

Determination of volatile organic compounds in different microenvironments by multibed adsorption and short-path thermal desorption followed by gas chromatographic–mass spectrometric analysis

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Received 21 March 2005; received in revised form 22 August 2005; accepted 26 August 2005

Available online 15 September 2005

Abstract

A multiphase assurance approach was developed for the accurate and precise determination of volatile organic compounds (VOCs) in different microenvironments. This approach includes (i) development of a method including adsorption of VOCs onto a multisorbent media followed by short-path thermal desorption (SPTD) pre-concentration and gas chromatography (GC) coupled to a mass spectrometry (MS) quantification, (ii) validation of the sampling and analytical method and (iii) validation of the data using a multidimensional procedure. Tenax TA and Carboxen B sorbent combinations were used to collect 102 individual VOCs ranging from C5 to C12. Method parameters including thermal desorption temperature, desorption time and cryofocusing temperature were optimized. The average recoveries and method detection limits (MDL) for the target analytes were in the range 80–100% and 0.01–0.14 ppbv, respectively. The method also showed good linearity ($R^2 > 0.99$) and precision (<8%) values. Validation of the method was performed under real environmental conditions at a gas station, in an office and a residential household to examine the influence of variation in meteorological conditions such as temperature and relative humidity and a wide range of VOC concentrations. The sampling and analytical method resulted in successful determination of VOC in different microenvironments. Finally, validation of the data was performed by assessing fingerprint and time series plots and correlation matrices together with meteorological parameters such as mixing height, wind speed and temperature. The data validation procedure provided detection of both faulty data and air pollution episodes.

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Keywords: Volatile organic compound; Multisorbent adsorption; Short-path thermal desorption; Gas chromatography–mass spectrometry

1. Introduction

Measurement of volatile organic compounds (VOCs) in different microenvironments has received significant attention over the past few years because of direct and indirect impacts of individual VOCs on human health and ecosystem. Many VOCs are either known or suspected carcinogens and some have toxic effects [1–3]. The 1990 US Environmental Protection Agency (EPA) Clean Air Act [4] includes 189 hazardous air pollutants (HAP) that are mostly VOCs. Volatile organic compounds also play a critical role in formation of tropospheric ozone [5,6].

Ambient VOC data can be used as input to receptor models to apportion pollution sources or to photochemical models to assess the effectiveness of various emission control measures [7]. In both cases accurate and reliable data are essential because the resulting source contributions or consequence analysis are dependent on the quality of these ambient data. Indoor data, on the other hand, can be used in personal exposure studies, health risk assessments and workplace environment monitoring [8–10]. Therefore, accurate and precise measurements of VOCs are crucial for the determination of effective mitigation measures and VOC management plans.

There are different methods for determination of VOCs in air. Collection of VOCs on active or passive sorbents with subsequent preconcentration by thermal desorption is one of the most popular methods used today [11–21]. Adsorption onto

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solid sorbents provides advantages such as higher sensitivity due to selectively collecting the compounds and ease of use because of the small size of sampling apparatus. Sampling onto adsorbent tubes can also achieve high recovery of polar and reactive compounds, which can pose problems for whole air samples collected in canisters [22]. Active sampling is preferred when time resolved data are required.

Usually adsorption tubes were used with single sorbent. Tubes with more than one sorbent, packed in order of increasing sorbent strength have become popular in recent years and they are used to facilitate quantitative retention and desorption of VOCs over a wide volatility range [23–27]. However, method parameters, particularly, breakthrough and storage stability should be evaluated for the multi sorbent adsorption tubes [28]. As the data given in the literature on the performance characteristics of sorbents are mostly for single sorbents and are limited for multisorbent media combinations, a detailed evaluation of the sampling and analytical method is required for new sorbent combinations.

Thermal desorption provides enhanced sensitivity and it has an advantage over solvent desorption in the non-use of solvent, with consequent implications for laboratory safety and waste disposal [28–31]. Short-path thermal desorption (SPTD) provides maximum sensitivity by minimizing artifacts, losses and carry-over effects [32].

This research was aimed at the development of a multiphase assurance approach for the accurate and precise determination of VOCs in different microenvironments. This approach includes (i) development of a method including adsorption of VOCs onto a multisorbent media (Tenax TA and Carboxen B) followed by short-path thermal desorption (SPTD) preconcentration and gas chromatography coupled to a mass spectrometry (GC–MS) quantification, (ii) validation of the sampling and analytical method under variety of conditions and (iii) validation of the data through a multidimensional procedure.

The performance of the method depends on many factors, including target compounds (e.g., concentration, species and mixture), the method (e.g., sorbent selection, procedures for conditioning, desorption, separation and analysis of VOCs) and meteorological conditions present during sampling (e.g., temperature and humidity). A comprehensive performance evaluation of the method including an assessment of blanks, method detection limit (MDL), precision, linearity, collection efficiency in terms of retention efficiency and breakthrough, recovery and storage stability was conducted in the laboratory and the field under a wide range of conditions. Field validation studies were conducted at a gas station and two indoor environments. One of the microenvironments used in the study was an office building and the other was a residential building. Optimal desorption and analysis conditions were suggested.

There are few limited data available for speciated VOCs in Turkey. The method was utilized for the collection of 411 time and space resolved data in Ankara, the capital of Turkey, in the summer of 2003 and the winter of 2004. The measurement of speciated VOCs in indoor air was performed for the first time in Turkey. A multidimensional data validation procedure was developed and applied to this data.

2. Experimental

2.1. Reagents, supplies and equipments

A gas phase mixture of VOCs including 148 individual compounds ranging from C2 to C12 was supplied by Environment Technology Center, Environment Canada (Ottawa, Canada). A calibration gas containing 2–20 $\mu\text{g m}^{-3}$ of each compound was prepared in a pressurized 15-L SUMMA polished canister by mixing standards having purity of 98% or higher and seven different stock gas mixtures that were purchased from Scott Specialty Gases (Plumsteadville, PA, USA). The calibration gas was analyzed and quantified against standard reference material SRM 1800 (non-methane hydrocarbon compounds in nitrogen) and 1804a (volatile organics in nitrogen) provided by the National Institute of Standards and Technology (NIST) (Gaithersburg, MD, USA).

Tenax TA (2,6 diphenylene oxide) and Carboxen B (graphitized carbon black) were used as sorbent materials. They had particle sizes of 60/80 and were supplied by Supelco (Bellefonte, PA, USA).

A microprocessor-controlled high- and low-flow vacuum pump, supplied by SKC Universal (SKC, PA, USA), was used in the field application. The pump has a flow capacity of 5–5000 mL min^{-1} and can be set up to sample for up to 7 days onto a single sorbent tube. An SKC quad tube holder was used during the field application. An SKC portable dual ball rotameter that provides 5–245 mL min^{-1} low-flow and 235–5000 mL min^{-1} high-flow reading was used both in the field and laboratory. Humonics Veri-Flow 500 electronic flow meter (Supelco, Bellefonte, PA, USA) having a flow range of 5–500 mL min^{-1} with an accuracy of $\pm 2\%$ was used in the method development and validation works. The flow meter is multiple-point calibrated to NIST-certified volumetric standards for nitrogen, helium, hydrogen and air. Thermal gas mass flow controllers (MFC) supplied by Aalborg (New York, USA) were used for controlling 0–500 mL min^{-1} and 0–5000 mL min^{-1} flow rates. These flow meters have calibration certificates confirming NIST-traceable standards and operate at inlet pressures between 5 and 60 psi and at gas temperatures between 59 and 77 °F (15–25 °C) while maintaining $\pm 1.5\%$ full-scale accuracy and linearity. Oakton Acorn series thermocouple thermometer (Oakton Instruments, IL, USA) with an accuracy of $\pm 0.25\%$ reading plus 1 °C for temperature less than 99.9 °C and $\pm 0.2\%$ of reading plus 0.5 °C for temperature greater than 99.9 °C was used.

2.2. Instrumentation

A SIS (Scientific Instrument Services, NJ, USA) Model TD 4 SPTD system was used in this study. The system consists of a thermal desorption unit and an electronics control unit. The Thermal Desorption Unit is placed directly on top of the GC injection port, where it is utilized for the direct desorption of samples into the GC injection port and column. Due to its “short path” of sample flow, this system overcomes shortcomings of previous desorption systems by eliminating transfer lines, which

are easily contaminated by samples, and by providing for the optimum delivery and therefore maximum sensitivity of samples to the GC injector via the shortest path possible, i.e., direct injection into the GC [32]. Analytes of interest were thermally desorbed from the sorbent tubes and directly entered into the GC inlet. Desorbed analytes were cryogenically cooled and trapped at the very front of the analytical column. Cryogenic trap was quickly heated for rapid introduction of the analytes into column for separation by the GC and identification and quantification by the MS.

The microprocessor-controlled electronic system, included in the thermal desorber system, permits either manual operation or automated operation including automatic injection, timed desorption, temperature ramp of heater blocks, control of GC cryotrap accessory, and remote starting of GC, mass spectrometer and recorder. The maximum desorption temperature permissible with the system was 350 °C and the heater blocks could be ballistically heated or temperature programmed at ramp rates up to 40 °C min⁻¹. Normal desorption times vary from 3 to 15 min, however, longer desorption times up to 100 min are also possible.

GC–MS analysis of desorbed analytes were performed on a HP (Agilent Technologies, Palo Alto, CA, USA) model 5973 MS and 6890 GC system. Analytical column was a 60 m × 0.32 mm J&W (Palo Alto, CA, USA) DB-1 with 1 µm dimethylpolysiloxane coating. HP ChemStation software was used for data acquisition. Liquid carbon dioxide (CO₂) was used both for column and cryotrap cooling.

2.3. Procedures

2.3.1. Multisorbent adsorbent tubes

There are three general types of adsorbents namely porous polymers (e.g., Supelpak-2, Tenax, Chromosorb 106), graphitized carbon blacks (e.g., Carbotrap, Carbopack), and carbon molecular sieves (e.g., Carbosieve SIII, Carboxen). Hydrophobicity, temperature stability, surface area and particle size characteristics affect the selection of adsorbent material. In this study, Tenax TA and Carbopack B were chosen for determination of C5–C12 hydrocarbons due to their low affinity to water and their temperature stability.

Stainless steel glass-lined thermal desorption tubes (GLT) with inner diameter of 4 mm and length of 10.6 cm were cleaned in ultrasonic shaker with methanol for 2 h and dried in oven at 100 °C for 1 h. Clean tubes were then packed with 100 mg of Tenax TA and 50 mg of Carbopack B separated by a glass wool plug and plugged at both ends with the same material. There was 1.5 cm empty space at the sampling end of tube.

Tubes were conditioned after packing and prior to use. A custom-made conditioning oven with a ten-tube conditioning capacity was used. The conditioning oven had a heating capacity of up to 400 °C and high purity nitrogen (N₂) gas flow of up to 500 mL min⁻¹ per tube. The temperature of the heater blocks was kept constant by a thermostat and the oven was calibrated by thermometer prior to use in the laboratory. Nitrogen gas flow was controlled by a MFC. Conditioning parameters were optimized after several trials at 200, 250, 300 and 350 °C conditioning tem-

peratures; 2, 4, 6 and 12 h conditioning durations, and 20, 50, 100 and 200 mL min⁻¹ N₂ flow rates. Low conditioning temperatures and durations were not effective in cleaning the tubes. Low N₂ flow rate was not effective while very high N₂ flow rates resulted in flushing the sorbents from the tubes. After each trial, background chromatograms of the adsorbent tubes were investigated and 300 °C, 12 h and 100 mL min⁻¹ were found to be optimum conditioning parameters for the initial conditioning after packing. If conditioned tubes were stored for a long period of time without any use, 2 h conditioning time with the same conditioning temperature and flow rate resulted in satisfactory background levels (i.e., no target compound was found) for later conditioning of these tubes prior to field use.

Conditioned tubes were capped tightly with brass caps having PTFE seals and kept in pre-cleaned glass tubes to prevent possible contamination. Glass tubes were filled with charcoal and anhydrous calcium sulfate at the bottom and fixed with glass wool to provide dry and hydrocarbon free air for storage. Glass tubes were also capped with PTFE caps and placed in freezer at -18 °C for storage. This procedure was applied to both clean and sample tubes for storage prior to use or analysis.

2.3.2. Sample collection

Tenax TA is a weak and Carbopack B is a strong sorbent since they have surface areas of 35 and 100 m² g⁻¹, respectively. Therefore, samples were collected at the Tenax TA end of the tube in order to collect the heavier hydrocarbons first. Air samples were collected using SKC vacuum pumps. An external MFC was not used since the pump had an internal MFC unit. However, the flow rate was controlled by a rotameter at the beginning, after 30 min and at the end of the sampling and recorded in the field datasheets. For the total of 411 samples collected at Ankara field campaign, ±3% change in flow rate was observed in 46% of samples.

A cabinet made of aluminum sheets was used at outdoor sampling to keep sampling apparatus at safe and under constant temperature to provide proper operation of instruments. An air fan was installed inside the cabinet in the summer to lower the inner temperature and a heater equipped with a thermostat was used in winter to keep the temperature inside the cabinet at around 10 °C. The sample inlet port was located at 1.5 m from the ground for the purpose of determining human exposure concentrations.

Current meteorological conditions, nearby potential pollution sources and problems encountered during sampling were recorded in the field datasheets in addition to the sampling information (i.e., tube number, start time, initial flow rate, etc.). This information was used during quality control (QC) of the analytical data to trace back the possible field problems. Samples were immediately brought to the laboratory in coolers in summer and in winter after collection. They were recorded in the laboratory datasheets and stored at -18 °C prior to analysis.

2.3.3. GC–MS analysis

External standard calibration and internal standard (I.S.) addition method was used for the GC–MS quantification. Four I.S. used in this study were bromochloromethane,

1,4-difluorobenzene, chlorobenzene-d₅, and 1-bromo-4-fluorobenzene (BFB), which are recommended by the EPA [42]. A 10 mL of gas phase I.S. was added to all sample tubes prior to analysis. Quantification was performed according to relative response factor (RRF) calculations.

The MS analysis was carried out in scan mode during compound identification and characteristic ion determination. One target and two qualifying ions were selected to identify target analytes. The quantitative determination was carried out using the mass values corresponding to the molecular ions of the different VOCs, which refers to selected ion monitoring (SIM) mode of analysis that increases sensitivity. Performance of the GC–MS was controlled by conducting autotune with perfluorotributylamine (PTFBA) before calibration and when required and by the daily analysis of a medium level calibration mixture. Responses of the I.S. compounds were also monitored to observe any significant changes in the instrument response.

3. Results and discussion

The SPTD/GC–MS method was developed for a wide range of VOCs including aromatics, olefins, paraffins, halogenated and biogenic compounds that may be present both in ambient and indoor air. The target analyte selection criteria for this study were based on several factors: (i) the prevalence of a compound in indoor and outdoor air, (ii) the presumed potential for a compound to induce adverse health effect, (iii) the potential for a compound to act as a tracer for specific sources such as petroleum, cleaning solvents, printing, painting, etc. and (iv) the inclusion of compounds that has been frequently used as target analytes by other investigators so as to compare findings with the literature [2,3,14,25,33–40].

The GC–MS parameters that were optimized for the determination of 98 target VOCs are presented in Table 1. Retention times as well as target and qualifying ions used in the SIM mode of GC–MS operation are given in Table 2. The optimum GC–MS parameters provided good chromatographic peak resolution for almost all target analytes. Fig. 1 shows the total ion chromatogram of calibration standard and a typical sample acquired with GC–MS under optimized conditions. In order to attain the optimization of stability and response, the effects

of SPTD parameters have been considered and optimum SPTD parameters were determined.

3.1. Optimization of the SPTD parameters

An appropriate desorption temperature was evaluated to ensure that all analytes were completely desorbed from the multisorbent tubes in order to reach the highest sensitivity and to avoid carryover. Very high desorption temperatures shorten the adsorbent resin life, cause excessive levels of undesired higher boiling compounds to enter the GC injection port, contribute to injection port and septa contamination. Lower desorption temperatures, on the other hand, result in poor recovery of target analytes. Thus, it was important to choose the lowest thermal desorption temperature needed to achieve complete volatilization and purging of analytes from the adsorbent. Adsorbent tubes were injected with gas phase VOC mixture at the sampling end and thermally desorbed and analyzed in the reverse direction to the sample flow. Fig. 2 shows the dependence of the analyte recovery on the desorption temperature for selected target analytes. It was obtained that the peak area responses for all target analytes increased with increasing desorption temperature up to 200 °C. The area responses were still high at 220 °C for some analytes but the variation was higher. The peak area responses decreased with increasing temperature after 220 °C. The decrease may be due to the decomposition of analytes. Thus, the optimum desorption temperature was chosen as 200 °C.

Fig. 3 shows the dependence of analyte recovery on desorption time. The desorption time exhibited relatively small influence on the analyte recovery. Optimum desorption time should be long enough to ensure complete desorption of target analytes from multisorbent tubes. Desorption time of 5 min and higher were found appropriate for this purpose. For isoprene, however, desorption time higher than 5 min resulted in loss of analyte and yielded zero recovery. This may be due to decomposition of isoprene under elevated temperature for extended period of time. Thus, 5 min was selected as the optimum desorption time.

Fig. 4 shows the dependence of the analyte recovery on cryotrap temperature. Cryofocusing of the analytes provide rapid injection and thus narrow bands resulting in good resolution [41]. As can be seen in Fig. 4, cryotrap temperature has significant influence on analyte recovery providing higher recovery

Table 1
Optimized GC–MS and SPTD parameters

GC–MS parameters		SPTD parameters	
Injector	Splitless, 230 °C	Dry purge flow rate (mL min ⁻¹)	40
Column flow rate (mL min ⁻¹)	1.6	Dry purge time (min)	1
Linear velocity (cm s ⁻¹)	31	Injection time (min)	0.30
Carrier gas	He	Desorption temperature (°C)	200
Temperature program	–30 °C hold 3 min, 6 °C min ⁻¹ to 220 °C, hold 1 min	Desorption flow rate (mL min ⁻¹)	20
		Desorption time (min)	5
		Guard column	None
EI condition (eV)	70	Cryo trap temperature (°C)	–70
Mass range (amu)	30–300	Cryo heat temperature (°C)	250
MS quad temperature (°C)	150	Cryo heat time (min)	5
MS source temperature (°C)	230	Cryo liquid	Liquid CO ₂

Table 2
Retention time, target and qualifying ions used in GC-MS analysis

No.	Compound name	RT ^a	TI ^b	QI1 ^c	QI2 ^d	No.	Compound name	RT	TI	QI1	QI2	No.	Compound name	RT	TI	QI1	QI2
1	Pentane	12.62	43	41	27	34	Dibromomethane	20.92	174	93	176	67	Ethylbenzene	27.29	91	106	-
2	Isoprene	12.84	67	68	53	35	1,2-Dichloropropane	20.98	63	62	-	68	<i>m,p</i> -Xylene	27.57	91	106	-
3	<i>t</i> -2-Pentene	13.11	55	42	70	36	Trichloroethene	21.34	130	132	95	69	Bromoform	27.64	173	171	175
4	<i>c</i> -2-Pentene	13.51	55	42	70	37	1-Heptene	21.44	56	41	70	70	Styrene	28.18	104	78	103
5	2-Methyl-2-butene	13.76	55	41	70	38	2,2,4-Trimethylpentane	21.44	57	41	-	71	1,1,2,2-Tetrachloroethane	28.32	83	85	-
6	2,2-Dimethylbutane	14.49	57	71	43	39	Heptane	21.84	43	57	71	72	<i>o</i> -Xylene	28.37	91	106	-
7	<i>t</i> -1,2-Dichloroethene	15.54	61	96	98	40	<i>c</i> -3-Heptene	21.89	69	98	-	73	1-Nonene	28.48	55	41	69
8	3-Methyl-1-pentene	15.63	41	69	55	41	<i>t</i> -2-Heptene	22.01	55	56	41	74	Nonane	28.85	57	43	85
9	2,3-Dimethylbutane	16.02	43	42	41	42	<i>c</i> -2-Heptene	22.01	56	55	41	75	<i>iso</i> -Propylbenzene	29.41	105	120	-
10	<i>t</i> -4-Methyl-2-pentene	16.23	69	84	-	43	<i>c</i> -1,3-Dichloropropene	22.55	75	77	110	76	3,6-Dimethyloctane	30.18	57	-	-
11	2-Methylpentane	16.28	43	42	71	44	2,2-Dimethylhexane	22.69	57	41	56	77	<i>n</i> -Propylbenzene	30.33	91	120	-
12	<i>c</i> -4-Methyl-2-pentene	16.23	69	84	-	45	Methylcyclohexane	22.68	83	98	-	78	3-Ethyltoluene	30.55	105	120	-
13	3-Methylpentane	16.95	57	56	41	46	2,5-Dimethylhexane	23.15	57	43	71	79	4-Ethyltoluene	30.62	105	120	-
14	1-Hexene/2-methyl-1-pentene	17.24	56	55	41	47	2,4-Dimethylhexane	23.15	57	43	85	80	1,3,5-Trimethylbenzene	30.78	105	120	-
15	<i>c</i> -1,2-Dichloroethene	17.36	61	96	98	48	<i>t</i> -1,3-Dichloropropene	23.3	75	77	110	81	2-Ethyltoluene	31.13	105	120	-
16	Hexane	17.77	57	41	43	49	Bromotrichloromethane	23.69	117	119	-	82	1,2,4-Trimethylbenzene	31.59	105	120	-
17	Chloroform	17.83	83	85	47	50	2,3,4-Trimethylpentane	23.77	43	71	-	83	Benzyl chloride	31.8	91	126	-
18	<i>t</i> -2-Hexene	17.98	55	42	84	51	Toluene	23.94	91	92	-	84	1,4-Dichlorobenzene	31.86	146	148	-
19	<i>c</i> -2-Hexene	18.36	55	42	84	52	4-Methylheptane	24.3	70	71	-	85	<i>iso</i> -Butylbenzene	32.05	91	92	134
20	<i>c</i> -3-Methyl-2-pentene	18.87	69	41	55	53	1-Methylcyclohexene	24.34	81	96	-	86	<i>sec</i> -Butylbenzene	32.13	105	134	91
21	2,2-Dimethylpentane	18.78	57	43	85	54	Dibromochloromethane	24.52	129	127	-	87	1,2,3-Trimethylbenzene	32.44	105	120	-
22	1,2-Dichloroethane	18.84	62	64	27	55	3-Methylheptane	24.59	43	57	85	88	<i>p</i> -Cymene	32.5	134	119	-
23	Methylcyclopentane	18.87	56	41	69	56	<i>c</i> -1,3-Dimethylcyclohexane	24.78	97	55	112	89	1,2-Dichlorobenzene	32.68	146	148	-
24	2,4-Dimethylpentane	19.05	43	57	85	57	<i>t</i> -1,4-Dimethylcyclohexane	24.85	97	55	112	90	1,4-Diethylbenzene	33.38	119	105	-
25	1,1,1-Trichloroethane	19.2	97	61	99	58	1,2-Dibromoethane	24.88	107	109	-	91	<i>n</i> -Butylbenzene	33.41	91	92	-
26	2,2,3-Trimethylbutane	19.25	57	56	85	59	2,2,5-Trimethylhexane	24.98	57	71	41	92	1,2-Diethylbenzene	33.57	105	119	134
27	1-Methylcyclopentene	19.8	67	82	-	60	1-Octene	25.09	55	41	70	93	Undecane	34.78	57	43	71
28	Benzene	19.83	78	77	-	61	Octane	25.5	43	57	85	94	1,2,4-Trichlorobenzene	36.77	180	182	-
29	Carbontetrachloride	20.04	117	119	121	62	<i>t</i> -2-Octene	25.61	55	41	70	95	Naphthalene	37.02	128	127	-
30	Cyclohexane	20.22	84	41	56	63	<i>t</i> -1,2-Dimethylcyclohexane	25.74	97	112	55	96	Dodecane	37.12	57	43	71
31	2-Methylhexane	20.56	43	85	57	64	Tetrachloroethene	25.62	166	164	-	97	Hexachlorobutadiene	38.05	225	223	227
32	2,3-Dimethylpentane	20.64	56	71	57	65	<i>c</i> -1,4/ <i>t</i> -1,3-Dimethylcyclohexane	25.74	97	112	55	98	Hexylbenzene	38.88	91	162	-
33	3-Methylhexane	20.91	43	70	57	66	Chlorobenzene	26.66	112	77	114						

^a Retention time.
^b Target ion.
^c First qualifying ion.
^d Second qualifying ion.

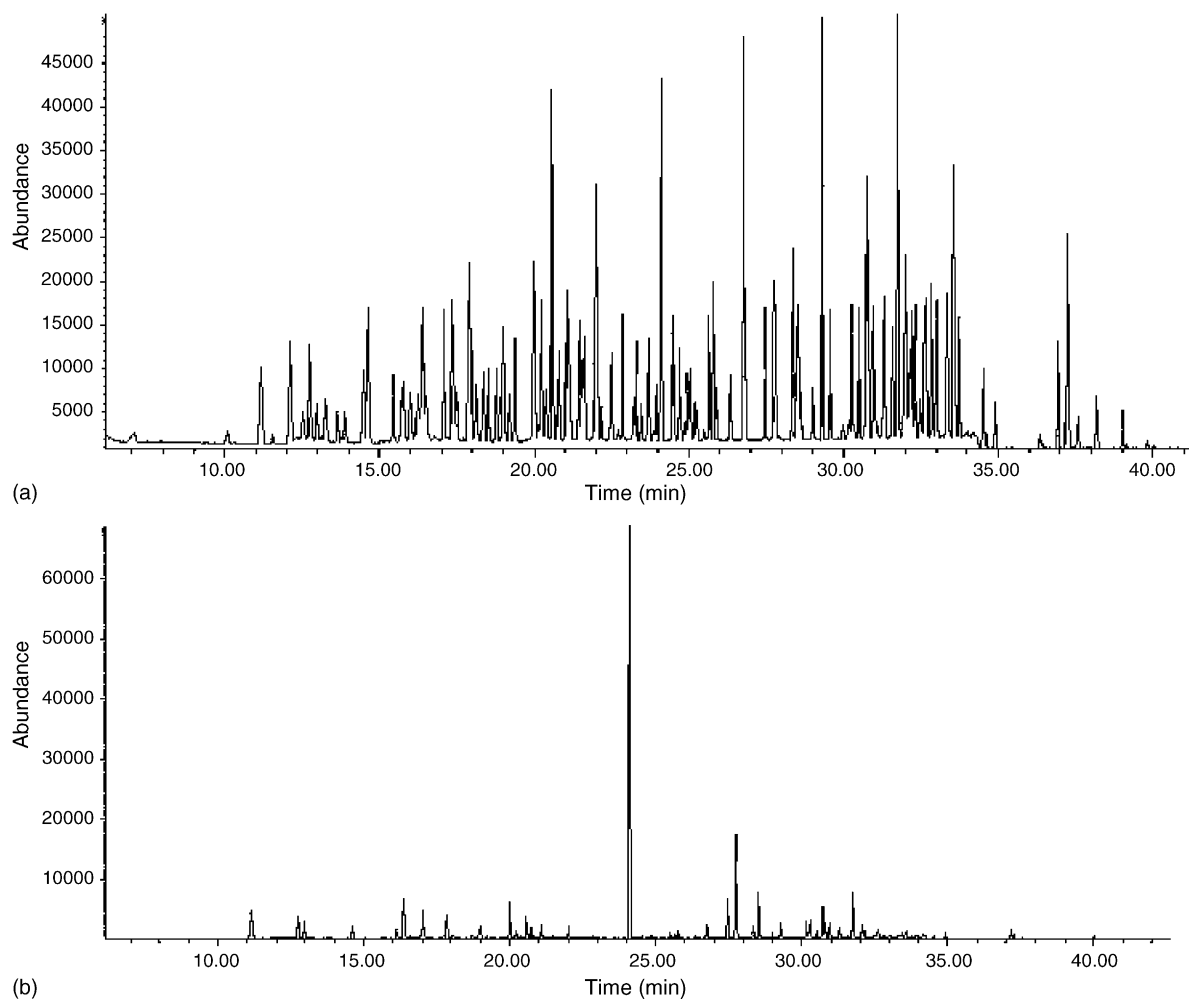


Fig. 1. Total ion chromatogram of (a) calibration standard and (b) a typical sample.

at lower temperatures. Therefore, a cryotrap temperature of -70°C was chosen as the optimum. The results were presented only for selected target analytes but the similar patterns and conclusions were valid for all other target analytes.

Desorption flow rate was set to 20 mL min^{-1} which provided a good recovery of all target analytes. The optimum SPTD parameters that were determined for the multisorbent tube type

and target analyte list described in this study are summarized in Table 1.

3.2. Method performance evaluation

Extensive validation was conducted for sampling and analytical methodology. Table 3 provides method detection limit, precision, and recovery (desorption efficiency) values for all target analytes in chromatographic elution order. Gas phase

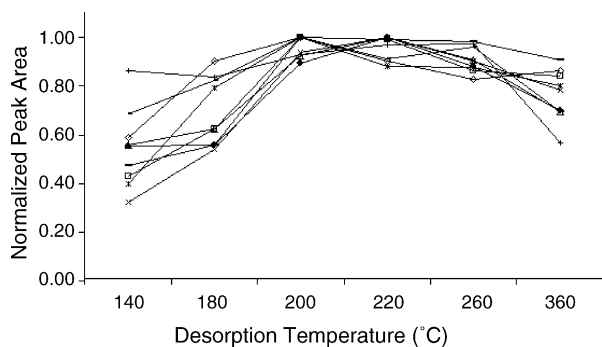


Fig. 2. Dependence of analyte recovery on desorption temperature. The peak area has been normalized to the maximum value for each individual compound. Symbols: (\diamond) benzene; (\square) toluene; (Δ) ethylbenzene; (\times) *m,p*-xylene; ($*$) *o*-xylene; (\blacklozenge) 1,2,4-trimethylbenzene; ($+$) isoprene; ($-$) 1-heptene and ($-$) heptane.

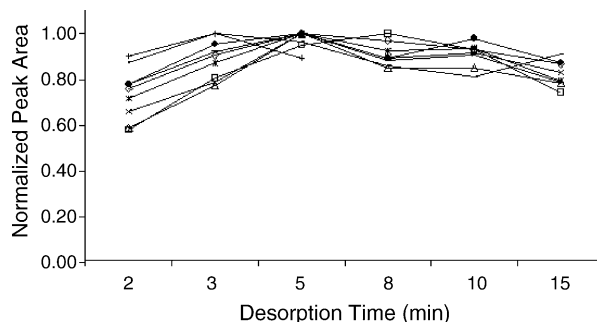


Fig. 3. Dependence of analyte recovery on desorption time. For symbols see Fig. 2.

Table 3
Selected method performance parameters

No. ^a	MDL (ppbv)	Precision ^b (n = 6)	Recovery ^c (%)	Detected ^d (%)	No. ^a	MDL (ppbv)	Precision ^b (n = 6)	Recovery ^c (%)	Detected ^d (%)	No. ^a	MDL (ppbv)	Precision ^b (n = 6)	Recovery ^c (%)	Detected ^d (%)
1	0.13	9.34	100.00	98.30	34	0.03	5.97	95.00	7.47	67	0.06	7.14	97.15	100.00
2	0.06	7.31	100.00	94.60	35	0.04	4.07	95.00	9.28	68	0.12	12.81	95.00	100.00
3	0.04	8.88	100.00	76.08	36	0.05	3.94	65.00	71.02	69	0.01	4.66	65.00	61.48
4	0.03	7.71	95.00	71.34	37	0.02	5.03	100.00	92.20	70	0.07	14.41	95.00	94.63
5	0.02	6.99	100.00	82.89	38	0.02	6.58	95.00	13.44	71	0.03	10.94	97.71	10.58
6	0.11	9.00	100.00	95.82	39	0.10	5.22	100.00	99.04	72	0.04	9.30	95.00	100.00
7	0.03	9.85	95.00	0.16	40	0.03	4.67	95.00	34.07	73	0.04	15.72	81.48	93.74
8	0.04	6.45	95.00	3.38	41	0.02	2.59	95.00	23.04	74	0.01	12.57	100.00	97.69
9	0.03	5.88	100.00	98.35	42	0.04	2.66	95.00	27.49	75	0.03	7.99	95.00	93.73
10	0.03	6.47	95.00	56.01	43	0.01	7.40	95.00	0.14	76	0.01	21.81	94.87	18.41
11	0.14	8.16	85.41	99.04	44	0.01	6.56	95.00	10.73	77	0.02	7.39	97.83	98.84
12	0.03	6.50	95.00	50.56	45	0.01	5.92	100.00	99.86	78	0.03	10.17	97.30	98.84
13	0.08	8.22	91.24	98.09	46	0.01	4.84	95.00	71.63	79	0.05	5.84	96.39	98.84
14	0.06	5.44	100.00	84.13	47	0.02	4.22	95.00	72.91	80	0.03	8.61	97.87	99.00
15	0.02	6.19	95.00	7.35	48	0.02	9.87	95.00	0.16	81	0.02	8.00	98.30	98.46
16	0.08	12.00	94.00	98.35	49	0.02	9.98	95.00	0.14	82	0.06	8.62	100.00	97.96
17	0.04	8.24	84.62	91.43	50	0.01	4.86	95.00	65.18	83	0.05	6.18	83.07	77.11
18	0.04	4.47	95.00	27.55	51	0.08	5.80	92.88	100.00	84	0.03	11.21	100.00	99.45
19	0.01	4.91	95.00	40.41	52	0.01	5.53	95.00	0.00	85	0.03	8.52	100.00	93.34
20	0.10	11.25	83.64	77.39	53	0.06	7.00	95.00	12.38	86	0.03	7.93	96.08	74.54
21	0.03	4.39	100.00	85.97	54	0.04	5.66	70.00	2.64	87	0.03	9.02	80.00	89.94
22	0.04	6.16	95.00	12.54	55	0.01	5.10	100.00	93.50	88	0.02	9.22	95.00	97.99
23	0.05	5.97	84.85	98.49	56	0.01	6.98	100.00	85.62	89	0.03	7.80	80.00	5.42
24	0.03	4.10	85.71	93.33	57	0.01	6.34	95.00	82.67	90	0.05	9.50	100.00	78.04
25	0.10	3.75	100.00	99.60	58	0.03	5.39	95.00	25.09	91	0.02	10.07	95.00	89.70
26	0.02	6.71	95.00	27.31	59	0.01	4.25	95.00	5.59	92	0.02	10.55	88.57	69.46
27	0.04	6.61	100.00	71.12	60	0.05	6.17	87.88	80.90	93	0.04	9.60	95.00	99.73
28	0.13	8.28	93.73	100.00	61	0.06	10.97	94.00	97.09	94	0.05	10.37	88.00	12.25
29	0.02	5.01	75.00	100.00	62	0.02	5.83	95.00	20.98	95	0.01	19.21	89.36	99.43
30	0.03	8.24	100.00	94.66	63	0.01	6.12	94.87	34.65	96	0.02	11.33	95.00	92.78
31	0.03	13.61	100.00	96.78	64	0.04	5.80	95.00	99.86	97	0.02	9.03	95.00	0.00
32	0.02	5.82	100.00	96.27	65	0.01	5.81	80.00	44.86	98	0.03	8.89	95.00	4.85
33	0.02	6.39	100.00	94.14	66	0.03	3.81	90.43	58.99					

^a Please see Table 2 for compound names corresponding to these numbers.

^b RSD (%).

^c Desorption efficiency.

^d Percent of field samples at which the individual compound was detected for a total of 411 sample.

calibration mixture was injected onto multisorbent tubes via a T-shaped loading apparatus every time. High-purity N₂ gas was passed through the apparatus in horizontal direction at a constant flow rate controlled by MFC while injecting the calibration mixture from the top seal of apparatus by using Hamilton gas tight syringe. Different concentration levels were obtained by adjust-

ing the volume of the gas phase calibration mixture injected into the apparatus.

3.2.1. Method detection limit

The method detection limit was calculated from seven replicate measurements of the target analytes at a concentration near (within a factor of five) the expected detection limit [42]. Standard deviation values for the seven replicate concentrations were computed and multiplied by Student's *t*-value for 99% confidence for seven replicate. The computed MDL values range from 0.02 to 0.26 μg m⁻³ with an average value of 0.17 μg m⁻³ (i.e., 0.04 ppbv).

3.2.2. Precision and linearity

The precision of the method was determined by performing six replicate measurements of the adsorbent tubes, which were injected with gas phase VOC mixtures containing 0.2–2.64 ng tube⁻¹ of each analyte. The resulting relative standard deviation (RSD) values range from 2.6% to 15.7% with an average value of 7.7%. Most of the target analytes have preci-

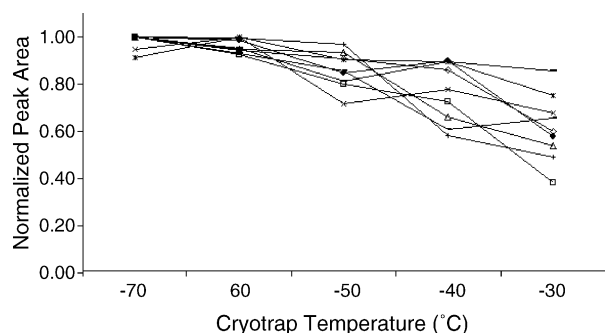


Fig. 4. Dependence of analyte recovery on cryotrap temperature. For symbols see Fig. 2.

sion value of less than 10% with the exception of naphthalene (19.2%) and 3,6-dimethyloctane (21.8%). The later compound was only detected at 18% of the 411 field samples, thus the poor precision of this compound had no significant influence on the overall performance of the method. The linearity of the method was evaluated with the correlation coefficient (R^2) of the regression line that was drawn for the five-point calibration curve ranging between 0.5 and 160 ng tube⁻¹. The method showed a good linear behavior with R^2 -values detected for most of the compounds being higher than 0.99.

3.2.3. Blanks

Laboratory and field blanks were evaluated. Laboratory blanks were evaluated to control both the efficiency of conditioning and any contamination in the instrumental system. Conditioned tubes were analyzed as the first and second run of the day on every analysis day. GC inlet, GC column and MS auxiliary connection were baked at 300 °C for 30 min if contamination was observed in the first run of laboratory blank tube. Field blanks were subjected to the same field condition as sample tubes. They were kept at the site for 5 min while the caps were open and then the caps were closed. A total of 17 laboratory blanks and 13 field blanks were analyzed under the same conditions of analysis and resulting chromatograms confirmed that no significant impurities were presented which could disturb the gas chromatographic analysis. Results were similar and even lower than the literature values provided for single adsorbent or different combination of multisorbent tubes [32,43]. Results of the sample chromatograms, however, corrected for the field blanks (average of 0.31 ng total VOC tube⁻¹), which were slightly higher than the laboratory blank values (average of 0.25 ng total VOC tube⁻¹).

3.2.4. Desorption efficiency

Desorption efficiencies for each VOCs are evaluated as the fraction of the mass recovered from the sorbent compared to that injected into the sorbent tube [32,44]. A sorbent tube spiked with gas phase VOC mixture with an average concentration of 7 µg m⁻³ was re-analyzed just after it was analyzed to calculate recoveries. Recoveries for the most analytes ranged between 80% and 100% with an average of 95.7%. However, three compounds (trichloroethene, dibromochloromethane, and bromoform) showed poor desorption efficiencies of less than 75%. Although all of these compounds are halogenated hydrocarbons, this should not be generalized as poor desorption efficiency values to all halogenated hydrocarbons since there were many other halogenated compounds in target analyte list that showed good recoveries. These three compounds were extracted from the target compound list for further analysis due to their poor recoveries.

3.2.5. Collection efficiency

Collection efficiency was evaluated in terms of both retention efficiency and breakthrough, under a range of conditions. The retention efficiency and breakthrough volumes for certain adsorbents and analytes were provided in the literature [43,45] but these literature values were given for single adsorbent tube

designs. The various studies available in the literature for multisorbent tubes that are limited to analyte number and adsorbent tube combinations [11,21,46]. Therefore, laboratory and field studies for the determination of collection efficiencies applicable for target analytes and multisorbent tube combination were conducted in this study.

Determination of retention efficiency at the laboratory was conducted by utilizing elution analysis technique, by combining two adsorption tubes in series [47]. A liquid mixture of DWM-550 aromatic hydrocarbons purchased from Ultra Scientific (North Kingstown, RI, USA) was injected into the sampling end of adsorbent tube with a concentration of 2 mg L⁻¹. A back adsorbent tube was connected to the front tube and high purity He gas at a total volume of 0.3 L was passed through the tubes that were attached to the thermal desorber instrument. Analysis of both the front and the back adsorbent tubes demonstrated that no significant breakthrough was observed for a very high concentration of analytes for a short period of elution time indicating collection efficiency close to 100%.

Studies [15,32,48] showed that breakthrough volume considerably responds to the change in relative humidity and temperature. It has also shown that breakthrough volume depends on VOC concentrations [15]. Breakthrough tests were conducted in the field under actual environmental conditions in order to account for changes in the breakthrough volume under real relative humidity, temperature and concentration values. Field study was conducted at a gas station in order to simulate maximum concentrations of VOCs in ambient air. Breakthrough was determined by connecting three sets of identical adsorbent tubes in series and sampling via SKC Universal microprocessor-controlled low-flow vacuum pump at a rate of 20 mL min⁻¹ for 1, 2 and 3 h sampling durations. The ambient concentrations were between 0.5 and 55 µg m⁻³ for different analytes. There was no significant breakthrough of analytes except 2-methylbutane (30% breakthrough) after 3 h sampling period. Field tests were also performed at residential, roadside and tunnel environments under summer and winter conditions using flow rate of 20 mL min⁻¹ for 3 and 4 h sampling durations. For a total of 15 samples collected, breakthrough was observed for 2-methylbutane, Freon 11, 1-pentene, and 2-methyl-1-butene at values ranging between 15% and 40%. These analytes were excluded from the target analyte list for the further evaluations.

3.2.6. Storage stability

Storage stability was evaluated for spiked samples. Six adsorbent tubes were injected with gas phase mid-level VOC mixture containing 1–13 µg m⁻³ of each analyte and sealed. Spiked samples were stored at -18 °C. Four samples were analyzed after a storage period of 2 days and two samples were analyzed after 9 days of storage. Recovery rates for stored samples were calculated as the fraction of the concentration measured in the tubes that were analyzed immediately after loading. The average recoveries for the storage of target analytes on multisorbent tubes were 102% and 87% for 2 and 9 days of storage periods, respectively. There was no significant change in sample amount after 2-day storage. On the other hand, increase in the amount of target

analytes due to sample degradation or decrease in the amount due to sample loss was observed for 9-day storage period. For the 2-methylbutane, 1-pentene and 2-methyl-1-butene, however, storage recoveries (i.e., 50%, 62% and 64%, respectively) were poor even for the 2-day storage. Samples were analyzed within an average of 3 days after collection to minimize the potential for losses and sample degradation.

3.3. Field validation

The sampling and analytical method were validated under various environmental conditions in three microenvironments: (i) ambient air at a gas station, (ii) indoor air in an office building and (iii) indoor air in a residential home household. Samples were collected only on 1 day for the field validation purposes. The ambient temperature was 32 °C and relative humidity was 31% during sampling, which are representative of the summer conditions in Ankara [49]. Samples were collected for 2 h at a 20 mL min⁻¹ flow rate at gas station and no breakthrough of target analytes was observed.

Indoor air samples were collected for 1 h at a sampling flow rate of 30 mL min⁻¹. This is the first study done in Turkey to measure such a wide range of VOCs in indoor microenvironment. Table 4 presents concentrations of total non-methane hydrocarbons (TNMHC) and the most abundant VOCs that account for 80%, 81% and 83% of the total VOC concentration measured in the office, the residential home and the gas station, respectively. The measured TNMHC concentrations covered a wide range between 522 and 41 µg m⁻³ at the gas station and the office, respectively. The concentration of individual VOCs also showed a high variation between 0.59 µg m⁻³ for styrene in the office and 54.91 µg m⁻³ for 1-hexene/2-methyl-1-pentene at the gas station. Rank and type of the most abundant species in the three microenvironments were different. VOCs associ-

ated with household cleaning chemicals such as chloroform and carbon tetrachloride were detected only in the office whereas 1,4-dichlorobenzene, another compound associated with cleaning products, was detected in both the office and the residential home. VOCs originated from printing ink solvent such as 1,2,4-trimethylbenzene and styrene were among the most abundant species measured in the office building. Isoprene, a biogenic VOC marker, was also abundant in the office whereas isoprene concentration was negligible in the air in the residential home and the gas station. The isoprene could infiltrate from outdoor air into the office since the university has significant number of pine trees on its campus. Naphthalene was in the third rank with a concentration of 9.01 µg m⁻³ in the residential home. This may be due to common use of mothballs in homes in Turkey. Most of the compounds in residential indoor air were associated with motor vehicle emissions indicating contribution of traffic emission to air in residential homes. The abundant VOCs measured in air of the gas station were originated from gasoline vapor and motor vehicle exhaust.

The field validation tests demonstrated that the sampling and analytical method described in this paper was promising for the measurement of a variety of speciated VOCs under different environmental conditions.

3.4. Multidimensional data validation procedure

Given the complexity involved in the chromatographic analysis of VOCs, it is justifiable to explore new techniques of quality control or standardization procedure to reduce artifacts or systematic errors in the analysis. It is imperative to be confident about the quality of the data before performing any interpretation of the data set. The anomalies in the data set may arise from (i) problems that may be encountered during sample collection on the field, (ii) analytical problems that may occur

Table 4
Concentration of abundant VOCs measured in indoor and gas station air

Office building—indoor		Residential house—indoor		Gas station—ambient	
Compound name	Concentration (µg m ⁻³)	Compound name	Concentration (µg m ⁻³)	Compound name	Concentration (µg m ⁻³)
1,4-Dichlorobenzene	9.83	Toluene	13.91	1-Hexene/2-methyl-1-pentene	54.91
Pentane	3.90	1-Hexene/2-methyl-1-pentene	9.60	2-Methylpentane	52.73
Toluene	2.40	Naphthalene	9.01	Toluene	52.28
Chloroform	2.19	Hexane	6.57	<i>m,p</i> -Xylene	43.11
Dodecane	2.05	2-Methylpentane	5.92	3-Methylpentane	37.24
Isoprene	1.98	<i>c</i> -3-Methyl-2-pentene	5.08	Benzene	27.52
Undecane	1.48	3-Methylpentane	5.04	Pentane	26.05
<i>m,p</i> -Xylene	1.34	Pentane	4.60	2,2-Dimethylbutane	24.89
2-Methylpentane	1.33	<i>m,p</i> -Xylene	3.66	Hexane	23.72
Hexane	1.09	1,4-Dichlorobenzene	3.25	1,2,4-Trimethylbenzene	20.53
Carbontetrachloride	1.05	Methylcyclopentane	2.99	2,3-Dimethylbutane	15.61
Benzene	0.96	2-Methylhexane	2.13	<i>o</i> -Xylene	15.43
1,2,4-Trimethylbenzene	0.85	3-Methylhexane	2.13	Ethylbenzene	11.47
3-Methylpentane	0.80	Dodecane	2.03	3-Methylhexane	10.33
Naphthalene	0.80	Benzene	1.96	3-Ethyltoluene	9.67
Styrene	0.59	1,2,4-Trimethylbenzene	1.59	2-Methylhexane	9.41
TNMHC	40.71	TNMHC	98.21	TNMHC	522.10

during instrumental analysis, (iii) inaccuracy in integration of the chromatogram, (iv) anomalies in meteorological parameters and (v) change in source strength. It is important to distinguish whether it is a systematic error or a problem in a single data point. These outliers may result in misleading information on the interpretation. Therefore, quality control of the data set in order to investigate anomalies must be performed.

A multidimensional data validation procedure was applied to a data set including 411 sampling intervals and 40 278 data points. The data set belonged to a field campaign that was conducted in Ankara for 2 months in the summer of 2003 and for 2 months in the winter of 2004 at four different sites for the determination of VOCs. The data validation procedure, similar to chromatographic techniques, was very complex and time consuming. Independent parameters, including time, compound and meteorology, influence overall concentration pattern of the data. These dimensions were evaluated in the two phase of the data validation procedure. The initial phase of the procedure included generation of (i) times series, (ii) scatter plots and (iii) fingerprint plots for individual species and for each session. SPLUS 6.0 computer software was used to handle QC of the large data set. The second phase covered evaluation of the plots to identify anomalies and to find the reasons behind these anomalies. In case any anomalies were observed, chromatograms were re-evaluated for misidentification or misquantification. In addition, field and laboratory logbooks were re-evaluated for any possible contamination or problem. Meteorological parameters such as mixing height, temperature and wind speed were evaluated to understand if the anomaly was due to a pollution episode.

Time series plots were drawn for each species. These plots showed variation in the species concentration along with time of campaign. Time series plots were inspected for large “jumps” or “dips” in concentrations, periodicity of peaks, calibration

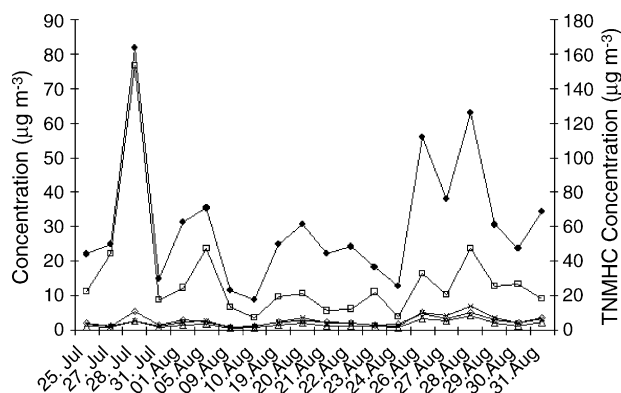


Fig. 5. Fingerprint plot for the benzene, toluene, ethylbenzene and xylenes (BTEX) measured at residential sampling site during summer of the 2003. Symbols: (●) TNMHC; for other symbols see Fig. 2.

carry-over, expected diurnal behavior (e.g., lower concentrations of isoprene during night time), expected relationships among species, and high single-hour concentrations of less abundant species.

Fingerprint plots were drawn for each individual session including all target compounds. These plots provided an overall view of daily changes. Morning, noon, afternoon, evening, and night sessions were inspected separately. These plots were inspected for outliers that were indicated by deviation from general pattern. Scatter plots were drawn to demonstrate correlations between individual species and between individual specie and total non-methane hydrocarbon. The plots were inspected for benzene versus toluene, species that elute close together, and isomers. Anomalies such as scattered data points contrary to the general correlation of the data were inspected.

Fig. 5 presents a fingerprint plot drawn for the selected compounds measured at residential station during a morning session

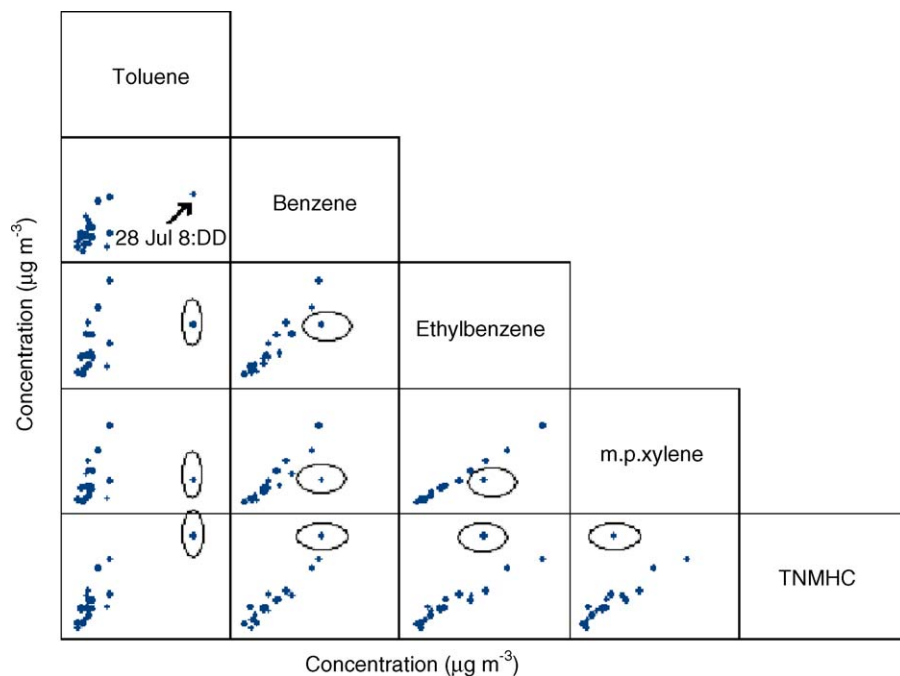


Fig. 6. Scatter plot matrices for the BTEX compounds measured at residential sampling site during summer of the 2003.

of the summer campaign in Ankara. It is clearly seen from the figure that there was a significant increase in the concentrations of compounds and especially in the concentrations of toluene on 28 July 8:00 session. Fig. 6 shows scatter plot matrices drawn for benzene, toluene, ethylbenzene, *m*- and *p*-xylene and TNMHC for the same data set. Correlation plots for two compounds in terms of concentrations are presented in matrix format in this figure. A single data point that was clearly separated from the other data points also stands for the results of 28 July 8:00 session. The data validation procedure was successful for the identification of this anomaly.

4. Conclusion

Accurate and precise determination of VOCs is critical due to utilization of the data for formation or monitoring of mitigation measures. Sampling and analysis of VOCs require significant consideration due to their low (i.e., ppb to ppt) concentrations and the susceptibility of methods to contamination and loss in performance. A complete evaluation of a method must be performed before utilization in order to obtain reliable results.

A multiphase assurance approach was successfully developed and implemented for the determination of 102 individual VOCs in indoor and ambient air. The three-phase approach covered development of sampling and analytical method, validation of the method both in the field and the laboratory and finally the validation of the quantification data through a multidimensional procedure, which provided both identification of faulty data and air pollution episodes. The laboratory and field results indicate that the multisorbent air sampling followed by SPTD preconcentration and GC–MS quantification method established in this study is well suited for quantitative analysis of the target compounds. The system exhibited capabilities of detection at a ppb level. The multiphase assurance approach presented in this research was a very valuable tool for the determination of VOCs in different microenvironments.

Acknowledgements

The authors thank Gürkan Kuntasal, Ozan Aktan and Kutay Erbayat for their enormous helps during field campaign and Professor Stuart Batterman from University of Michigan for his valuable comments during method development and validation parts through personal communication. This work was supported partly by the Middle East Technical University Research Fund, project number 2001-07-02-00-76.

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