

Short communication

Measurement of toxic volatile organic compounds in indoor air of semiconductor foundries using multisorbent adsorption/thermal desorption coupled with gas chromatography–mass spectrometry

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Abstract

A method for the qualitative and quantitative analysis of volatile organic compounds (VOCs) in the air of class-100 clean rooms at semiconductor fabrication facilities was developed. Air samples from two semiconductor factories were collected each hour on multisorbent tubes (including Carbopack B, Carbopack C, and Carbosieve SIII) with a 24-h automatic active sampling system and analyzed using adsorption/thermal desorption coupled with gas chromatography–mass spectrometry. Experimental parameters, including thermal desorption temperature, desorption time, and cryofocusing temperature, were optimized. The average recoveries and the method detection limits for the target compounds were in the range 94–101% and 0.31–0.89 ppb, respectively, under the conditions of a 1 L sampling volume and 80% relative humidity. VOCs such as acetone, isopropyl alcohol, 2-heptanone, and toluene, which are commonly used in the semiconductor and electronics industries, were detected and accurately quantified with the established method. Temporal variations of the analyte concentrations observed were attributed to the improper use of organic solvents during operation.

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1. Introduction

The monitoring of volatile organic compounds (VOCs) in ambient air has received substantial attention over the past several years because certain VOCs are known to be hazardous to human health [1–3]. A thermal desorption method with new types

of solid adsorbents, such as graphitized carbon blacks and carbon molecular sieves, is widely used for ambient VOC monitoring in the sub-ppb range [4]. The method is based on the preconcentration of an air sample using a multisorbent collection tube, followed by thermal desorption to release the compounds to the gas chromatography–mass spectrometry (GC–MS) detector for analysis [5]. Depending on the sampled volume, sensitivities in the low and sub-ppb range can readily be achieved for active sampling, so this sampling has preferentially

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been used in air analysis. Although blank levels can be made extremely low (down to sub-ppb) by meticulous conditioning of the solid adsorbents, the danger of artifact formation during storage and exposure may be unavoidable and needs to be considered [6].

The semiconductor and electronics industries have grown significantly in Taiwan over the past two decades. Production routinely requires a diverse range of volatile organic compounds (VOCs) in the factories; however, little is known about the quality of indoor air in the so-called class-100 clean rooms at semiconductor fabrication facilities. The use of Tenax-TA adsorption for the measurement of toxic organic compounds in workplace air of surface coating industries using thermodesorption/gas chromatography has been evaluated [7]. The method was found to be reliable for monitoring nonpolar VOCs in the workplace environment. In the present work, adsorptive (active) sampling on multibed tubes followed by thermal desorption GC–MS was used. An analytical protocol was developed for the analysis of nonpolar and polar VOCs in workplace air during the processing of semiconductors and electronics. To obtain the best performance, the parameters of the thermal desorption cryofocusing system were studied in detail.

2. Experimental

All VOCs (acetone, isopropyl alcohol, benzene, trichloroethylene, toluene, butyl acetate, cyclopentanone, *m,p*-xylene, 2-heptanone, and *o*-xylene) were obtained from Chemservice (West Chester, PA, USA) with purity greater than 99.5%. Gas standards were prepared by injecting a certain amount of the liquid standards containing a mixture of the 10 VOCs into a Model 232 Tedlar (SKC, USA) sampling bag filled with a known amount of helium gas as the dilution gas with a relative humidity of $80 \pm 5\%$. The concentration of each VOC in the gas standards was prepared at a level of approximately 100 ppmv by the static method.

The multibed collection tubes were custom-made of glass (16 cm \times 4 mm I.D. and a wall thickness of 2 mm). Each tube contained 0.2 g of Carboxpack C, 0.2 g of Carboxpack B, and 0.2 g of Carboxieve SIII

(Supelco, Bellefonte, PA, USA). The adsorbents were held in place by a small amount of deactivated quartz wool. Prior to sampling, all tubes were conditioned for 3 h at 350 °C using nitrogen gas (>99.999%) at 120 mL/min.

Samples were collected in the air of class-100 clean rooms at two different semiconductor fabrication facilities (sites A and B) in May to June 2000. Active sampling was performed using a sequential tube sampler (Perkin-Elmer STS 25, Norwalk, CT, USA). The flow-rate was regulated by a needle valve and calibrated by a rotameter (Drycal BIOS, USA). Typical sample volumes in the range of 1 L were taken over a period of 1 h at a sampling rate of 10 to 20 mL/min. Before and after sampling, all tubes were plugged tightly with special 1/4 in. Teflon screw caps and stored in a clean plastic container filled with active charcoal at room temperature.

An automatic thermal desorption cryofocusing injector system (Tekmar 6016 and Tekmar 6000, Cincinnati, OH, USA) was connected by a transfer line maintained at 180 °C to a Hewlett-Packard 5890 A GC system equipped with a HP 5971 A mass selective detector (Palo Alto, CA, USA). The automated Tekmar thermal desorption device can process up to 16 samples automatically. The multisorbent tubes were thermally desorbed at 230 °C for 10 min. The desorbed analytes were retrapped at -150 °C for 7 min by a Teflon tube (10 cm \times 1.6 mm I.D.) filled with 2 cm deactivated glass beads (mesh 60/80). After sample concentration, the trap was flash-heated to 200 °C at 50 °C/s for 7 min, and the trapped analytes were introduced into a moisture control system to remove water vapor before being injected into the GC–MS system. The thermodesorption and cryofocusing conditions are discussed below.

The analytical column was a DB-Wax fused-silica capillary column of 60 m \times 0.32 mm I.D. with 0.5 μ m film thickness (J&W Scientific, Folsom, CA, USA). The inlet pressure of the ultra-pure helium carrier gas (>99.9995%) was set at 0.36 bar. Oven temperature was programmed as follows: start at 35 °C for 7 min; ramp at 7 °C min^{-1} to 91 °C; ramp at 9 °C min^{-1} to 154 °C and hold for 5 min; finally, ramp at 20 °C min^{-1} to 194 °C and hold for 5 min. The total analysis time was 34 min. The mass selective detector with electron ionization was operated in scan mode at a rate of 6.1 scans s^{-1} from 40

to 260 amu. From a comparison of both the retention times and major fragments with those of the standards, the peaks of the real samples were identified when they exhibited >85% match.

3. Results and discussion

The target compounds in this study are widely used in the semiconductor and electronics industries as cleaning solutions or solvents of photoresists. Displayed in Fig. 1 is a total ion chromatogram of a mixed standard under the optimization of the multisorbent adsorption/thermal desorption analytical method. Except for *m*-xylene and *p*-xylene, which were not resolved, all the VOCs could be well separated and identified.

The appropriate desorption temperature was evaluated to ensure that all analytes were completely desorbed from the multisorbent tubes. Fig. 2 shows the dependence of the analyte recovery on the

desorption temperature. Except for the desorption temperature, the thermodesorption conditions of the cryofocusing system were set the same as those in optimization. It was found that the signals for all analytes increased initially with increasing desorption temperature of the multisorbent collection tubes, and then decreased gradually when the temperature was above 240 °C. The decrease may be due to the decomposition of analytes. Therefore, the optimal desorption temperature of the adsorbent tube was chosen to be 230 °C for subsequent experiments. Fig. 3 shows the dependence of the analyte recovery on the desorption time. A desorption time of 10 min was sufficient to ensure total desorption and no peaks appeared in the chromatogram corresponding to the analysis of the adsorbent tube prior to re-use. Fig. 4 shows the dependence of the analyte recovery on the cryotrap temperature. Usually, a cryofocusing trap is needed before GC analysis, to provide narrow bands entering the capillary columns, and thus good resolution [8]. Due to the weak adsorption of the glass

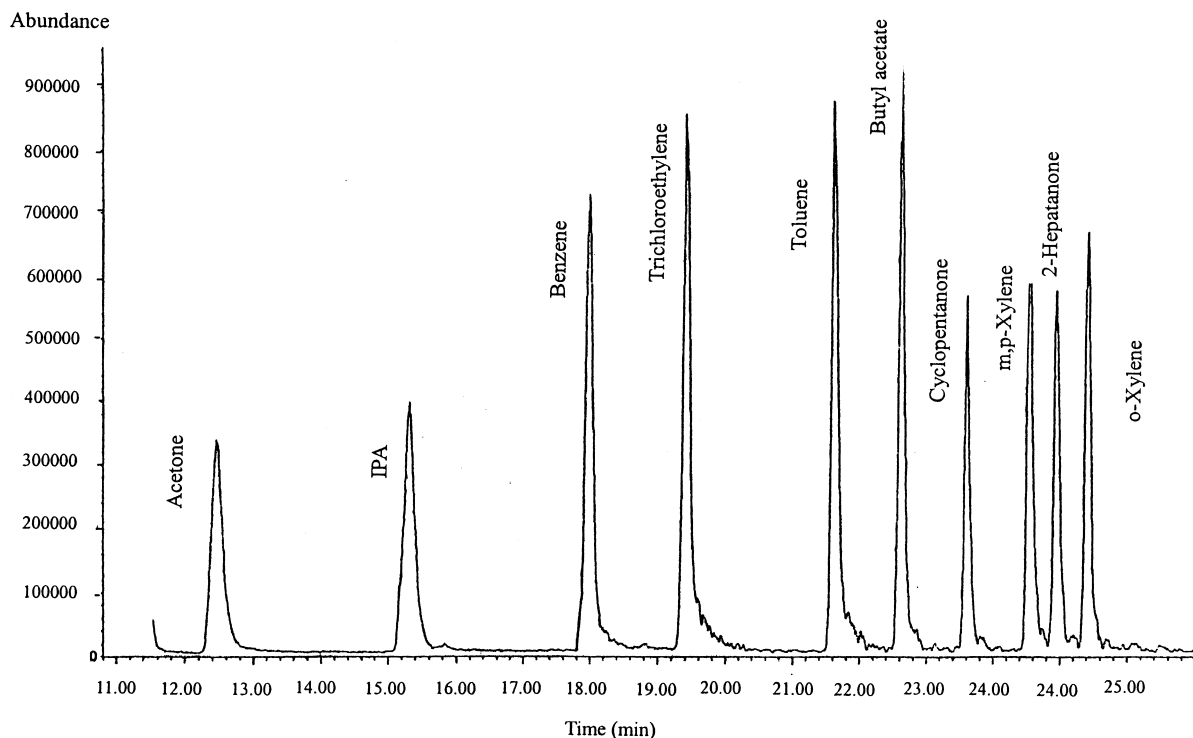


Fig. 1. Chromatogram of the 10 VOCs reference standard acquired with GC–MS under the optimized conditions. Chromatographic conditions are described in the Experimental section.

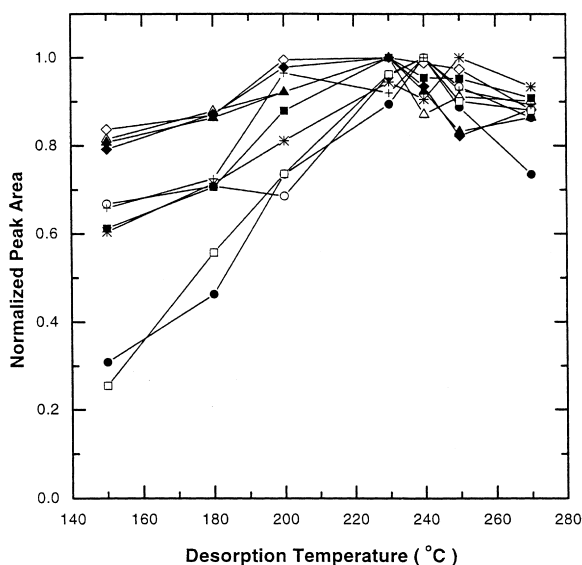


Fig. 2. Dependence of analyte recovery on the desorption temperature for the multibed adsorbent tube. The peak area has been normalized to the maximum value for each individual compound. Symbols: (○) acetone; (●) IPA; (△) benzene; (▲) trichloroethylene; (◇) toluene; (◆) butyl acetate; (□) cyclopentanone; (■) *m,p*-xylene; (+) 2-heptanone; (*) *o*-xylene. Other conditions as in the Experimental section.

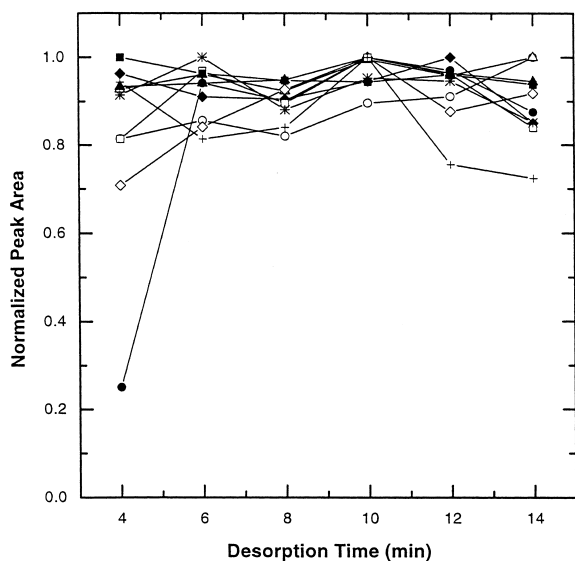


Fig. 3. Dependence of analyte recovery on the desorption time for the multibed adsorbent tube. Peak area and notation as in Fig. 2. Other conditions as in the Experimental section.

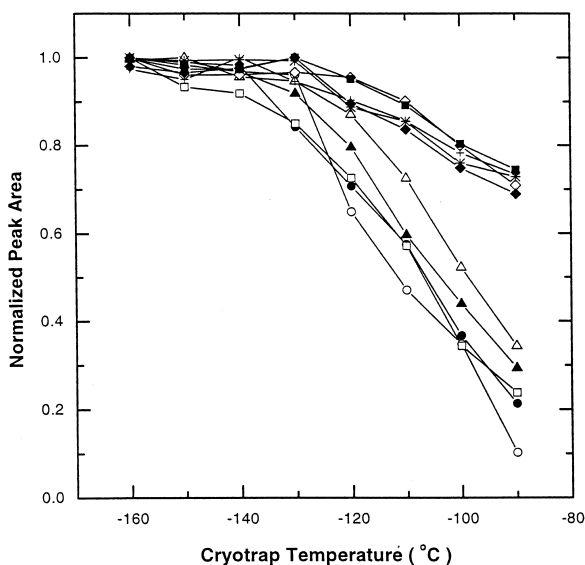


Fig. 4. Dependence of analyte recovery on the cryotrap temperature. Peak area and notation as in Fig. 2. Other conditions as in the Experimental section.

beads with analytes in the cryotrap tube, the cryotrap temperature was highly correlated with the efficiency of the cryofocusing system. As a conclusion, -150°C was considered as the optimized cryofocusing temperature for further studies. Fig. 5 shows the dependence of the analyte recovery on the desorption time of the cryofocusing desorber at 200°C . The profile indicates that the desorption time has little influence on the desorption efficiencies for acetone, benzene, and trichloroethylene and the desorption efficiencies for the other analytes reach plateau within 7 min. Therefore, a desorption time of 7 min was selected for best recovery and further studies.

The recovery, method detection limit (MDL), and reproducibility of the target compounds are listed in Table 1. Recovery for the standards from the collection tube were determined from three replicate experiments, using a standard gas containing 24–47 ppb of each compound. The average recoveries of all the analytes range from 94 to 101%. The MDLs were calculated as three times the standard deviation of seven replicate measurements at 1–4 ng, close to the blank concentration. The system exhibited detection capabilities at the ppb level. The reproducibility expressed in terms of the coefficient of variation (C.V.) was found to be in the range 2.6–6.5%.

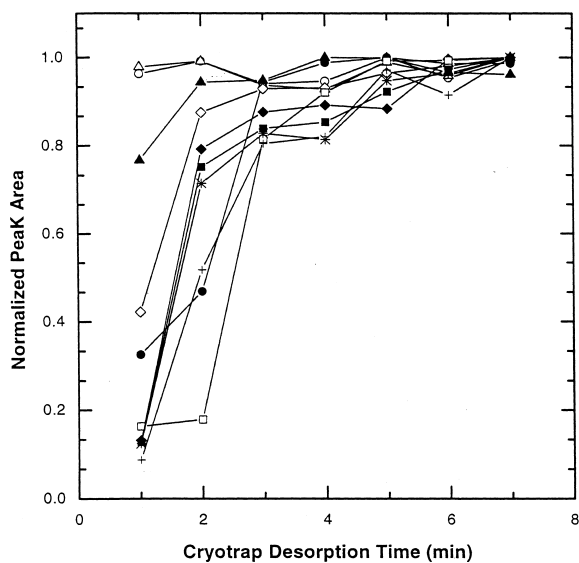


Fig. 5. Dependence of analyte recovery on the desorption time of the cryofocusing desorber. Peak area and notation as in Fig. 2. Other conditions as in the Experimental section.

Table 1
Summary of recovery yield, method detection limit, and reproducibility

Compound	Recovery ^a (%)	MDL ^b (ppb)	Reproducibility ^c (C.V.) (%)
Acetone	97	0.42	3.1
IPA	95	0.56	6.4
Benzene	101	0.89	3.7
Trichloroethylene	98	0.54	5.7
Toluene	97	0.44	4.2
Butyl acetate	99	0.31	2.6
Cyclopentanone	94	0.73	6.5
<i>m,p</i> -Xylene	97	0.60	5.5
2-Heptanone	100	0.65	5.1
<i>o</i> -Xylene	96	0.87	4.1

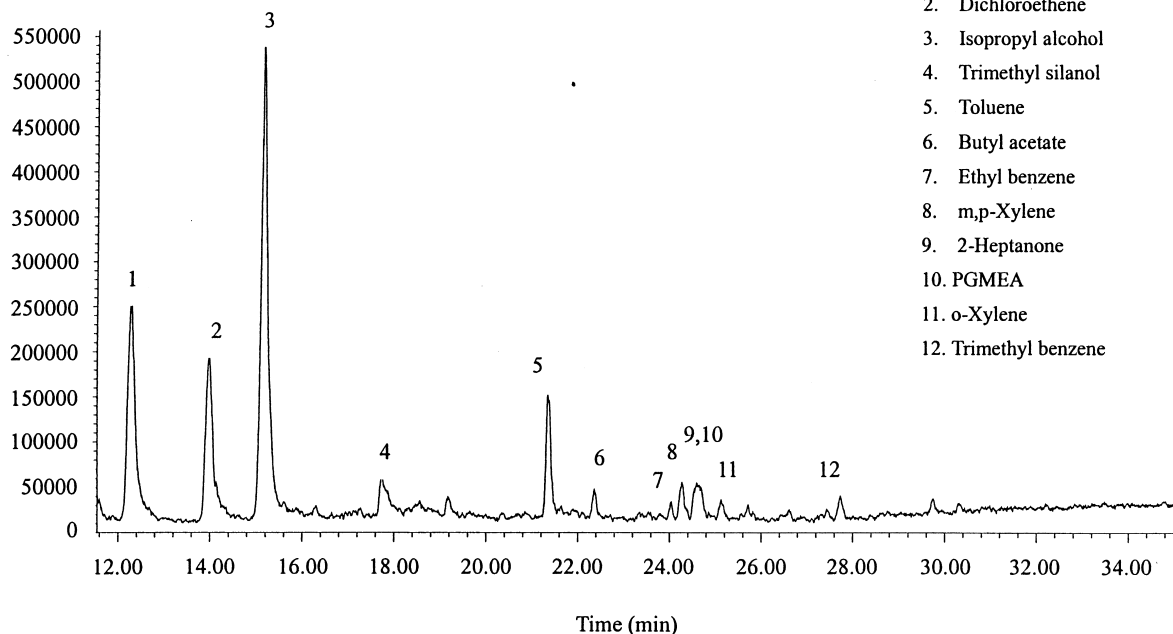
^a Three replicate measurements were used.

^b Sampling volume was 1 L.

^c Seven replicate measurements were used. C.V., coefficient of variation.

Under optimization of the analytical method, all analytes exhibited good linearity over two orders of

Abundance



1. Acetone
2. Dichloroethene
3. Isopropyl alcohol
4. Trimethyl silanol
5. Toluene
6. Butyl acetate
7. Ethyl benzene
8. *m,p*-Xylene
9. 2-Heptanone
10. PGMEA
11. *o*-Xylene
12. Trimethyl benzene

Fig. 6. Total ion chromatogram of 600 mL air sample collected with adsorbent tubes in semiconductor factory A on 23 May 2000.

magnitude. The linear correlation coefficients, r^2 , were better than 0.996.

Exposure to VOCs in the workplace is subject to regulations and has to be monitored regularly. The air samples were collected from class-100 clean rooms at two semiconductor fabrication facilities (A and B). Fig. 6 presents a typical chromatogram for VOCs in workplace air. The results show that 12 compounds have been detected and seven of them could be well quantified with the established method. As an example, the temporal variations in the analyte concentrations observed at factory A are shown in Fig. 7. In factory A, the results show that concentrations of acetone and IPA were the two highest among those of VOCs detected at any time. Other VOCs, such as toluene, butyl acetate, 2-heptanone, and xylene, were present at 10–200 ppb levels. The peak concentrations of acetone and IPA in the workplace air occurred between 7 and 10 a.m. and between 1 and 6 p.m., indicating that a significant amount of VOCs were emitted during working hours. Acetone, IPA, toluene, and 2-heptanone were the four major variable compounds during the day. The fluctuations of their concentrations were possibly due to the improper use of organic solvents and thus intermittent release of these species during operation. Similar to factory A, acetone and IPA were the two major contaminants during the day in

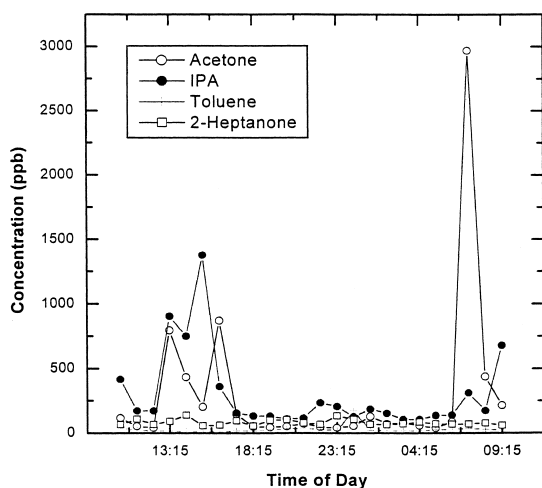


Fig. 7. Hourly measurements of major VOCs determined with adsorbent tubes in semiconductor factory A during the period 23–24 May 2000.

Table 2

Average and range of VOC concentrations in the workplace air of semiconductor foundries in May–June 2000

Compound	Average (ppb)	Range (ppb)
Acetone	251	39–2970
IPA	356	105–1378
Benzene	ND	ND
Trichloroethylene	ND	ND
Toluene	31	12–172
Butyl acetate	18	10–27
Cyclopentanone	ND	ND
<i>m,p</i> -Xylene	54	15–36
2-Heptanone	22	17–138
<i>o</i> -Xylene	20	11–34

ND, not detectable.

factory B (data not shown). Most of the contaminants found in factory A were also detected in factory B, but with a slightly different concentration profile. The average and range of VOC concentrations in the workplace air of factories A and B are listed in Table 2. As seen in Table 2, the concentration of total VOCs in the workplace air ranged from 10 to 3000 ppb, of which more than 80% was attributed to acetone and IPA. The monitoring showed that concentrations of VOCs in the class-100 rooms were significantly higher than those in outdoor air [9,10]. Trimethyl silanol, a potentially toxic compound, was identified in the air samples, though not quantified. Further development of a method for the quantification of silanols is required.

4. Conclusion

A method for the qualitative and quantitative analysis of volatile organic compounds (VOCs) in the air of class-100 clean rooms at semiconductor fabrication facilities has been developed with high precision and good linearity. The thermal desorption method with multisorbent tubes, including Carbo-pack B, Carbo-pack C, and Carbosieve SIII, has been successfully applied to the analysis of VOCs in workplace air. Optimal adsorption/thermal desorption conditions have been determined and analysis can be completed in 40 min. The system has been demonstrated to be capable of measuring the temporal variations of trace levels of VOCs with a short time resolution.

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