.25 mm x 0.25 mm methyl silicone bonded phase capillary
Approximate flow:	1.5 mL/min
Temp. program:	50°C (5 min), 10°C/min to 200°C, 5°C/min to 300°C (5 mins)
Sample:	0.5 µL cocktail and 0.3 µL d10 anthracene standard injected onto pre-heat conditioned quartz wool inside an empty sample tube.

Note that routine air monitoring would be carried out using tubes packed with quartz wool (10 mm) backed up by well conditioned Tenax TA 35-60 mesh (50 mm.)

UNITY:	"High Boilers" Cold trap U-T1HBL-2S
Cold trap low:	+30°C
Inlet split:	Off
Desorb flow:	45 mL/min
Outlet split flow:	20 mL/min
Desorb	200°C for 12 minutes
Flow path:	200°C
Cold trap high:	250°C for 20 minutes

Results of the preliminary study using TD-GC with flame ionisation detection

Chromatograms are considered in the order they appear.

Chromatogram 1 shows the results of desorption of the liquid standard loaded onto a silcosteel tube and analysed on a Markes UNITY™ thermal desorber with GC/FID. The correct number of peaks were observed with no evidence of either activity (peak tailing) or degradation.

Chromatogram 2 shows a repeat desorption of the same tube with the blank profile, indicating no observable carryover.

Chromatogram 3 represents a second injection of the same liquid standard onto a bed of quartz wool packed into a plain stainless steel tube, showing evidence of component degradation during analysis. Peak areas for some of the higher boiling components were relatively low and additional peaks (probably artefacts from analyte degradation) can be observed between 15 and 20 minutes retention time.

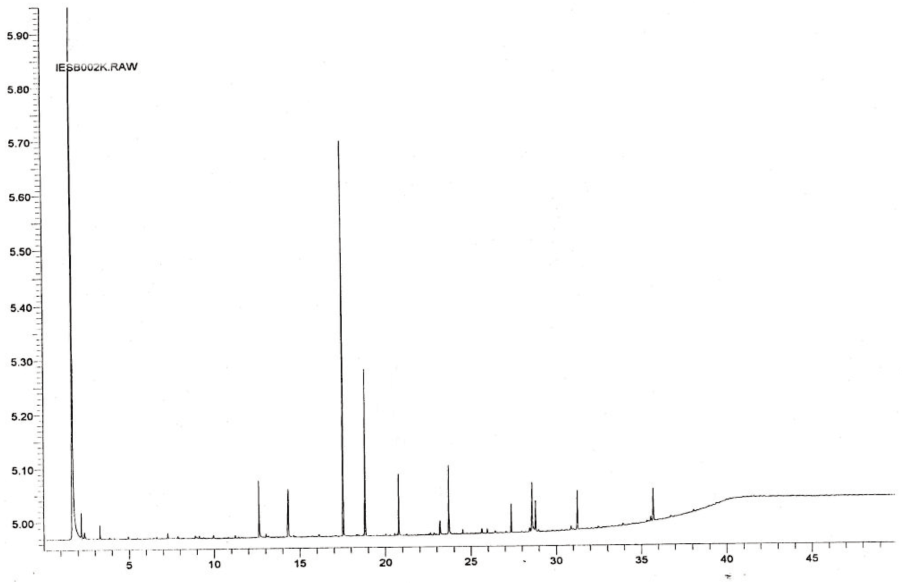
The results of these tests were encouraging as the flow path of Markes International UNITY (manual) and TD-100 (automated 100-tube) thermal desorption systems are constructed of short, narrow-bore lengths of silcosteel tubing. No untreated/coated stainless steel (or other metal) is used for flow path construction. Lack of carryover also indicated that there was no condensation or deposition in the sample flow path of the analytical system.

More detailed study of the recovery of isobornyl methacrylate – A key indicator of analytical system performance

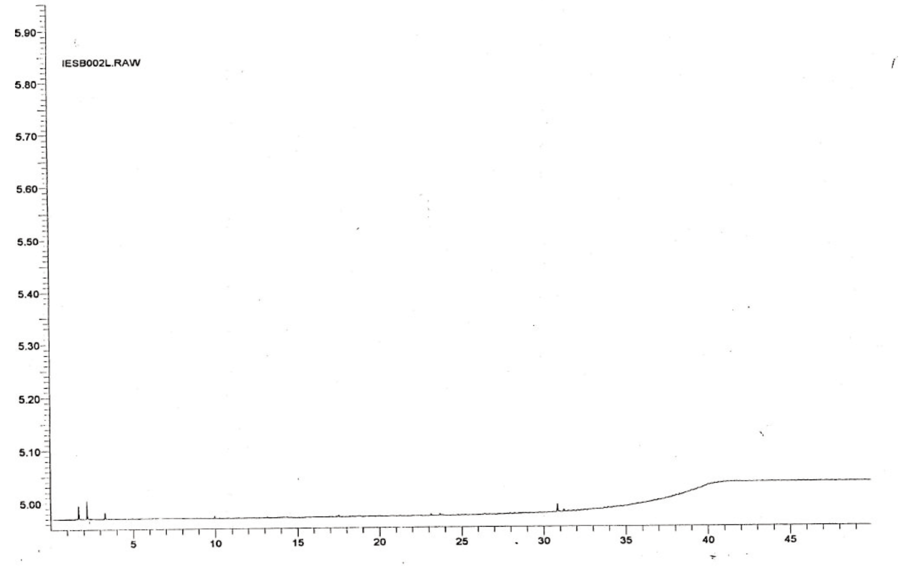
One of the most important clean room air contaminants is isobornyl methacrylate (IBMA). IBMA is a highly reactive species and monitoring of IBMA levels has traditionally proved difficult as it degrades to camphene during TD-GC(MS) analysis if there is any activity in the analytical flow path.

Chromatogram 4 shows desorption of a liquid standard containing IBMA and some high boiling point plasticisers (*e.g* dioctyl phthalate). This mix was loaded onto a Silcosteel TD tube and analysed using a Markes TD-100™ thermal desorber with GC/MS detection. No camphene was detected despite the high flow path temperature (200°C) used for analysis thus demonstrating the compatibility of Markes TD technology with this challenging compound.

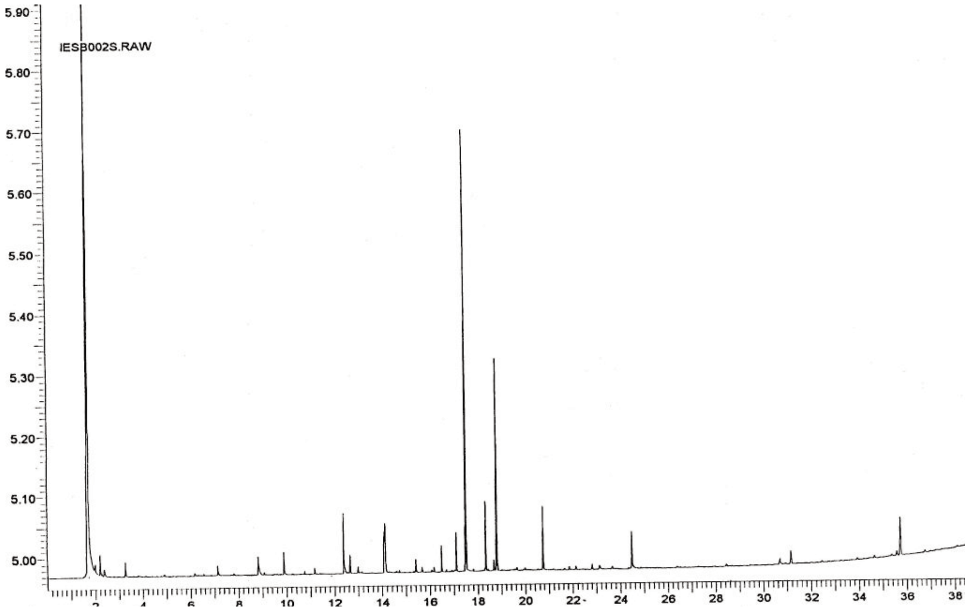
Quantitative recovery of IBMA was further demonstrated using SecureTD-Q (See TDTS 24). This facility is available on all Markes TD systems and allows re-collection and repeat analysis of the original sample. Figure 1 shows the IBMA levels observed over a series of nine desorption/re-collection/repeat analysis cycles of the original sample. The recovery of IBMA following each re-collection is consistent with that expected from the TD split ratio and therefore demonstrates complete recovery of IBMA through the flow path of the thermal desorber. This can only be achieved with a chemically inert and uniformly-heated flow path.



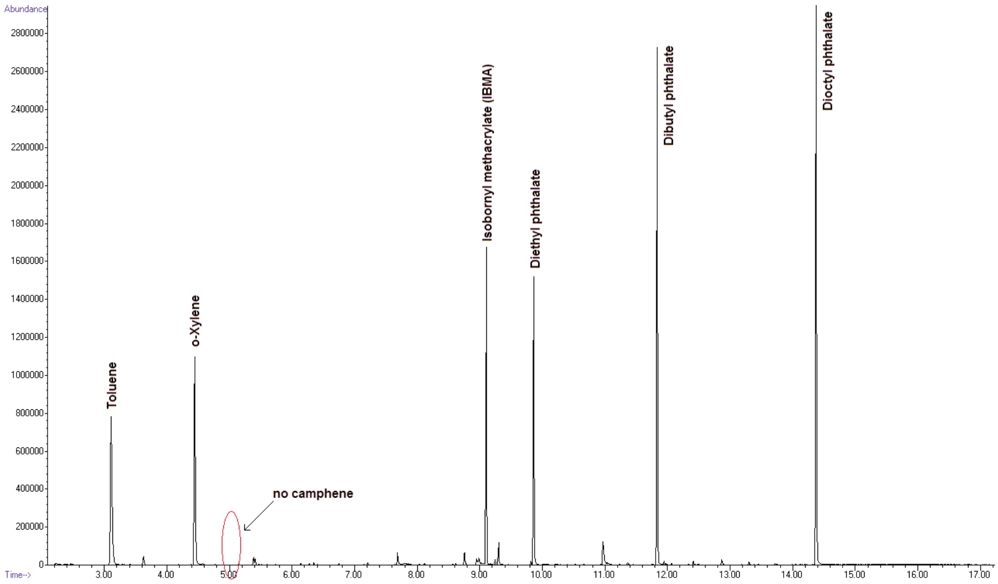
Chromatogram 1



Chromatogram 2



Chromatogram 3



Chromatogram 4. Standard containing toluene, o-xylene, IBMA, diethyl phthalate, dibutyl phthalate and dioctyl phthalate (300 ng/µL). 1µL injected onto the sorbent tube and analysed by Markes TD-100-GC/MS

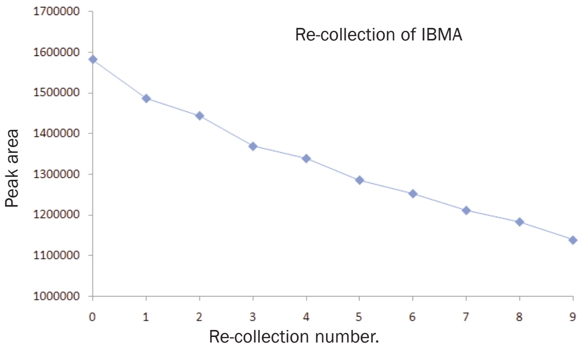


Figure 1. IBMA levels determined in a series of nine consecutive re-collections and repeat analyses of the original IBMA liquid standard mix. Re-collection of each analysis was at a split ratio of approximately 40:1

Summary

These data demonstrate the inertness of Markes' TD systems and that, provided a suitably inert tube material is used for sample/standard loading, both UNITY and TD-100 can be used to analyse trace levels of the labile, semi-volatile contaminants of most interest to cleanroom environments. The SecureTD-Q™ facility of all Markes TD systems allows re-collection and repeat analysis of all samples thus overcoming the one-shot limitation of traditional TD technology and allowing simple validation of complete recovery through the TD analytical system during analysis.

Trademarks

Silcosteel® is a registered trademark of Restek Inc, USA

Revised May 2010