

Application Note 014

Monitoring labile, high-boiling organic vapours such as those found in cleanroom air in semiconductor plants

Summary

This Application Note describes how Markes' thermal desorption technology can be used to detect semi-volatile organic compounds (SVOCs) in air – an application that is of particular relevance to sampling in the cleanroom facilities of semiconductor plants.

Introduction

The presence of VOC and SVOC 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 concentrations of these contaminants in semiconductor fabrication facilities is thus a critical issue, and must be controlled with respect to both particulates and vapours.

Volatile organic compounds (VOCs) are predominantly present in the atmosphere in the vapour phase, and range in volatility up to n-C₁₆. 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 organic compounds (SVOCs) are less volatile than n-C₁₆, and 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 semiconductor production. Some SVOCs are also chemically reactive and prone to oxidative degradation, making them difficult to analyse.

This Application Note demonstrates the suitability of Markes' TD technology to sample SVOCs. For details of sampling methods and examples of relevant applications please see Application Note 062.

Experimental

0.5 µL of a cleanroom/semiconductor check-standard (Table 1) was injected onto a small bed of pre-heated, conditioned quartz wool which was placed inside a inert-coated stainless steel TD tube. Inert-coated tubes have an extremely thin layer of quartz bonded to the surface of the stainless steel tube and primary (front) sorbent retaining gauze, making the sampler inert and suitable for dealing with reactive species.

Compound	Formula	Molecular weight
Palmitic acid	C ₁₆ H ₃₂ O ₂	256
Butylated hydroxy toluene	C ₁₅ H ₂₄ O	220
Triphenyl phosphate	C ₁₈ H ₁₅ O ₄ P	326
Oxybenzone	C ₁₄ H ₁₂ O ₃	228
Caprolactam	C ₆ H ₁₁ NO	113
Hexadecane	C ₁₆ H ₃₄	226
DC704 (phenyl silicone)	[(C ₆ H ₅) ₂ SiO] _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 ₆ H ₁₅ O ₄ P	182
Anthracene-d ₁₀ (internal standard)	C ₁₄ H ₁₀	178

Table 1: Components of the cleanroom/semiconductor check-standard used in this study.

TD:

Instrument: UNITY™
 Cold trap: U-T1HBL-2S ('high boilers')
 Cold trap low: 30 °C
 Inlet split: Off
 Desorb flow: 45 mL/min
 Outlet split flow: 20 mL/min
 Desorb: 200 °C for 12 min
 Flow path: 200 °C
 Cold trap high: 250 °C for 20 min

GC:

Column: 30 m × 0.25 mm × 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 min)

Sample: 0.5 µL cocktail and 0.3 µL anthracene-d₁₀ standard, injected onto pre-heated 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 bed) backed up by well-conditioned Tenax® TA (35/60 mesh) (50 mm bed).



Results and discussion

1. Preliminary study using TD-GC-FID

Figure 1A shows the results of desorption of the liquid standard loaded onto an inert-coated stainless steel tube and analysed on Markes' UNITY thermal desorber by GC-FID. The correct number of peaks were observed with no evidence of either activity (peak tailing) or degradation.

Figure 1B shows a repeat desorption of the same tube with the blank profile, indicating no observable carryover.

Figure 1C represents a second injection of the same liquid standard onto a bed of quartz wool packed into a plain stainless steel tube. There is some indication of component degradation – peak areas for some of the higher-boiling components are relatively low, and additional peaks are present between 15 and 20 minutes.

The results of these tests were encouraging, as the flow paths of Markes' UNITY and TD-100™ systems are constructed solely of short, narrow-bore lengths of inert-coated tubing. Lack of carryover (Figure 1B) also indicated that there was no condensation or deposition in the sample flow path of the analytical system.

2. Recovery of isobornyl methacrylate

One of the most problematic cleanroom 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.

Figure 2 shows desorption of a liquid standard containing IBMA and some high-boiling plasticisers (e.g. dioctyl phthalate). This mix was loaded onto an inert-coated TD tube and analysed by TD-GC-MS using Markes' TD-100 thermal desorber. No camphene was detected despite the high flow path temperature (200 °C) used for analysis, thus demonstrating the ability of Markes' TD technology to handle this challenging compound.

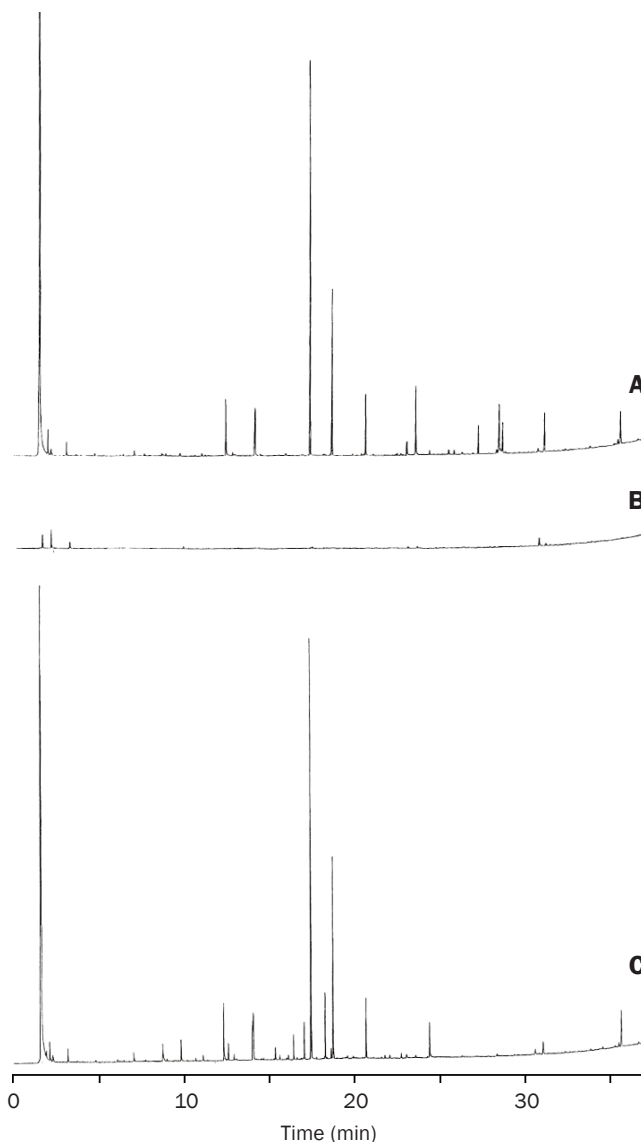


Figure 1: GC-FID analysis of a liquid standard containing SVOCs:
(A) Desorption from an inert-coated stainless steel tube;
(B) Repeat desorption of the same tube; **(C)** Desorption from a plain stainless steel tube.

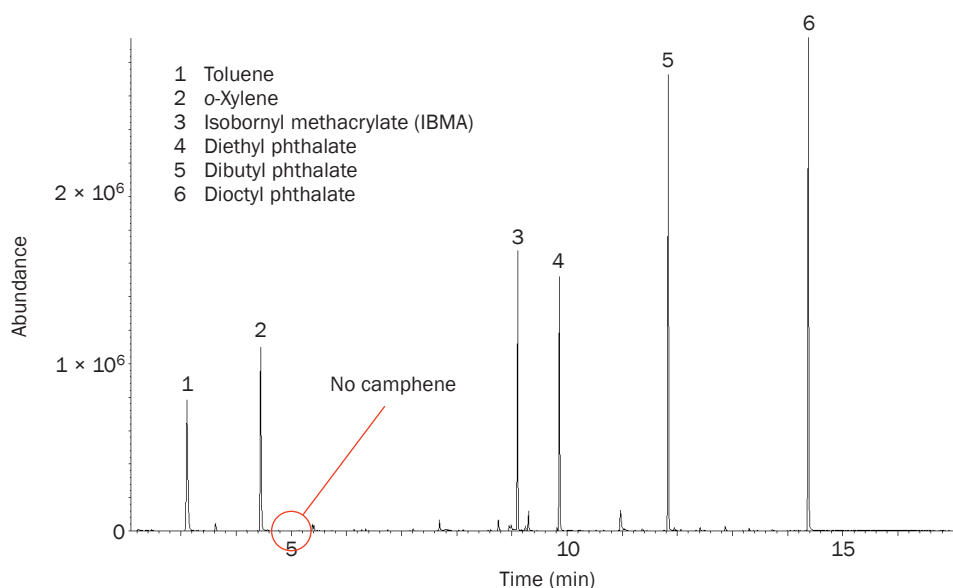


Figure 2: Desorption of 1 µL of a 300 ng/µL liquid standard containing IBMA. The absence of a camphene peak indicates no degradation of IBMA in the flow path of the TD instrument.

Quantitative recovery of IBMA was further demonstrated using by re-collection and repeat analysis of the original sample (SecureTD-Q™ – see Application Note O24 for more details). Figure 3 shows the IBMA levels over a series of nine consecutive desorption–re-collection cycles of the original sample. The recovery of IBMA following each re-collection is consistent with that expected from the TD split ratio, demonstrating 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.

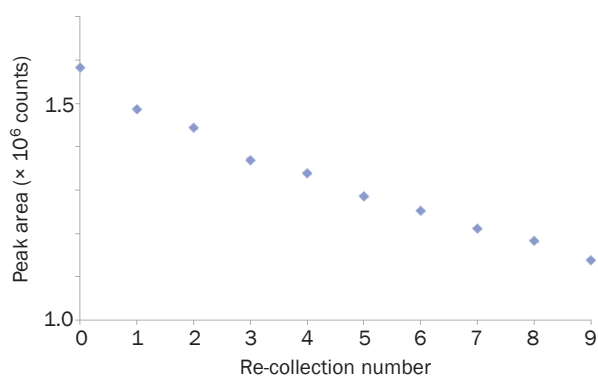


Figure 3: IBMA levels determined in a series of nine consecutive desorption–re-collections of the original IBMA liquid standard mix. Re-collection was carried out using a split ratio of approximately 40:1.

Conclusions

The results described in this Application Note demonstrate the inertness of Markes' TD systems. It is clear that, provided a suitably inert tube material is used for sample/standard loading, either UNITY or TD-100 can be used to analyse trace levels of the labile, semi-volatile contaminants of greatest relevance to cleanroom environments.

Furthermore, the SecureTD-Q ability 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

SecureTD-Q™, TD-100™ and UNITY™ are trademarks of Markes International.

Tenax® is a registered trademark of Buchem B.V., The Netherlands.

Applications were performed under the stated analytical conditions. Operation under different conditions, or with incompatible sample matrices, may impact the performance shown.

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