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DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN PALM-BASED POLYURETHANE FOAMS USING STATIC HEADSPACE GAS CHROMATOGRAPHY MASS SPECTROMETER

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ABSTRACT

Volatile organic compounds (VOC), in combination with other environmental factors, are potential health and environmental hazards. Studies have shown that an abundance of VOC were released from home and personal care products, building and transportation materials. A direct method employing a static headspace sampler (HS), a gas chromatography (GC) and a mass spectrometer detector (MS) has been developed and validated for semi-quantitative analysis of VOC emitted from palm-based polyurethane (PU) foams. In this method, PU foams were heated and the volatiles were extracted and then analysed by GC-MS. The conditions of the HS-GC-MS system were optimised to achieve high recovery and sensitivity. Method validation was performed and it demonstrated an average recovery of 95% and 89% for DABCO 33LV and NIAX A1 (volatile amines), respectively. The limit of detection was 0.66 ppm while the limit of quantitation was 1.32 ppm. Analyses performed on commercial and palm-based PU foams showed that the concentration of overall VOC detected did not exceed the limits set by car manufacturers (maximum at 50 ppm). The VOC detected were mainly DABCO 33LV and NIAX A1. The method developed was found to be effective and considered rapid without laborious sample preparation and can be used by PU manufacturers to monitor the level of VOC in their products.

Keywords: static headspace, volatile organic compounds, polyurethane foams, volatile amines, gas chromatography.

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INTRODUCTION

Volatile organic compounds (VOC) are components which, at room temperature, are susceptible to be released from materials or products in the form of gases. VOC, in combination with other environmental factors, can cause damage to human and environment. Studies have shown that an abundance of VOC were released from home and personal care products, building and transportation materials (Crump *et al.*, 1995).

Plastic materials are viewed as the culprits for the VOC emission in vehicle cabins. Fregni and Fanget (2010) reported that approximately 13 kg of polyurethane (PU) foams are used in a car; applications range from seat cushions to head rests, instrument panel foams and headliners. These materials are regarded as potential causes of the VOC emissions.

There are significant numbers of established methods for determining VOC emission. The US Environmental Protection Agency (EPA, 1996) has

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established the EPA Method 8260B to determine the VOC in a variety of solid waste matrices.

Pfannkoch and Whitecavage (2000) compared several techniques to analyse volatiles in solids. Samples of polyethylene packaging were analysed using Static Headspace Gas Chromatography (HS-GC), Thermal Desorption System (TDS) and Solid Phase Microextraction (SPME) sample introduction method. The volatiles were then injected into the same gas chromatography instrument. Kusch and Knupp (2004) described a method for identification of VOC released from expandable polystyrene (EPS). Headspace-solid phase micro extraction (HS-SPME) with a 75-μm carboxen/polydimethylsiloxane fibre was used as sample preparation technique before the determination of VOC by gas chromatography-mass spectrometry (GCMS) was carried out.

Sonney *et al.* (2002) reported two methods that were used to determine VOC in a material. The first method, developed by Volkswagen (VW), was based on static headspace. The sample was introduced in a headspace vial and equilibrated at 120°C for 5 hr. An aliquot of the headspace gas was then introduced into a GC equipped with flame ionisation detector (FID). Results were reported in μg carbon per gramme sample (μg C g^{-1}) and were based on an external calibration, using acetone as the calibration substance. A modification of this method was studied as well in which the FID detector was replaced by a mass spectrometer (MS) and the acetone was replaced by perdeuterotoluene (C7D8). Results were reported in μg C7D8 per gramme sample. The other method, developed by Daimler Chrysler, was based on a dynamic headspace method. The sample was heated at 90°C and purged for 30 min with an inert gas. The volatile substances emitted during the process were transferred to a GC, where they were first cryofocused at -150°C in a cryogenic trap before injection by quickly heating the trap to 280°C. The focused substances were separated by a capillary column and detected by MS. Results were reported in ppm, using toluene as the calibration substance.

Fabio *et al*. (2002) found that the major contributor of VOC from PU foams was amine catalyst used in the formulation. VOC, notably volatile amines, were extracted using headspace sampler (HS) before being analysed by GC and detected by MS.

In this study, a method employing static headspace sampling prior to GC for semi-quantitative analysis of VOC, notably volatile amines in PU foams, was developed and validated. Optimisation of the headspace conditions was performed to enable maximum recovery of VOC from the PU foams. The chromatographic performance of the GC was made more efficient by investigation through some selected capillary columns. The developed method was validated for the detection system used and was further applied for the determination of VOC, notably volatile amines, in PU foams.

MATERIALS AND METHODS

Materials

Palm-based PU foams were obtained from the Polymer and Composite Group, Advanced Oleochemical Technology Division, Malaysian Palm Oil Board (MPOB). There were two types of PU foam *i.e.* high resilient PU foams (density of 45-50 kg m^{-3}) and viscoelastic PU foams (density = 60-70 kg m^{-3}). The methylene diphenyl diisocyanate (MDI)-based PU foams were produced by handmixing and box foams; and were crushed. All of the foams were aged at room temperature for at least seven days before analysis (ASTM D3574).

Commercial PU foams were collected from four local PU foam manufacturers (A, B, C and D). The foams were TDI-based viscoelastic PU foams and were produced on continuous slabstock machines. The foams from manufacturers A, B and D were high resilient PU foams while the foams from manufacturer C were viscoelastic type.

Amine standards, DABCO 33LV (A33) and NIAX A1 (A1), were purchased from Aldrich (St Louis, MO). The A33 is a 33% (in weight) solution of triethylenediamine in dipropylene glycol while A1 contains 70% of bis (2-dimethylaminoethyl) ether. Internal standard, toluene-d8, was purchased from Acros Organics (New Jersey, USA).

HS-GC-MS Conditions

Static HS-GC-MS analyses were carried out using an Agilent Technologies GC model 7890A equipped with an Agilent Technologies HS model G1888 and an Agilent Technologies inert MS detector model 5975C with Triple-Axis Detector. The Headspace sample was collected through a 3 ml sample loop and was automatically transferred to the GC via a heated transfer line. A split/splitless GC injector equipped with a direct 0.2 mm i.d. glass liner was used. The system operation, as well as data acquisition, collection, and evaluation, were accomplished using the Agilent Enhanced MSD ChemStation software.

Two chromatographic columns of the fused silica capillary type were investigated. These were ZB-1701 (30 m × 0.25 mm i.d. × 1.00 μm film thickness, Zebron) and HP-5ms (30 m × 0.25 mm i.d. × 1.00 μm film thickness, J&W Scientific) columns. The ZB-1701 is a low/medium polar column while HP-5ms is a non-polar column. The optimum GC conditions were achieved using a ZB-1701 column with a 1:1 split injection at 230°C.

Sample Preparation

Samples were taken from the centre of the foam bun. Using a cutting tool, 0.5 g of the foam was cut into small pieces and was then placed in a 20 ml headspace vial with PTFE/silicone-coated septa and closed with an aluminium crimp cap. About 50 µg of the internal standard solution of toluene-d8 was added into the vial.

Sample Analysis

All the samples were analysed using identical chromatographic conditions (*Table 1*) and toluene-d8 was spiked into all samples as an internal standard. The sample, placed in a vial, was heated at 120°C for 60 min in the headspace oven. The headspace sample was then transferred to the GC before being detected by MS detector. The semi-quantitative results were obtained via an internal standard procedure. The sum of the areas of all volatiles was compared with the area of a known concentration of the internal standard. MS responses were assumed to be identical for all identified components.

RESULTS AND DISCUSSIONS

This study was conducted based on the standard method GMW8081:2005, *Static Headspace GC-MS for Interior Materials* (GM, 2005). The test method was used for the semi-quantitative determination of emissions for interior materials via HS-GC-MS. Through emission spectra, emissions of interior materials can be compared, resultant emissions can be identified and relative emissions can be calculated.

Method development has to be performed for A33 and A1 in order to achieve the preferred recovery, sensitivity and validation. Studies by Fabio *et al*. (2002) showed that the major contributor of VOC from PU foams was amine catalyst additive, which is generally used in PU formulation. Preliminary studies done on palm-based and commercial PU foams also showed that VOC detected were A33 and A1.

Optimisation of HS-GC-MS Conditions

The conditions of the HS-GC-MS system were optimised by studies done on parameters such as type of column and carrier gas flow. The total ion current (TIC) chromatograms in *Figures 1*, *2* and *3* show that the low/medium polar ZB-1701 column gave greater sensitivity than the non-polar HP-5ms column. Signal-to-noise ratio (S/N) obtained for A33 and A1 using HP-5ms column was 7 and 9, respectively, while S/N obtained for A33 and A1 using ZB-1701 column was 42 and 49, respectively. The S/N is obtained by calculating the ratio of

TABLE 1. OPTIMISED INSTRUMENTAL CONDITIONS

Agilent HS G1888	
Carrier gas flow	20 ml min^{-1}
Vial size	20 ml
Oven temperature	120°C
Loop temperature	140°C
Transfer line temperature	160°C
Vial equilibration time	60 min
Vial pressurisation time	0.1 min
Loop fill time	0.1 min
Loop equilibration time	0.1 min
Injection time	1.0 min
Agilent GC 7890A	
Inlet temperature	230°C
Split ratio	1:1
Type of column	ZB 1701
Oven temperature	50°C (1 min) then 10°C min^{-1} to 240°C (10 min)
MSD transfer line temperature	240°C
Agilent MS 5975C	
SIM/Scan mode	Scan
Mass range	30 – 300 amu

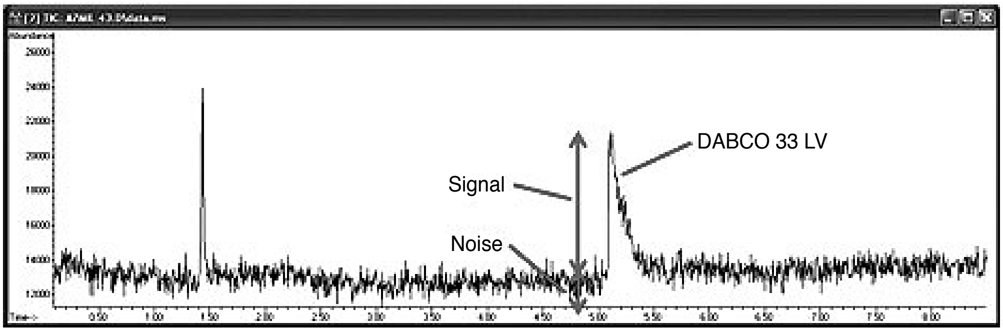


Figure 1. The total ion current chromatogram of 0.1 g of A33 using HP-5 ms column.

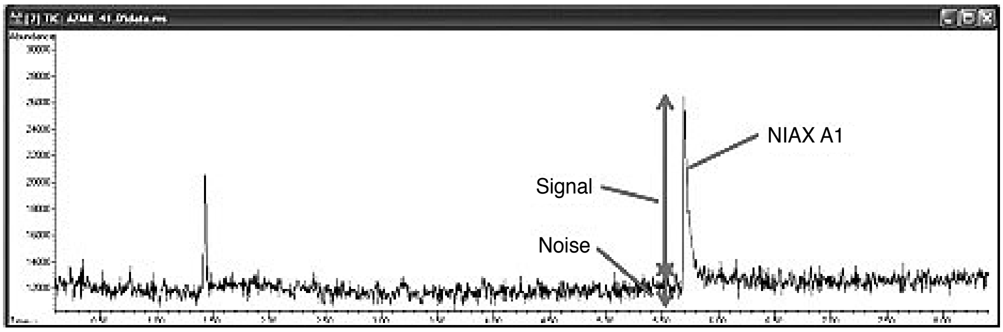


Figure 2. The total ion current chromatogram of 0.1 g of A1 using HP-5 ms column.

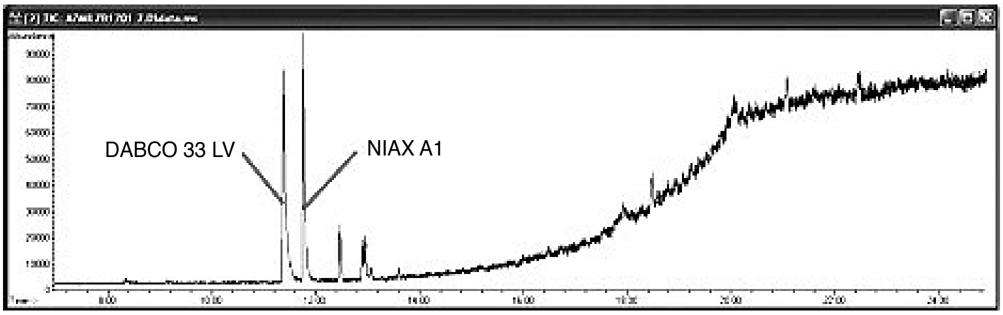


Figure 3. The total ion current chromatogram of 0.1 g of A33 and 0.1 g of A1 using ZB-1701 column.

heights between analyte and noise. The greater the S/N value, the more sensitive is the column. Furthermore, the peaks obtained using ZB-1701 column have better resolutions and separations than the peaks obtained using HP-5ms column.

For Headspace configuration, different carrier gas flows were studied to optimise the sensitivity of detection. *Figure 4* shows abundances of A33 and A1 obtained by varying the carrier gas flow. Results showed that lower carrier gas flow (20 ml min^{-1}) gave better sensitivity than higher carrier gas flow (37 and 50 ml min^{-1}). The ZB-1701 column and carrier gas flow of 20 ml min-1 were, thus, chosen for the method development since they provided a good compromise between acceptable resolution and sensitivity.

Method Validation

Static Headspace method was developed for semi-quantitative analyses of VOC in PU foam using HS-GC-MS system via internal standard procedure. Based on *ICH Harmonised Tripartite Guideline Validation of Analytical Procedures: Text and Methodology Q2(R1)* (2005), this method was validated with respect to trueness (recovery), sensitivity [limit of detection (LOD) and limit of quantitation (LOQ)], linearity, working range and repeatability using the optimised instrumental conditions in *Table 1*.

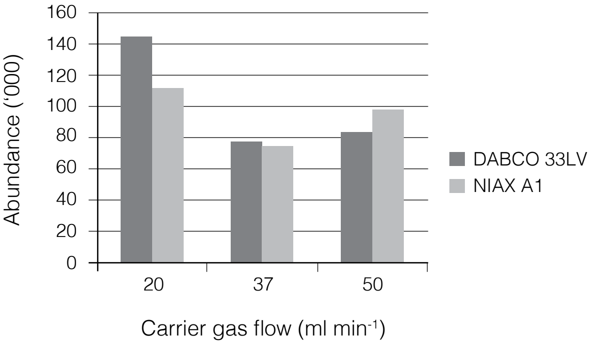


Figure 4. Abundances of A33 and A1 at different carrier gas flow.

Recovery studies were done by spiking 100 μg of A33, 100 μg of A1 and 50 μg of toluene-d8 (as internal standard) into a blank PU foam sample. Four replicates were analysed. Recovery value (in %) was obtained by calculating the ratio between concentration of analyte determined by analysis and concentration of analyte injected. An average recovery of 95% and 89% was obtained for A33 and A1, respectively.

Sensitivity is reflected by the LOD and LOQ, defined as the concentration at which $S/N \geq 3$ and $S/N \geq 10$, respectively. For the determination of LOD and LOQ, several analyses were done with the amount of A33 spiked into PU was varied between 0.5 and 4.0 ppm. The S/N was then measured and calculated. The LOD and LOQ determined was 0.66 ppm and 1.32 ppm, respectively.

The working range and the linearity of the method were assessed by constructing the calibration curves, where the relationship between detector responses and the concentration of A33 and A1 injected was studied. A series of concentrations of A33 and A1 ranging from 10 to 60 ppm were spiked into 0.5 g of foam sample. The spiked samples were then analysed using the Static Headspace method.

Figures 5 and *6* show the calibration curve for A33 and A1, respectively. Good linearity was observed for both A33 and A1 with a correlation coefficient (R^2) of 0.9954 and 0.9910, respectively.

The repeatability of the method was determined by analysing six replicates of both A33 and A1 at 30 ppm by the same analyst and using the same instrumentation. The resultant coefficient of variation (% CV) obtained for A33 and A1 was 11.4% and 12.8%, respectively, which are considered acceptable (<15%). Overall, the validation data confirmed the sensitivity and usefulness of the Static Headspace method to determine VOC in PU foams.

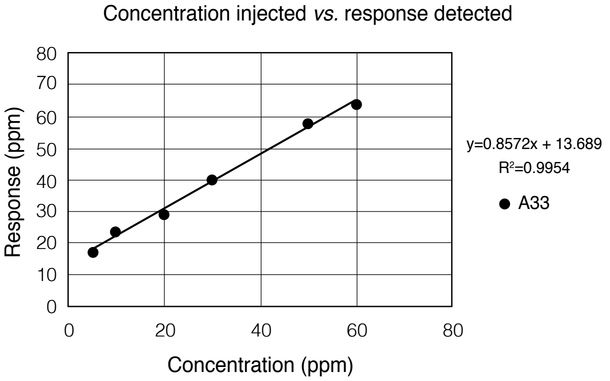


Figure 5. Calibration curve for A33.

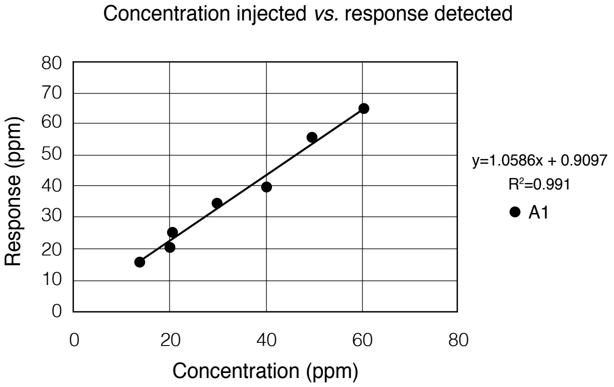


Figure 6. Calibration curve for A1.

Analyses of Commercial and Palm-based PU Foams

The developed Static Headspace method was applied for semi-quantitative analysis of VOC in commercial and palm-based PU foam samples. Quadruplicate determinations were performed for each foam sample. The results shown in *Table 2* and *3* indicated that the overall VOC detected were well below the Original Equipment Manufacturer (OEM) limits of 50 ppm. The standard deviations of quadruplicate determinations of each foam sample were relatively low when compared to the overall VOC values.

The VOC detected in the commercial and palm-based PU foams were generally volatile amines (A33 and A1). The TIC chromatogram in *Figure 7* shows the presence of A1 in commercial PU foam A3 while the TIC chromatogram in *Figure 8* shows the presence of A33 and A1 in palm-based PU foam HR 16#1. The compounds were identified based on the consultation of NIST08 library. *Figures 9*, *10* and *11* show the MS spectra of the peaks at 5.9, 11.3 and 11.7 which correspond to toluene-d8, A33 and A1, respectively. The library database showed good match for the three compounds detected. These results are in agreement with the fact that A33 and/or A1 were used in a small amount (0.1%-0.2% weight) in the PU foam formulation.

Typical components of PU foam formulations are diisocyanates, polyols and a number of ancillary chemicals and processing aids. These include reactive amine catalysts, cross-linkers, surfactants, water (as blowing agent), chain extenders and fillers (Allport *et al.*, 2003). The basic reaction between a diisocyanate and a polyol produces a PU addition polymer with the liberation of heat. It was reported that the foam temperature was close to 100°C when cell opening occurred (Klempner and Sendijarevic, 2004). Therefore, it can be assumed that during the production of PU foams, most of the VOC were evaporated from the system. However, reactive amine catalysts such as A33 and A1 were regenerated at the end of the process. This explains why A33 and A1 were detected in the foams.

TABLE 2. DETERMINATION OF VOLATILE ORGANIC COMPOUNDS (VOC) CONCENTRATION IN COMMERCIAL POLYURETHANE (PU) FOAM SAMPLES OBTAINED FROM FOUR DIFFERENT PU FOAM MANUFACTURERS (A, B, C and D)

Foam designation	Foam properties		Concentration of VOC, ppm (mean ± SD)			
	Type	Density (kg m^{-3})	A33	A1	Others	Overall
Foam A1	High resilient	60 - 70	11.8	ND	ND	**11.8** ± 3.4
Foam A2			13.1	ND	ND	**13.1** ± 2.4
Foam A3			10.2	ND	ND	**10.2** ± 1.7
Foam A4			10.0	ND	ND	**10.0** ± 1.3
Foam B1		25	9.7	ND	ND	**9.7** ± 1.3
Foam C1	Viscoelastic	60 - 90	0.9	4.1	ND	**5.0** ± 1.6
Foam C2			1.3	4.0	ND	**5.3** ± 1.8
Foam C3			0.3	3.8	ND	**4.1** ± 1.7
Foam D1	High resilient	20 - 40	10.2	ND	ND	**10.2** ± 1.8
Foam D2			9.0	ND	ND	**9.0** ± 0.8
Foam D3			3.5	ND	ND	**3.5** ± 1.0
Foam D4			7.4	ND	ND	**7.4** ± 1.8

Note: A33 - DABCO 33LV. A1 - NIAX A1. ND - not detected.

TABLE 3. DETERMINATION OF VOLATILE ORGANIC COMPOUNDS (VOC) CONCENTRATION IN PALM-BASED POLYURETHANE (PU) FOAM SAMPLES PRODUCED IN ADVANCED OLEOCHEMICALS TECHNOLOGY DIVISION, MPOB

Foam designation	Foam properties		Concentration of VOC detected, ppm (mean ± SD)			
	Type	Density (kg m^{-3})	A33	A1	Others	Overall VOC
HR14 #3	High resilient	45 - 50	0.5	8.9	ND	**9.4 ± 2.9**
HR16 #1			0.9	8.8	ND	**9.7 ± 1.0**
HR1-R3			ND	4.1	ND	**4.1** ± 1.2
BM 3			0.2	3.8	ND	**4.0** ± 0.7
BM 5			ND	5.5	ND	**5.5** ± 0.9
BM 7			ND	6.1	ND	**6.1** ± 1.2
PC 0			ND	2.5	ND	**2.5** ± 0.5
PC 5			ND	4.6	ND	**4.6** ± 0.7
PC 3			ND	3.2	ND	**3.2** ± 0.5
PC 7			0.2	2.6	ND	**2.8** ± 0.5
VE	Viscoelastic	60 - 70	0.1	1.7	ND	**1.8 ± 0.3**
VE19			ND	2.0	ND	**2.0 ± 0.7**
VE20#2			ND	ND	ND	**ND**
VE25			ND	ND	ND	**ND**
VE27			ND	ND	ND	**ND**
VE Q10M2			1.7	13.9	ND	15.6 ± 3.2

Note: A33 - DABCO 33LV. A1 - NIAX A1. ND - not detected.

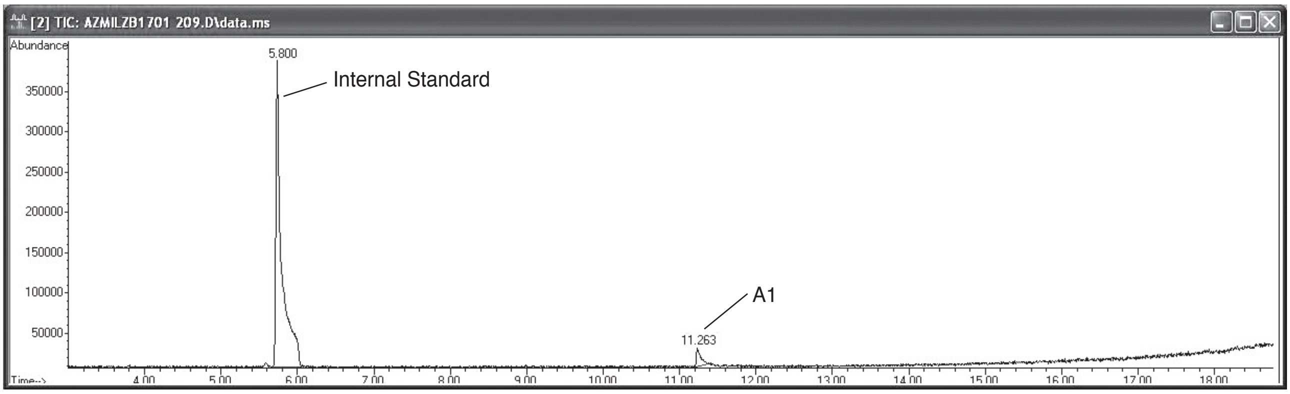


Figure 7. The total ion current chromatogram of commercial polyurethane foam A3.

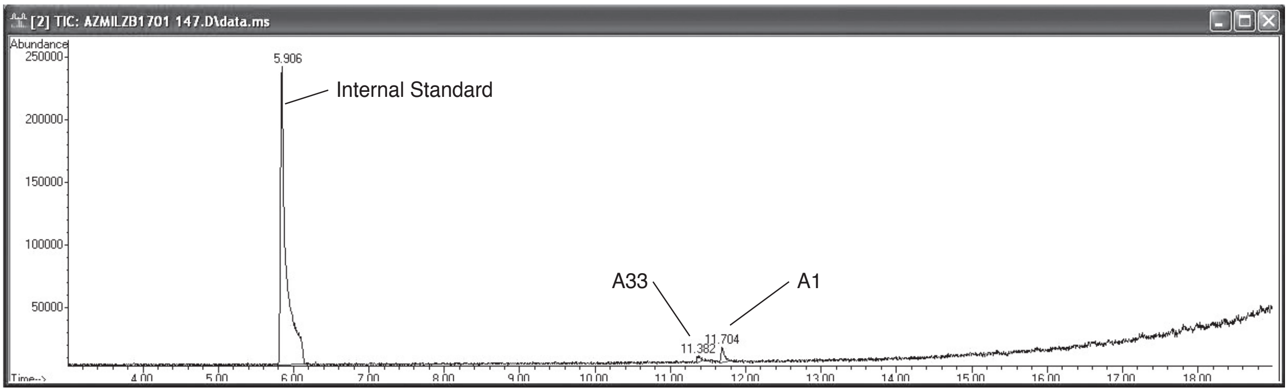
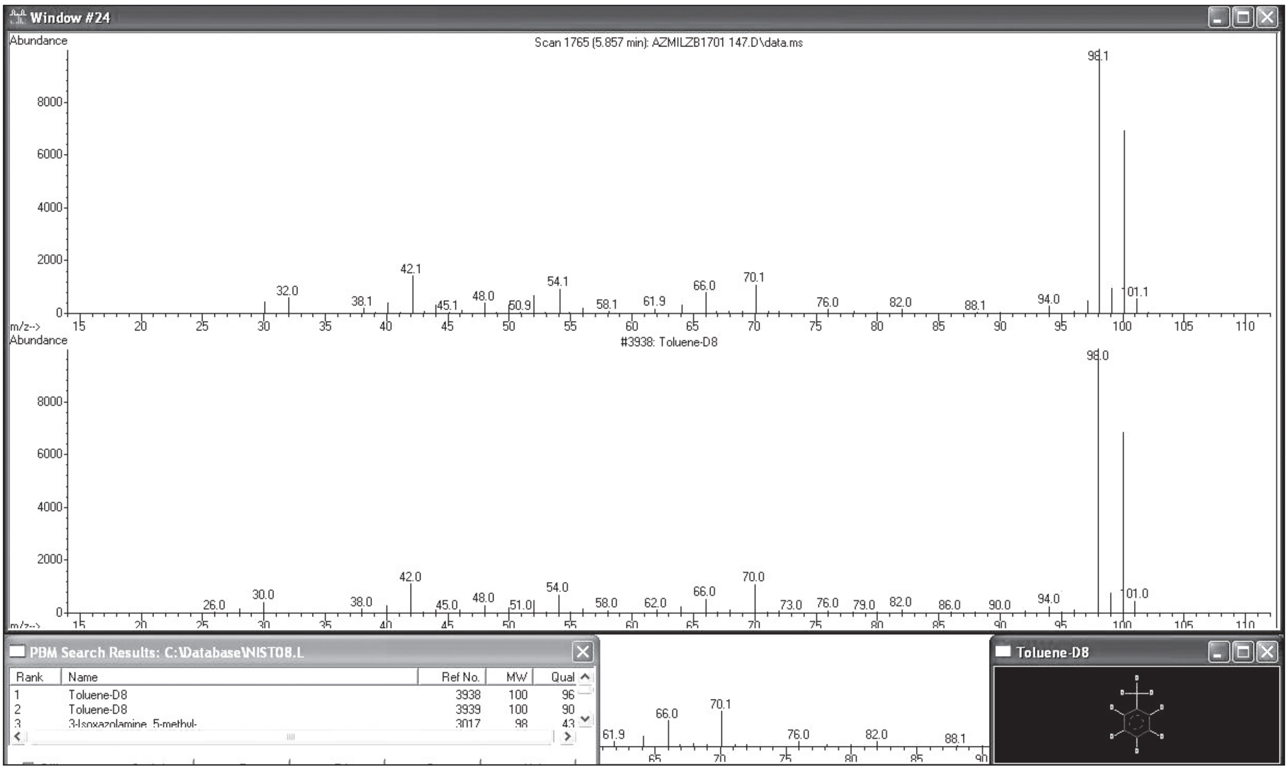


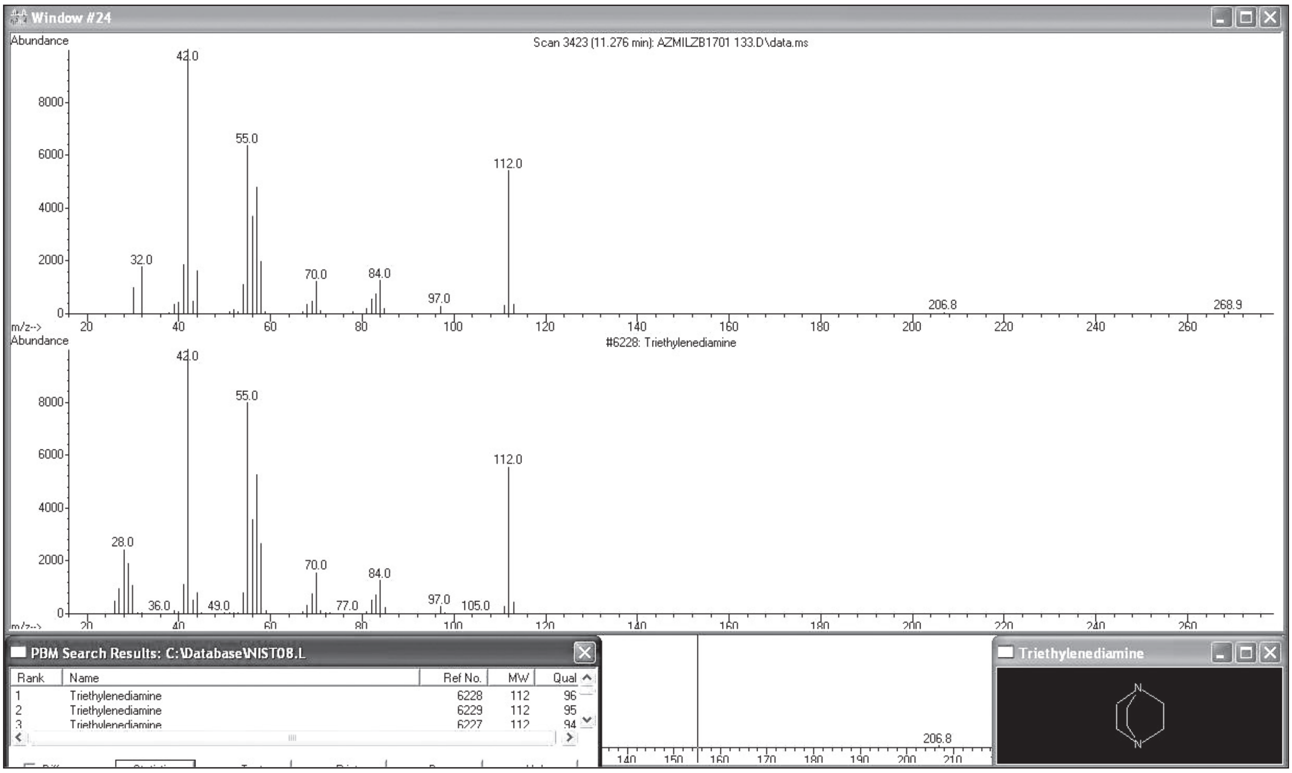
Figure 8. The total ion current chromatogram of palm-based polyurethane foam HR 16#1.



PBM Search Results: C:\Database\NIST08.L

Rank	Name	Ref No.	MW	Qual
1	Toluene-D8	3938	100	96
2	Toluene-D8	3939	100	90
3	3-Isoxazolamine, 5-methyl-	3017	98	43

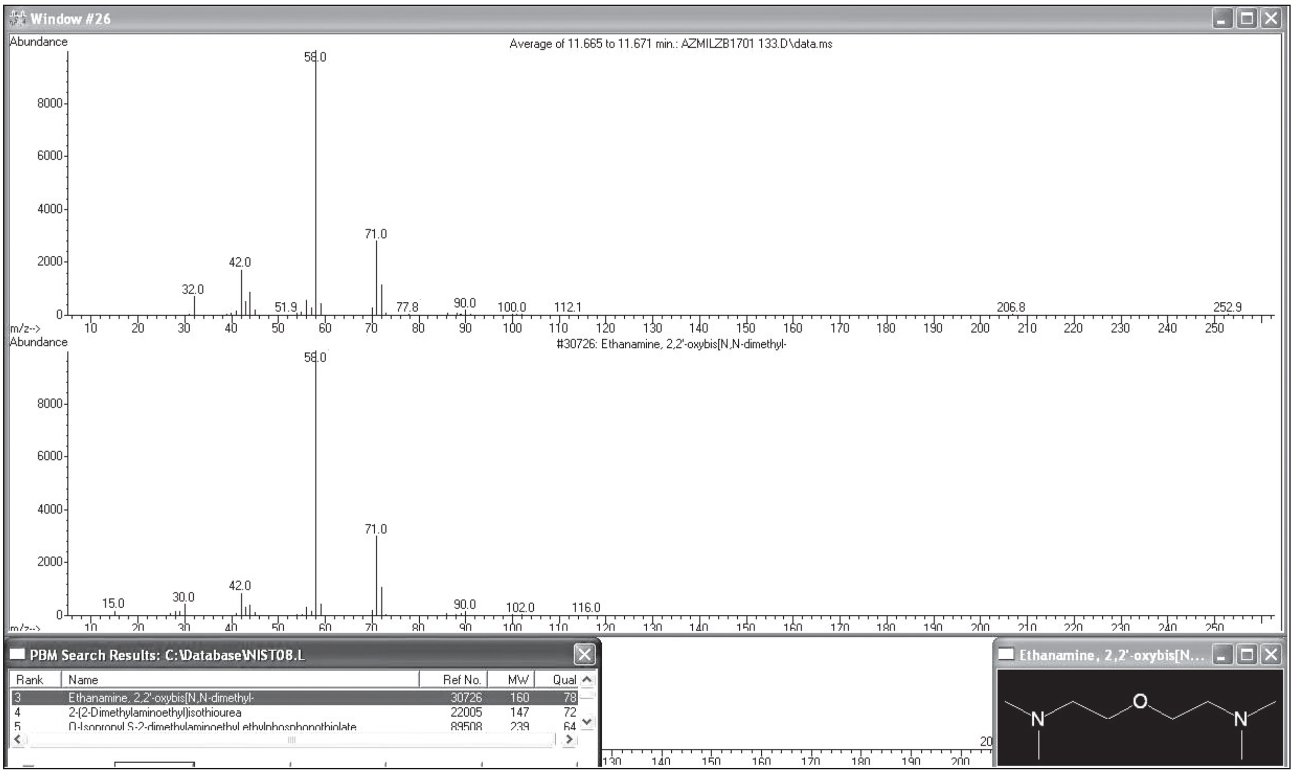
Figure 9. Mass spectrometer spectrum of toluene-d8.



PBM Search Results: C:\Database\NIST08.L

Rank	Name	Ref No.	MW	Qual
1	Triethylenediamine	6228	112	96
2	Triethylenediamine	6229	112	95
3	Triethylenediamine	6227	112	94

Figure 10. Mass spectrometer spectrum of A33.



PBM Search Results: C:\Database\NIST08.L

Rank	Name	Ref No.	MW	Qual
3	Ethanamine, 2,2'-oxybis[N,N-dimethyl-	30726	160	78
4	2-(2-Dimethylaminoethyl)isothiourea	22005	147	72
5	O-Isopropyl S-2-dimethylaminoethyl ethylphosphonothiolate	89508	239	64

Figure 11. Mass spectrometer spectrum of A1.

CONCLUSION

The Static Headspace method was developed and has proven able to provide an effective mean for simple and rapid quantitative analysis of VOC, notably volatile amine additives, in PU foams. The advantage of this method over other methods that employ TDS and SPME is that the sample preparation step and the total analysis time are much shorter and it is fully automated and solvent-free. This method offers satisfactory recovery and sensitivity of A33 and A1 for MS as a GC detector. Analysis of samples using the validated method showed that A33 and A1 were emitted and quantitated at low concentration. This method can be used by PU foam manufacturers to monitor the VOC emission in their products.

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