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Development of an analytical technique and stability evaluation of 143 C_3–C_{12} volatile organic compounds in Summa® canisters by gas chromatography–mass spectrometry

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A technique using Summa® canisters with cryogenic preconcentration and gas chromatographic–mass spectrometric (GC-MS) detection was developed to determine 143 C_3–C_{12} volatile organic compounds (VOCs) including alkanes, alkenes, aromatics and halohydrocarbons in ambient and indoor air. The method detection limits and practical quantification limits were sensitive at 0.02 and 0.10 ppbv, respectively, and the method precision and accuracy were also satisfactory. The stability of C_3–C_{12} VOC standards at ppbv levels under elevated pressure in canisters was assessed over various time intervals (from 1 week to 4 months after preparation) and most of the compounds were found to be acceptably stable with a mean recovery of 85.6 ± 9.9% during the course of a 4-month study. However, a small fraction (approximately 6%) of the compounds, including two halohydrocarbons (bromotrichloromethane and benzyl chloride) and six alkenes (2-methylbuta-1,3-diene (isoprene), *cis*-4-methylpent-2-ene, *cis*-3-methylpent-2-ene, hept-1-ene, oct-1-ene and styrene) displayed relatively low recoveries in the range 34.6–67.9%. The loss of these compounds is most probably caused by their physical adherence to the active sites of the canister surface, chemical decomposition and/or reactions with other species. The results indicated that one must be cautious in attempting to measure these compounds owing to their instability in canisters. Overall, this analytical technique, which has been used for the determination of the VOCs under study in the toxic air pollutant monitoring network administered by the HKSAR Government, was amenable to the measurement of airborne VOCs collected both outside and inside a semi-confined car park in the present study.

Introduction

Volatile organic compounds (VOCs) are one of the major groups of global atmospheric pollutants. Large amounts of VOCs enter the troposphere every year and an estimated 350–375 million tons yr^{-1} of methane and 60–140 million tons yr^{-1} of non-methane organic hydrocarbons (NMHCs) were produced from anthropogenic activities (such as fossil fuel combustion, transport and evaporation, chemical treatment and other domestic and industrial discharges) world-wide.[1,2] This substantial anthropogenic emission has profound adverse impacts on human health and crop production.[3] VOCs play a vital role in the formation of various secondary pollutants through photochemical reactions in the presence of sunlight and nitrogen oxides.[4,5] Furthermore, some VOCs could contribute to the atmospheric ozone depletion and the build-up of persistent pollutions in remote areas.[6,7] As a consequence, VOCs have attracted significant attention and have been considered as an important environmental issue over the last two decades.

A thorough understanding of the formation, distribution, transportation, stability and reactivity of VOCs in the atmosphere requires the availability of sensitive and specific analytical methods for measuring these compounds. Sorbent-based or canister-based methods have been successfully developed and frequently used in the collection of ambient VOCs. A cryogenic preconcentration process is often applied to air samples concentrating the VOC content, prior to chromatographic separation and detection of VOCs by various gas chromatographic techniques. In sorbent-based methods, whole air is pulled through metal or glass tubes that have been pre-packed with appropriate packing materials such as activated charcoal, Tenax, XAD-2, Carbotrap and Carboseive. Attention must be paid on the choice of these sorbent materials because they have variable selectivity towards different types of VOCs. The physical properties and applicability of VOCs sorbents have been compared and discussed recently.[8] In canister-based methods, air is pumped at adjustable flow rates into cleaned and evacuated stainless steel canisters. Canisters of 2–15 L capacity are usually used to hold air samples up to 40 psig and offer a convenient means for multiple analyses. However, the inner wall of the canisters must be thoroughly cleaned before sampling, otherwise contamination and recovery problems might arise.[9,10]

Reviewing the applicability and limitations of sorbent-based and canister-based methods,[11,12] it was decided to adopt the canister-based sampling method followed by cryogenic preconcentration and GC-MS detection in our study of 143 ambient VOCs because of the following concerns:

(1) The time required to arrange transportation of the collected samples to the laboratory, tight resources and other factors may lead to a period of several days between sampling and analysis. The lead time makes sorbent-based methods less favourable as VOCs have been found to be less stable upon storage in sorbents.[13]

(2) This work was primarily targetted at monitoring a broad range of ambient VOCs, so canister-based sampling would have advantages as sorbents are normally selective in, if not limited to, adsorbing/absorbing certain classes of VOCs.

(3) It is difficult to anticipate the possible concentration of analytes under various environmental conditions as it is not easy

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to adjust the sampling volume to circumvent the breakthrough of analytes that is often encountered in sorbent-based methods. Extreme precautions are required for ensuring reproducible and good quality results.

(4) The generation of artifacts that are frequently found in sorbents (*e.g.*, benzene and toluene are the major artifacts reported on Tenax and Carbotrap)[14,15] might create additional technical difficulties in its application.

On the other hand, the canister-based technique is thought to be unsuitable for collecting polar compounds such as aldehydes and terpenes.[16] Several studies[17–20] have indicated that the storage stability of VOCs within the canisters is a critical issue of the methodology, although the employment of new types of canister coated with fused silica might offer increased sample integrity.[21] Those studies[17–20] only considered a small selected group of hydrocarbons, halohydrocarbons and simple aromatics, hence comprehensive stability information on the majority of VOCs was scarce. Furthermore, the stability data for VOCs in the literature were found to be relatively inconsistent. This paper presents our work on the evaluation of the suitability and investigation of the stability of 143 C_3–C_{12} VOCs covering a broad range of alkanes, alkenes, halohydrocarbons and aromatic compounds at low ppb levels in pressurized canisters. A sampling and analytical protocol, based on USEPA Method TO-14,[12] was also developed and piloted to measure the concentration of VOCs inside and outside a semi-confined car park environment. The protocol has been adopted by the Government Laboratory of the HKSAR as one of the standard methods in the toxic air pollutant (TAP) monitoring network since early 1999. Results and details of the TAP monitoring work using the above technique will be reported later.

Experimental

Apparatus

Air samples in canisters, ranging from 25 to 1000 mL, were withdrawn through an autosampler (Nutech 3600, Graseby Andersen, GA, USA) into a cryogenic preconcentrator (Nutech 3550A) and a cryofocuser (Nutech 354A). The flow rate of air samples was regulated by a mass flow controller (MFC). VOCs in the standards or samples were dried with the aid of a Nafion® permeable membrane dryer (Purma Pure, NJ, USA) and then concentrated cryogenically prior to gas chromatographic separation and detection by a mass spectrometer. The GC-MS system (Hewlett-Packard, Rockville, MD, USA) consisted of a Model 6890 gas chromatograph and a Model 5973 mass spectrometer fitted with a 60 m × 0.32 mm id, 1 µm film thickness DB-1 capillary column (J&W Scientific, Folsom, CA, USA). Ultrapure grade helium gas (Hong Kong Oxygen, Hong Kong) was used as the carrier gas and was cleaned with gas purifier (Supelco, Bellefonte, PA, USA) and hydrocarbon purifier (Alltech, Deerfield, IL, USA). Canisters were cleaned by three repeated cycles of pressurization with humidified zero air generated by a zero air generator *in situ* by a zero air generator (737-10, Aadco, Clearwater, FL, USA) and a laboratory-made humidifier (a stainless steel container filled with HPLC grade water), followed by evacuation at 100 °C under high vacuum (<0.065 mbar) for 1 h using a VOC cleaning system (Nutech 3650). Cleaned canisters were analysed as for field samples to ensure that the residual VOC content was less than the method detection limit (MDL) before use. A schematic diagram of the analytical system is illustrated in Fig. 1.

Operating conditions and procedure

A Nafion® permeable membrane dryer was operated at room temperature during the sample drying process and purged with humidified air at 100 °C at 50 mL min^{-1} for 120 s after each analysis to prevent memory effects. VOCs in standards and air samples were concentrated in the cryotrap at -160 °C, desorbed at 150 °C and then cryofocused at -185 °C in the cryofocuser. The gas chromatograph was operated isothermally at -60 °C for 3 min, then programmed to 250 °C at 8 °C min^{-1} and finally held at 250 °C for 10 min. The carrier gas was maintained at a flow rate of 2.0 mL min^{-1} in the splitless mode. The mass spectrometer was operated in the positive electron ionization (EI) mode at 70 eV. The transfer line, the ion source and the quadrupole were set at 200, 230 and 150 °C, respectively. Data were acquired in the selective ion monitoring (SIM) mode and with a 5.0 min solvent delay time.

Daily mass tuning of the mass spectrometer at *m*/*z* 69, 219 and 502 was automatically performed by the Chemstation software (version 1.0, Hewlett-Packard). Additional tuning of bromo-4-fluorobenzene (BFB) and evaluation of the cleanliness of blank of zero air were conducted by drawing 500 mL of zero air together with 2 mL of 1 ppmv of internal standards through the autosampler, cryotrap and cryofocuser into the GC-MS system. Calibration curves were constructed using six calibra-

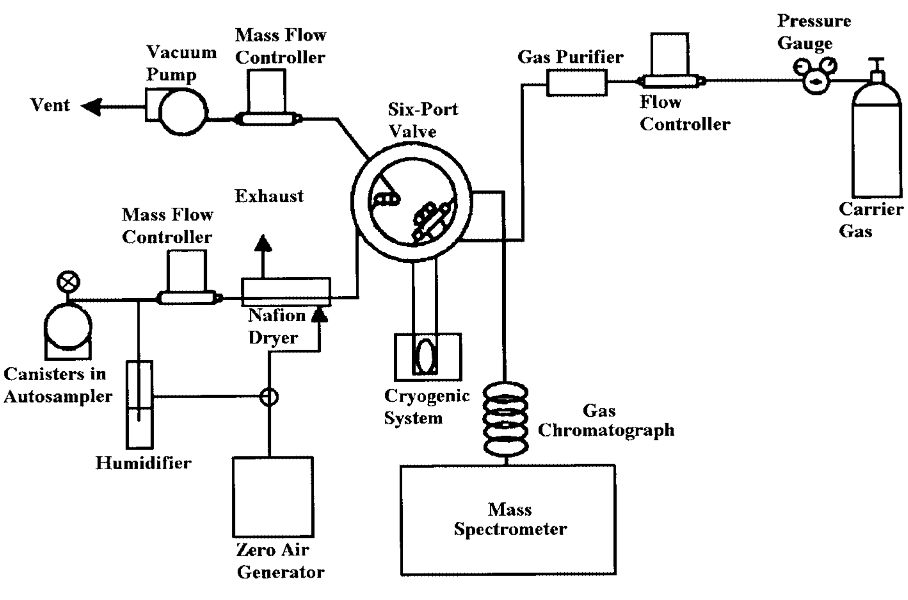

Fig. 1 Schematic diagram of the analytical system for VOCs analysis.

tion points in the range 0.20–4.0 ppbv by injecting 25–1000 mL of the working standard solutions into the GC-MS system. The linearity of the six-point calibration was considered acceptable if $r^2 > 0.99$. VOCs in samples were determined by withdrawing air volumes of 500 mL together with 2 mL of internal standard in a similar manner to the blank zero air. If the concentrations of analytes of interest were found to exceed the maximum calibration range, dilution of the sample with zero air using a gas dilution system (Environics S-4040, Tolland, USA) was required. Conversely, a larger volume (usually up to a maximum of 1000 mL in order to prevent moisture overloading) of sample was needed if the concentration of VOCs was below the calibration range. To achieve better sensitivity, the SIM mode was used and specific ion groups in multiple retention time windows were quantified. Baseline correction and quantification of the integrated results based on the specific response factor of individual VOCs and least squares analysis of the latest calibration curves were performed automatically by the software. All raw data affecting the identification and quantification results were manually checked as a quality control measure.

Chemicals and standards

Standard reference materials SRM 1800 and 1804a were purchased from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA). SRM 1800 and 1804a contain 15 and 19 VOC components, respectively, at approximately 5 ppbv in nitrogen. Ethane in SRM 1800 is not applicable to this method and benzene, toluene and *o*-xylene are common in both SRMs. A mixture of 41 NIST traceable VOCs that are listed in USEPA Method TO-14 at nominal concentrations of 1–2 ppmv in nitrogen was purchased from Matheson Gas Products (GA, USA) and Air Products and Chemical (Tamaqua, USA). The concentrations of these certified standards are given in Table 1. The NIST traceable VOCs mixture was diluted with humidified zero air in canisters to low ppbv levels and used as validity check standards in the study.

Stock gaseous standards of 26 VOC components (chloroethene, propane, propene, propyne, butane, isobutane, but-1-ene, 2-methylpropene, *cis*-but-2-ene, *trans*-but-2-ene, buta-1,3-diene, butyne, pentane, 2-methylbutane, 2,2-dimethylpropane, pent-1-ene, cyclopentene, hexane, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, hex-1-ene, cyclohexene, 1-methylcyclopentaene, heptene and 1-methylcyclohexene) were purchased from Scott Specialty Gases (San Bernardino, CA, USA). These mixtures usually contain 48 L of standards at 300 psig at approximately 10–15 ppmv. Standards of the remaining VOCs (most are liquids at room temperature and a few are crystalline solids) were purchased as commercial neat chemicals (Aldrich, BDH, Merck, *etc.*) with purity of not less than 98%. These standards were prepared in-house in the concentration range approximately 10–30 ppmv as described below.

Table 1 Certified concentrations of individual VOC component in NIST SRM 1800 and 1804a and TO-14 NIST traceable standards

SRM 1800	Concentration ± s (ppbv)	SRM 1804a	Concentration ± s (ppbv)	TO-14 NIST traceable standard	Concentration (ppmv) accuracy ± 5%
Ethane	5.1 ± 0.2	Chloroethene	5.26 ± 0.15	Dichlorodifluoromethane (Freon 12)	1.01
Propane	5.4 ± 0.2	Trichlorofluoromethane (Freon 11)	5.26 ± 0.08	Chloromethane	1.02
				1,2-Dichlorotetrafluoroethane (Freon 114)	1.03
Propene	5.2 ± 0.2	Buta-1,3-diene	5.39 ± 0.17	Chloroethene	1.04
IsoButene	5.5 ± 0.2	Dichloromethane	5.13 ± 0.25	Buta-1,3-diene	1.06
n-Butane	5.3 ± 0.2	1,1-Dichloroethene	5.58 ± 0.23	Bromomethane	1.03
		1,1-Dichloroethane	5.67 ± 0.13	Chloroethane	1.03
2-Methylbutane	5.8 ± 0.2	Trichloromethane	5.15 ± 0.16	Freon 11	1.01
n-Pentane	5.1 ± 0.2	1,2-Dichlorethane	5.09 ± 0.15	1,1-Dichloroethene	0.99
Pent-1-ene	5.1 ± 0.2	1,1,1-Trichloroethane	5.11 ± 0.12	Methylene chloride	1.01
n-Hexane	5.3 ± 0.2	Benzene	5.11 ± 0.12	1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)	1.00
Benzene	5.2 ± 0.2	Tetrachloromethane	5.12 ± 0.11	1,1-Dichloroethane	1.02
Octane	5.1 ± 0.2	1,2-Dichloropropane	5.12 ± 0.12	*cis*-1,2-Dichloroethene	1.01
Toluene	5.2 ± 0.2	Trichloroethene	5.16 ± 0.10	Chloroform	1.01
o-Xylene	5.1 ± 0.2	Toluene	5.00 ± 0.16	1,2-Dichloroethane	1.02
n-Decane	5.1 ± 0.2	1,2-Dibromoethane	4.88 ± 0.38	1,1,1-Trichloroethane	1.02
		Tetrachloroethene	5.13 ± 0.10	Benzene	1.03
		Chlorobenzene	5.11 ± 0.17	Tetrachloromethane	1.01
		Ethylbenzene	5.14 ± 0.17	1,2-Dichloropropane	1.02
		o-Xylene	5.34 ± 0.13	Trichloroethene	1.02
				cis-1,3-Dichloropropene	1.03
				trans-1,3-Dichloropropene	1.05
				1,1,2-Trichloroethane	1.02
				Toluene	1.03
				1,2-Dibromoethane	1.03
				Tetrachloroethene	1.01
				Chlorobenzene	1.01
				Ethylbenzene	1.01
				m-*p*-Xylene	2.04
				Styrene	1.01
				1,1,2,2-Tetrachloroethane	1.01
				o-Xylene	1.01
				4-Ethyltoluene	1.01
				1,3,5-Trimethylbenzene	1.03
				1,2,4-Trimethylbenzene	1.02
				Benzyl chloride	1.02
				1,3-Dichlorobenzene	1.00
				1,4-Dichlorobenzene	1.00
				1,2-Dichlorobenzene	0.99
				1,2,4-Trichlorobenzene	1.00
				Hexachlorobutadiene	1.00

Preparation of stock standard solutions from neat chemicals

An appropriate, selected volume of neat liquid standard was pipetted into a clean pre-weighed 50 mL calibrated flask with stopper *via* an autopipette. The flask was re-weighed on an analytical balance capable of reading to at least 0.1 mg. The process was repeated until all the liquid standards had been added to the flask. Crystalline standards were separately weighed on weighing paper and transferred into the liquid mixture. The weight fraction of each component was calculated. Allowing sufficient time for complete dissolution of solid components, approximately 1 mL aliquots of the homogenized stock standard solution were transferred to amber-coloured ampoules and sealed immediately. The ampoules were stored in an explosion proof refrigerator until use.

The seal was opened after the mixture in the ampoule had equilibrated at room temperature and exactly 10 μL were withdrawn using a syringe. The filled syringe was weighed on an analytical balance capable of reading to at least 0.1 mg. The liquid mixture was injected *via* a septum assembly into a 3 L dilution flask, the exact volume of which was pre-determined by the water displacement method, and the syringe was immediately weighed. The flask was allowed to stand at room temperature (25 °C) for at least 72 h before any of the stock gas mixture was withdrawn. From the weight of the mixture added to the flask, the weight fractions of components in the mixture and the volume of the flask, the gaseous concentration of each component was calculated as follows:

$$WF_X = \frac{\text{weight of component X in mixture}}{\text{weight of all components in mixture}}$$

Concentration of component X (ppmv) at 25 °C and 1 atm =

$$\frac{W_L \times WF_X \times 24.45}{F_V \times MW}$$

where W_L is the weight of mixture injected into dilution flask in μg, WF_X is the weight fraction of component X in the liquid mixture, F_V is the volume of dilution flask in litres at 25 °C and MW is the molecular weight of component X.

Preparation of working standard solutions

VOC working standard solutions were prepared by dilution of appropriate volumes of the stock VOC mixture with cleaned humidified zero air into a clean, fully evacuated 15 L canister. The evacuated canister was connected to a three-way stainless steel valve assembly which allows for the accurately metered introduction of clean humidified zero air, syringe delivery of stock gas mixtures and venting of the dilution air flow to the atmosphere when the desired fill volume has been achieved. With the valve in the ‘fill’ position, air was introduced into the canister *via* mass flow controllers (MFCs). The MFCs were regularly calibrated against a soap bubble flowmeter (Gillian Instruments, Wayne, USA) or a Dry Cal primary flow calibrator (BIOS International, Pompton Plains, USA). While filling the 15 L canisters with zero air at a selected flow rate, stock gaseous VOC mixtures were introduced sequentially into the canisters *via* gas tight syringes of appropriate volume (5, 10 or 25 mL). The three-way valve was switched to the ‘vent’ position when the canisters were filled with exactly 100 L of zero air. The working standard solutions were in the low ppb range and were subsequently verified with reference standards before use whenever possible.

Internal standards

Four compounds, bromochloromethane, 1,4-difluorobenzene, chlorobenzene-d_5 and BFB, were purchased from Matheson Gas Products as internal standards in the GC-MS analysis. The working level of these compounds was approximately at 1 ppmv. Unlike the VOC working standard solutions, the concentrations of internal standards need not be known with high accuracy as recalibration of analytical system is required upon first use of each batch of internal standard.

Method validation

Qualitative identification of VOCs was based on the match of the retention times and the ion ratios of the target ions and the respective qualifier ions. MDL values were calculated by seven replicate analyses of the 143 VOC working standard solutions at about 0.2 ppbv concentration according to an approach described previously.[22,23] MDLs were defined as $t_{(n-1,\,1\text{-}\alpha\,=\,0.99)}\,s$, where s is the standard deviation of consecutive analyses, t is Student’s t-value appropriate to a 99% confidence level and a standard deviation estimate with $n-1$ degrees of freedom; in this case $t = 3.14$. Practical quantification limits (PQL) were defined as five times the MDL. Precision in terms of relative standard deviation (RSD) was determined by analysing 10 consecutive working standard solutions at concentrations near the PQL and was also assessed through the relative percentage difference (RPD) of replicate analyses (n = 35) of samples collected at urban sites in Hong Kong during 1999 and 2000. In addition, the overall analytical bias was estimated using co-located samples at 3 month intervals and should not deviate by more than 25%.

Determination of the method accuracy for the 143 VOCs is not easy in practice since reference materials that are traceable to international and national standards for most of the VOCs under study are currently unavailable.[24] The commercial standards of 41 targeted VOCs as listed in USEPA Method TO-14 and SRM 1800 and 1804a from NIST together could only account for 51 out of the 143 VOCs. The NIST reference standards were primarily used to construct calibration curves in the range 1.0–9.0 ppbv for the verification of individual batch of working standard solutions. Conversely, the in-house working standard solutions were used to construct calibration curves in the range 0.20–4.0 ppbv for evaluating the percentage recovery of VOCs in the validity check standard (zero air diluted TO-14 reference standards). The percentage recovery of VOC concentrations in the in-house prepared working standard solutions was worked out against the nominal concentrations of the reference standards. The validity of the remaining VOCs was evaluated by comparison with the calculated values of the corresponding compounds against the mean relative response factors (RRF) that were established in the calibration using the nominal values during preparation. A working standard solution was accepted for use when the concentration values determined for all the components were within 20% of their respective nominal values.

A calibration check standard was used to check the validity of the calibration curves. Full calibration was performed once a month or whenever the criteria of the calibration check standard were not met. The difference between the RRF in the calibration check standard and the mean RRF in the most updated calibration curve should be within 30%.

In summary, the following analysis sequences were conducted for routine analyses: (1) GC-MS mass autotune, (2) BFB tune using internal standard in zero air, (3) full calibration or calibration standard check, (4) blank zero air, (5) field samples, (6) replicate sample and (7) calibration standard check. The key ions and ion abundance of the background-subtracted mass spectrum of BFB must meet the criteria specified by the MS manufacturer. The blank zero air should not contain any VOCs that exceed the PQL. If the concentrations of the VOCs lie between the MQL and PQL, the blank will be used for correction in the quantification. Sample data were considered valid if all the above QC parameters met the set acceptance requirements. Other requirements such as sample handling and storage were undertaken according to the Standard Operating Procedures of the Hong Kong Government Laboratory.[25]

Stability of working standard solutions

The stability of VOCs in the working standard solutions in pressurized canisters was assessed by the measurement of the percentage recovery, which was calculated as the ratio of the average of two consecutive measurements at various time intervals (1, 2 and 4 weeks and 2 and 4 months after preparation) to the mean initial values of the working standard solution. Mean initial values were the average of seven replicate analyses of the freshly prepared standard.

Site sampling

A VOC canister sampling system (Model 910A, Xontech, USA) was installed in a proper position at the sampling site. A certified clean evacuated canister was connected to the sampler and a built-in digital timer was programmed at designated times over 4 h to collect air samples. Whole air was drawn into the system through a stainless steel inlet tube and a 2 μm stainless steel filter from a glass manifold attached to a blower motor assembly. A minimum of at least 1 L min^{-1} of whole air was drawn from the inlet tube by a stainless steel diaphragm pump. A small portion was split by a MFC at a flow rate of 10 mL min^{-1} into the canister. The rest of the air was vented. The canister pressures were recorded immediately after field sampling and the canisters with a final pressure of not less than 18 psi were sent to the laboratory for VOC analysis.

Results and discussion

Precision and accuracy

As listed in Table 2, the MDLs of the 143 VOCs were within 0.02 ppbv and were similar to or up to twice as good as those in other studies,[26–28] and were consistent during regular reviews in the past 12 month period. The precision of 10 consecutive injections at about 0.2 ppbv was well within ±10%; the RPDs of replicates (n = 35) and co-located samples were less than 15% and 20%, respectively. The accuracy for 51 VOCs was within ±20% of the claimed values of NIST standards (88.4–110%) and NIST traceable reference standards (84.2–117%) and shown to meet the acceptance criteria. The mean recoveries of most VOCs in the five independently prepared working standard solutions were in the range 86.5–116% with RSDs of less than 10%. However, the variation for some aliphatic alkenes and styrene was relatively high (up to 19%). In a previous study it was reported[29] that C_5–C_6 alkenes exhibit high analytical variability owing to either their non-symmetrical peak shape on the non-polar DB-1 column or loss to water condensate in the analytical system. We believe the latter is probably the possible source of error because the peak shape for

Table 2 Summary of the validation data for the 143 VOCs of interest

											Precision		Accuracy (%RSD)		
Time window/min	No.	VOC (source)	Retention time/min	Target ions (m/z)	Qualifier ions (m/z)				MDL (ppbv)	PQL (ppbv)	RSD (%)^a	Diff. (%)^b	Mean recovery (%)^c	Mean recovery (%)^d	Mean recovery (%)^e
5.00	1	Propylene (G)	6.78	41	41	39	42		0.018	0.090	1.1	3.4	95.3 (9.9)	—	106 (5.7)
	2	Propane (G)	7.00	29	29	43	39		0.017	0.085	1.2	5.0	93.9 (5.3)	—	100 (6.2)
	3	Freon 22 (L)	7.42	51	51	67			0.016	0.080	2.3	2.6	—	—	99.2 (4.3)
	4	Freon 12 (L)	7.79	85	85	87	101		0.013	0.065	2.3	2.0	—	117 (8.9)	102 (6.3)
8.20	5	Prop-1-yne (G)	8.51	40	40	39	37		0.017	0.085	3.2	7.7	—	—	94.5 (5.4)
	6	Chloromethane (L)	9.03	50	50	52	15		0.015	0.075	2.0	2.7	—	114 (13)	98.9 (2.0)
9.50	7	Isobutane (G)	9.98	43	43	41	39		0.017	0.085	1.2	3.6	98.9 (8.6)	—	98.4 (7.2)
	8	Freon 114 (L)	10.3	85	85	135	87		0.009	0.045	2.2	3.1	—	108 (7.6)	98.6 (6.2)
	9	Chloroethene (G)	10.55	62	62	27	64		0.019	0.095	3.4	5.6	99.5 (6.5)	104 (4.0)	102 (6.8)
10.80	10	But-1-ene/isobutene (G/G)	11.15	41	41	39	56		0.015	0.075	0.9	5.3	—	—	110 (5.3)
	11	Buta-1,3-diene (G)	11.29	54	54	39	27	53	0.016	0.080	2.5	5.4	96.3 (6.5)	—	90.6 (4.0)
	12	Butane (G)	11.50	43	43	41	27	29	0.018	0.090	0.9	5.0	93.2 (13)	—	90.1 (8.9)
11.75	13	*t*-But-2-ene (G)	11.97	56	41	56	39	27	0.018	0.090	2.4	7.2	—	—	106 (6.3)
	14	2,2-Dimethylpropane (G)	12.04	57	57	41	29		0.009	0.045	1.2	—	—	—	112 (9.9)
	15	Bromomethane (L)	12.13	94	94	96	79		0.016	0.080	1.5	4.9	—	104 (17)	95.5 (3.5)
	16	But-1-yne (G)	12.29	54	54	39	53		0.015	0.075	2.2	—	—	—	91.6 (7.3)
	17	*c*-But-2-ene (G)	12.55	41	41	56	39		0.020	0.100	3.0	4.2	—	—	92.9 (8.0)
	18	Chloroethane (L)	12.84	64	64	27	29	66	0.014	0.070	3.2	3.1	—	102 (11)	96.6 (5.2)
13.60	19	2-Methylbutane (G)	14.44	43	43	42	41	57	0.016	0.080	1.4	2.5	94.7 (7.1)	—	97.0 (4.4)
	20	Freon 11 (L)	14.69	101	101	103	105		0.016	0.080	2.7	3.1	91.8 (6.3)	108 (3.7)	98.7 (7.7)
14.90	21	Pent-1-ene (G)	15.01	42	55	42	70	39	0.018	0.090	1.8	4.7	98.1 (14)	—	108 (12)
	22	2-Methylbut-1-ene (L)	15.27	55	55	39	42	70	0.017	0.085	3.0	6.6	—	—	103 (6.4)
	23	Pentane (G)	15.42	43	43	42	41		0.015	0.075	2.1	2.2	103 (5.8)	—	98.5 (6.8)
	24	Isoprene (L)	15.56	67	67	68	53	39	0.017	0.085	2.5	3.0	—	—	89.6 (8.2)
	25	Bromoethane* (L)	15.71	108	108	110	29		0.015	0.075	2.6	—	—	—	101 (9.6)
	26	*t*-Pent-2-ene* (L)	15.71	55	55	42	70	39	0.017	0.085	1.9	5.0	—	—	113 (13)
	27	1,1-Dichloroethene (L)	15.77	61	61	96	98	63	0.014	0.070	2.1	—	94.1 (4.6)	104 (7.1)	101 (8.9)
	28	*c*-Pent-2-ene (L)	15.98	55	55	42	70		0.015	0.075	1.0	4.5	—	—	92.1 (13)
	29	Methylene chloride (L)	16.06	49	49	84	86	51	0.017	0.085	2.5	3.0	88.4 (3.0)	116 (7.1)	110 (9.6)
	30	2-Methylbut-2-ene (L)	16.14	55	55	70	41	39	0.015	0.075	1.2	4.3	—	—	93.7 (11)
	31	3-Chloropropene (L)	16.21	41	41	76	39		0.017	0.085	3.4	—	—	—	96.9 (10)
16.35	32	Freon 113 (L)	16.50	151	151	103	101	85	0.015	0.075	2.3	4.1	—	106 (13)	118 (8.5)
	33	2,2-Dimethylbutane (G)	16.64	57	57	71	43	41	0.018	0.090	1.5	4.0	—	—	96.1 (9.8)
16.95	34	Cyclopentene (G)	17.21	67	67	68	53		0.016	0.080	2.2	6.3	—	—	96.3 (11)
	35	*t*-1,2-Dichloroethene (L)	17.33	61	61	96	98		0.013	0.065	2.7	3.1	—	—	100 (6.9)
	36	4-Methylpent-1-ene (L)	17.39	43	43	41	56	39	0.016	0.080	1.6	5.9	—	—	108 (11)

Table 2 continued on next page—

Table 2 *Continued—*

											Precision		Accuracy (%RSD)		
Time window/min	No.	VOC (source)	Retention time/min	Target ions (m/z)	Qualifier ions (m/z)				MDL (ppbv)	PQL (ppbv)	RSD (%)^a	Diff. (%)^b	Mean recovery (%)^c	Mean recovery (%)^d	Mean recovery (%)^e
	37	3-Methylpent-1-ene (L)	17.41	55	55	69	41	84	0.017	0.085	1.9	6.5	—		95.1 (12)
	38	1,1-Dichloroethane* (L)	17.56	63	63	65	27	83	0.016	0.080	2.4	1.9	95.5 (3.9)	107 (9.7)	99.4 (8.6)
	39	Cyclopentane* (L)	17.56	42	42	55	70		0.016	0.080	3.2	3.5	—	—	97.3 (5.2)
	40	2,3-Dimethylbutane (L)	17.67	43	43	42	41	71	0.016	0.080	3.4	3.2	—	—	98.9 (8.0)
	41	*t*-4-Methylpent-2-ene (L)	17.78	69	69	41	84		0.017	0.085	2.6	5.3	—	—	115 (14)
	42	2-Methylpentane (G)	17.83	43	43	42	71		0.017	0.085	1.3	3.6	—	—	101 (6.7)
	43	*c*-4-Methylpent-2-ene (L)	17.88	69	69	41	84		0.016	0.080	4.6	4.1	—	—	103 (10)
18.10	44	3-Methylpentane (G)	18.29	57	57	56	41	29	0.017	0.085	1.2	2.6	—	—	107 (3.7)
	45	*c*-1,2-Dichloroethene (L)	18.56	61	61	96	98		0.015	0.075	1.0	4.0	—	95.9 (14)	90.9 (9.8)
	46	*Chlorobromomethane (IS)*	18.73	49	49										
	47	Hexane (G)	18.85	57	57	43	41	56	0.017	0.085	2.5	2.5	104 (4.4)	—	96.1 (9.5)
	48	Chloroform (L)	18.91	83	83	85	47		0.016	0.080	2.3	1.7	94.3 (4.8)	102 (4.4)	105 (6.3)
	49	*t*-Hex-2-ene (L)	19.00	55	55	84	41	42	0.017	0.085	3.2	6.4	—	—	87.6 (12)
	50	2-Ethylbut-1-ene (L)	19.08	69	41	69	84		0.015	0.075	5.6	—	—	—	90.2 (11)
	51	*t*-3-Methylpent-2-ene (L)	19.18	41	69	41	55	84	0.020	0.100	4.8	6.8	—	—	113 (9.8)
	52	*c*-Hex-2-ene (L)	19.30	55	55	42	84	69	0.016	0.080	4.2	4.1	—	—	104 (13)
19.40	53	*c*-3-Methylpent-2-ene (L)	19.49	41	69	41	55	84	0.016	0.080	3.3	7.0	—	—	105 (12)
	54	1,2-Dichloroethane* (L)	19.69	62	62	64	27	49	0.010	0.050	1.6	2.2	91.3 (5.4)	109 (2.2)	91.3 (7.3)
	55	Methylcyclopentane* (L)	19.69	56	56	41	69	84	0.015	0.075	2.8	2.7	—	—	95.6 (7.8)
	56	2,4-Dimethylpentane (L)	19.82	43	43	57	56	85	0.017	0.085	3.0	4.3	—	—	94.8 (5.9)
	57	1,1,1-Trichloroethane (L)	19.95	97	97	99	61		0.011	0.055	1.7	2.2	92.1 (5.9)	100 (13)	101 (8.1)
	58	2,2,3-Trimethylbutane (L)	19.98	57	57	56	41	85	0.016	0.080	2.9	—	—	—	94.8 (6.9)
20.20	59	1-Methylcyclopentene (G)	20.40	67	67	82	39		0.016	0.080	2.2	5.1	—	—	96.1 (11)
	60	Benzene (L)	20.43	78	78	77	50		0.011	0.055	1.4	3.0	103 (3.8)	91.5 (6.6)	90.6 (8.2)
	61	Tetrachloromethane (L)	20.60	117	117	119	121		0.016	0.080	2.8	2.0	95.0 (7.8)	102 (9.6)	96.6 (7.9)
	62	Cyclohexane (L)	20.73	56	56	84	41	69	0.015	0.075	2.8	3.0	—	—	100 (5.6)
	63	1,4-Difluorobenzene (IS)	20.85	114	114	63	88								
	64	2-Methylhexane (L)	20.96	43	85	57	43	41	0.015	0.075	2.8	3.2	—	—	95.2 (7.0)
	65	2,3-Dimethylpentane (L)	21.03	56	56	57	43	71	0.017	0.085	1.4	3.5	—	—	98.2 (8.5)
	66	Cyclohexene* (G)	21.22	67	67	54	82	41	0.016	0.080	2.0	3.9	—	—	96.9 (7.8)
	67	3-Methylhexane* (L)	21.22	43	70	71	43	57	0.014	0.070	2.1	4.7	—	—	95.9 (9.6)
	68	Dibromomethane (L)	21.26	93	93	95	174		0.012	0.060	1.7	—	—	—	107 (7.2)
	69	1,2-Dichloropropane (L)	21.30	63	63	62	41	76	0.017	0.085	2.5	—	90.0 (8.2)	99.2 (15)	105 (7.3)
21.40	70	Bromodichloromethane (L)	21.50	83	83	85	129		0.013	0.065	1.1	—	—	—	86.2 (9.6)
	71	Trichloroethene* (L)	21.57	130	130	132	95	97	0.014	0.070	1.9	3.7	94.3 (6.3)	102 (6.7)	106 (8.4)
	72	1-Heptene* (L)	21.57	41	41	56	55	70	0.020	0.100	2.6	8.3	—	—	87.1 (14)
	73	2,2,4-Trimethylpentane (L)	21.64	57	57	56	41		0.017	0.085	3.0	5.6	—	—	93.3 (11)
21.75	74	*t*-Hept-3-ene (L)	21.86	41	41	56	69	98	0.007	0.035	11	—	—	—	110 (13)
	75	Heptane* (G)	21.92	43	43	57	71	100	0.015	0.075	2.5	5.5	—	—	111 (11)
	76	*c*-Hept-3-ene* (L)	21.92	69	41	56	69	98	0.017	0.085	3.5	8.3	—	—	91.9 (13)
	77	*t*-Hept-2-ene (L)	22.05	55	55	69	41	98	0.017	0.085	1.9	3.7	—	—	91.0 (12)
	78	*c*-Hept-2-ene (L)	22.29	56	56	98	41	69	0.017	0.085	1.6	—	—	—	105 (11)
	79	*c*-1,3-Dichloropropene (L)	22.47	75	75	39	77	110	0.011	0.055	1.8	—	—	91.1 (4.5)	108 (11)
	80	2,2-Dimethylhexane* (L)	22.59	57	57	56	41		0.015	0.075	2.9	—	—	—	106 (12)
	81	Methylcyclohexane* (L)	22.59	83	55	83	98	41	0.012	0.060	2.1	—	—	—	101 (12)
22.73	82	2,5-Dimethylhexane (L)	22.85	57	57	43	71	99	0.013	0.065	2.4	5.2	—	—	94.1 (11)
	83	2,4-Dimethylhexane (L)	22.92	43	43	57	85	41	0.016	0.080	3.1	4.4	—	—	109 (12)
	84	*t*-1,3-Dichloropropene (L)	23.02	75	75	77	110	39	0.017	0.085	2.6	—	—	84.2 (3.6)	92.9 (11)
	85	1,1,2-Trichloroethane (L)	23.22	97	97	83	85	61	0.015	0.075	2.9	—	—	114 (16)	97.1 (7.2)
	86	Bromotrichloromethane* (L)	23.40	117	117	119	163		0.014	0.070	2.2	—	—	—	96.3 (14)
	87	2,3,4-Trimethylpentane* (L)	23.40	43	70	71	57	43	0.015	0.075	3.0	3.6	—	—	109 (13)
	88	Toluene (L)	23.54	91	91	92			0.017	0.085	2.7	1.4	104 (3.1)	104 (7.5)	104 (7.1)
23.67	89	2-Methylheptane (L)	23.79	57	43	57	41	99	0.016	0.080	3.1	2.9	—	—	86.8 (11)
	90	1-Methylcyclohexene* (L)	23.84	81	81	67	68	96	0.017	0.085	2.6	4.2	—	—	102 (13)
	91	4-Methylheptane* (L)	23.84	43	43	70	71	41	0.018	0.090	3.3	6.4	—	—	109 (13)
	92	3-Methylheptane* (L)	23.99	43	43	57	85	29	0.013	0.065	2.7	4.1	—	—	107 (13)
	93	Dibromochloromethane* (L)	23.99	129	129	127	79		0.016	0.080	1.8	—	—	—	112 (10)
	94	1,2-Dibromoethane (L)	24.26	107	107	109	27		0.015	0.075	2.4	—	111 (7.3)	113 (7.3)	98.2 (7.2)
	95	2,2,5-Trimethylhexane (L)	24.31	57	57	56	71		0.011	0.055	2.6	—	—	—	102 (12)
	96	Oct-1-ene (L)	24.38	41	41	43	55	70	0.016	0.080	2.1	8.0	—	—	116 (13)
24.46	97	Octane (L)	24.68	43	43	57	71	85	0.017	0.085	3.0	2.0	90.1 (5.8)	—	92.1 (13)
	98	*t*-1,2-Dimethylcyclohexane (L)	24.74	97	55	97	112	41	0.019	0.095	6.1	2.2	—	—	90.1 (10)
	99	Tetrachloroethene (L)	24.82	166	166	164	129	131	0.011	0.055	1.3	1.6	95.6 (5.7)	112 (7.6)	97.7 (8.1)
25.30	100	Chlorobenzene-d_5* (IS)	25.55	117	117	119	82								
	101	*c*-1,2-Dimethylcyclohexane* (L)	25.55	55	55	70	97		0.018	0.090	1.8	—	—	—	93.5 (8.7)
	102	Chlorobenzene (L)	25.60	112	112	114	77		0.016	0.080	2.8	—	93.7 (7.1)	106 (9.8)	112 (10)
25.84	103	Ethylbenzene (L)	26.07	91	91	106			0.019	0.090	2.6	2.5	96.2 (4.3)	96.9 (10)	107 (13)
	104	1,2,4-Trimethylcyclohexane (L)	26.18	111	111	69	55	126	0.015	0.075	2.6	4.0	—	—	92.4 (12)
	105	*m*-,*p*-Xylene (L)	26.30	91	91	106			0.016	0.080	1.2	2.5	—	85.9 (3.0)	113 (6.4)
	106	Bromoform (L)	26.35	173	173	171	254	250	0.016	0.080	2.2	—	—	—	108 (13)
26.55	107	1,4-Dichlorobutane* (L)	26.74	55	41	55	62	90	0.016	0.080	2.7	—	—	—	110 (11)
	108	Styrene* (L)	26.74	104	104	103	78	51	0.019	0.095	3.7	6.9	—	101 (21)	87.8 (14)

Table 2 continued on next page—

Table 2 *Continued—*

											Precision		Accuracy (%RSD)		
Time window/min	No.	VOC (source)	Retention time/min	Target ions (*m*/*z*)	Qualifier ions (*m*/*z*)				MDL (ppbv)	PQL (ppbv)	RSD (%)[a]	Diff. (%)[b]	Mean recovery (%)[c]	Mean recovery (%)[d]	Mean recovery (%)[e]
	109	1,1,2,2-Tetrachloroethane (L)	26.85	83	83	85			0.019	0.095	2.5	—	—	95.4 (5.0)	114 (9.8)
	110	*o*-Xylene (L)	26.88	91	91	106			0.015	0.075	2.5	2.7	110 (5.0)	87.0 (2.2)	92.3 (5.5)
	111	1-Nonene (L)	26.93	56	55	56	69	41	0.017	0.085	2.5	7.3	—	—	87.8 (14)
	112	Nonane (L)	27.20	57	57	43	85		0.012	0.060	2.2	2.7	—	—	92.9 (11)
	113	*Bromofluorobenzene (IS)*	27.46	95	95	174	173	50							
	114	Isopropylbenzene (L)	27.66	105	105	120			0.018	0.080	3.3	5.0	—	—	90.0 (11)
27.90	115	3,6-Dimethyloctane (L)	28.22	57	57	71	43	41	0.012	0.060	2.8	8.2	—	—	96.5 (12)
	116	*m*-/*p*-Chlorotoluene (L)	28.30	91	91	126	89		0.016	0.080	1.5	—	—	—	106 (11)
	117	Propylbenzene (L)	28.37	120	91	120			0.018	0.090	3.5	3.3	—	—	105 (9.9)
	118	*o*-Chlorotoluene (L)	28.40	126	91	126	89		0.015	0.075	2.6	6.0	—	—	108 (11)
	119	3-Ethyltoluene (L)	28.52	105	105	120			0.008	0.040	1.4	2.6	—	—	101 (11)
	120	4-Ethyltoluene (L)	28.58	105	105	120			0.015	0.075	2.5	3.2	—	—	104 (10)
	121	1,3,5-Trimethylbenzene (L)	28.69	105	105	120			0.015	0.075	2.6	3.2	—	98.3 (11)	99.5 (11)
	122	2-Ethyltoluene (L)	28.96	105	105	120			0.013	0.065	2.7	2.2	—	—	92.9 (9.5)
29.12	123	Tertbutylbenzene* (L)	29.30	134	134	119	91		0.011	0.055	1.8	—	—	—	109 (10)
	124	1,2,4-Trimethylbenzene* (L)	29.30	105	105	120			0.019	0.095	3.1	3.0	—	89.4 (14)	105 (11)
	125	Dec-1-ene* (L)	29.30	56	55	56	70		0.013	0.065	2.9	5.5	—	—	86.5 (19)
	126	Benzyl chloride* (L)	29.51	91	91	126			0.020	0.100	3.5	6.3	—	—	96.4 (15)
	127	Decane* (L)	29.51	43	43	57	71	85	0.007	0.035	1.1	4.9	92.2 (6.0)	—	94.7 (7.2)
	128	1,3-Dichlorobenzene* (L)	29.51	146	146	148	111		0.017	0.065	2.7	3.5	—	109 (12)	90.1 (10)
	129	1,4-Dichlorobenzene (L)	29.62	146	146	148	111		0.017	0.065	2.8	—	—	101 (13)	101 (12)
	130	Isobutylbenzene (L)	29.66	91	91	92	134		0.015	0.075	2.8	2.2	—	—	107 (11)
	131	*sec*-Butylbenzene (L)	29.72	105	105	134			0.017	0.065	2.7	2.2	—	—	106 (12)
29.88	132	1,2,3-Trimethylbenzene* (L)	29.98	105	105	120			0.017	0.085	3.2	4.0	—	—	103 (10)
	133	4-Isopropyltoluene* (L)	29.98	119	119	134			0.016	0.080	2.8	4.3	—	—	93.5 (10)
	134	1,2-Dichlorobenzene (L)	30.15	146	146	148	111		0.016	0.080	2.7	—	—	101 (12)	110 (12)
	135	Indan (L)	30.27	117	117	118	115		0.011	0.055	1.9	6.5	—	—	93.9 (13)
	136	1,3-Diethylbenzene (L)	30.49	105	105	119	134		0.017	0.085	2.7	3.3	—	—	104 (11)
	137	1,4-Diethylbenzene (L)	30.65	119	119	105	134		0.015	0.075	2.5	4.5	—	—	99.4 (11)
	138	Butylbenzene (L)	30.68	92	91	92	134		0.015	0.075	2.2	5.3	—	—	109 (11)
	139	1,2-Diethylbenzene (L)	30.80	105	105	119	134	91	0.017	0.085	2.6	—	—	—	92.1 (11)
31.25	140	Undecane (L)	31.65	43	43	57	71	85	0.009	0.045	1.6	2.9	—	—	93.2 (11)
	141	1,2,3,5-Tetramethylbenzene (L)	32.01	119	119	134			0.015	0.075	2.5	8.0	—	—	88.9 (13)
	142	1,2,4,5-Tetramethylbenzene (L)	32.08	119	119	134			0.015	0.075	2.5	6.4	—	—	92.6 (14)
32.60	143	1,2,4-Trichlorobenzene (L)	33.22	180	180	182	145	184	0.017	0.085	2.2	2.6	—	105 (10)	89.9 (11)
	144	Naphthalene (L)	33.41	128	128	127	102		0.019	0.095	3.9	5.2	—	—	87.9 (13)
	145	Dodecane (L)	33.65	57	57	71	85	43	0.020	0.100	4.9	3.6	—	—	89.1 (14)
33.90	146	Hexachlorobutadiene (L)	34.16	225	225	223	227	260	0.011	0.055	1.6	—	—	—	85.3 (14)
	147	Hexylbenzene (L)	34.78	91	91	92	162		0.016	0.080	3.8	—	—	109 (8.5)	88.0 (10)

G = commercial stock gaseous mixture, L = in-house gaseous standards from neat chemical, IS = internal standards; precision in terms of [a] RSD of 10 consecutive injections at approximately 0.2 ppbv and [b] RPD of replicate analyses of samples collected at urban sites during 1999–2000 ($n = 35$), accuracy in terms of mean recovery ($n = 5$) in the [c] in-house working standards using NIST standard as calibration standards, [d] commercial NIST traceable standards using in-house working standards as calibration standards and [e] in-house working standards against the nominal concentrations during preparation; *represents co-eluted pairs. *t* = *trans*; *c* = *cis*.

alkenes was symmetrical in our chromatograms. Styrene was recognized to be difficult to determine accurately in our previous TO-14 study[30] and also studies undertaken by other laboratories.[23]

The blank zero air samples ($n = 100$) were free of analytes above the MDL or any other interference during the previous 12 month period [Fig. 2(a)]. The three repeated cleaning cycles of zero air filling and high temperature evacuation were proved to be successful in maintaining the cleanliness of canisters and the background contribution was considered negligible. Fig. 2(b)–(d) show typical chromatograms of the VOC analytes in the working standard and air samples collected outside and inside a semi-confined car park environment. The 143 VOC peaks were monitored separately in 26 retention time windows in the SIM mode. The majority of the peaks are reasonably resolved within 35 min on the DB-1 column and signs of broadening were not observed for those late eluting peaks. Table 2 illustrates co-eluted analytes under the chromatographic conditions applied such as bromoethane and *trans*-pent-2-ene, 1,1-dichloroethane and cyclopentane, and 1,2-dichloroethane and methylcyclopentane. These co-eluted pairs showed no quantification problems since the respective target ions and qualified ions are distinctively different from one another. However, this was not the case for three pairs of isomeric compounds, namely but-1-ene and isobutene, *m*- and *p*-xylene and *m*- and *p*-chlorotoluene, and thus the values were expressed as the total amount of these three pairs.

Use of humidified sample and purge gas

During the cryotrapping process of ambient samples, excessive moisture must be removed because it can block the cryotrap by the formation of ice, damage the GC capillary column, shift elution times and cause other undesirable effects in the quality measurements. As a consequence, a dryer is often recommended prior to cryogenic preconcentration in VOCs analysis. A Nafion® selective membrane type dryer is commonly used for this purpose. The mechanism is based on the dryer's material that is uniquely permeable to water molecules and water in the sample is removed by a counterflow of relatively dry air flowing between the membrane and the outer stainless steel tube. We preferentially employed a dryer to remove excessive moisture in all our samples, in particular the high moisture containing samples that were normally collected in the wet spring and summer seasons. However, the judicious use of this dryer with regard to the sample integrity in the analysis requires considerable attention and care. Although the sample recovery of some organic gases has been reported to be satisfactory when using a Nafion® dryer, the NMHC concentrations were reduced by nearly 20% and, in addition, the dryer introduced contaminants into the system in some cases.[31] The loss was mainly due to the dissolution of polar compounds in the moisture being removed and the rearrangement of compounds, particularly alkenes, under the regenerated conditions of the dryer's membrane between analyses. One study[32] reported that the degree of the loss of such sensitive compounds depends on the humidity of the sample and the purge gas. The recovery of C_4–C_6 alkenes was shown to be improved by 20–30% when using wet than dry purge air. It was proposed that the moisture could reduce the reactivity of the membrane towards alkenes although the exact mechanism is not known. In order to reduce the loss of the alkenes in the samples, the Nafion® dryer was constantly purged with humidified air before preconcentration (Fig. 1). The consistently good recovery for the working standard solution (Table 2) indicated that there was an insignificant loss of these olefinic compounds and the rearrangement problem associated with the dryer in VOCs analysis was not observed in our study.

Stability of VOCs in canisters

Working standard solutions at 0.2–9 μg m^{-3} were used to assess the stability of the 143 VOCs in canisters over a storage period of 4 months. As shown in Table 3, the extent of concentration decrease was not the same across different classes of VOCs. Some diminished faster in the first 2 weeks while the majority showed reasonably stable characteristics (loss $<15\%$) during the entire study period. The average loss of all the VOCs was calculated to be 7.3, 9.3, 10.6, 12.5 and 14.4% at 1, 2 and 4 weeks and 2 and 4 months after preparation, respectively (Fig. 3). In general, aliphatic alkenes were found to be the most unstable group of VOCs in the present study and their 4 month loss (mean ± *s*) was 21.8 ± 10.5%, followed by aromatics (15.5 ± 4.6%), halohydrocarbons (12.6 ± 11.4%) and alkanes (8.8 ± 4.6%). The concentrations of eight compounds or approximately 6% of the 143 VOCs were found to decrease by more than 30% upon storage in canisters. Two of them are halohydrocarbons, bromotrichloromethane and benzyl chloride, and the others are alkenes, isoprene, *cis*-4-methylpent-2-ene, *cis*-3-methylpent-2-ene, hept-1-ene, oct-1-ene, dec-1-ene and styrene. The low stability of these compounds might mainly arise from the chemical decomposition, adsorption/absorption on the canister's inner surface and chemical reactions with other species inside the canisters. A similar loss[31] (30 to 40%) was noted for C_6 alkenes after 3 months of storage, but the substantial losses for isoprene (100%) and styrene ($>60\%$) reported were not so evident in our study. Another study[32] on polar and non-polar VOCs in canisters revealed extremely good 30 day recoveries for Freon 12 (103%), isoprene (93%), styrene (95%), *trans*-4-methylpent-2-ene (117%), *cis*-4-methylpent-2-ene (104%), 2-ethylbut-1-ene (94%), *cis*-3-methylpent-2-ene (100%), hept-1-ene (99%) and *trans*-hept-3-ene (99%), but it showed various degrees of stability for prop-1-yne (72%), 1,2-dibromoethane (62%) and 2,3-dimethylbutane (23%) and unexpected high recoveries for *cis*-pent-2-ene (200%), tetrachloromethane (135%), 1,3-dimethylbenzene (175%) and *trans*-pent-2-ene (213%). The high recovery was explained by analytical interferences[29] but, as stated earlier, other workers

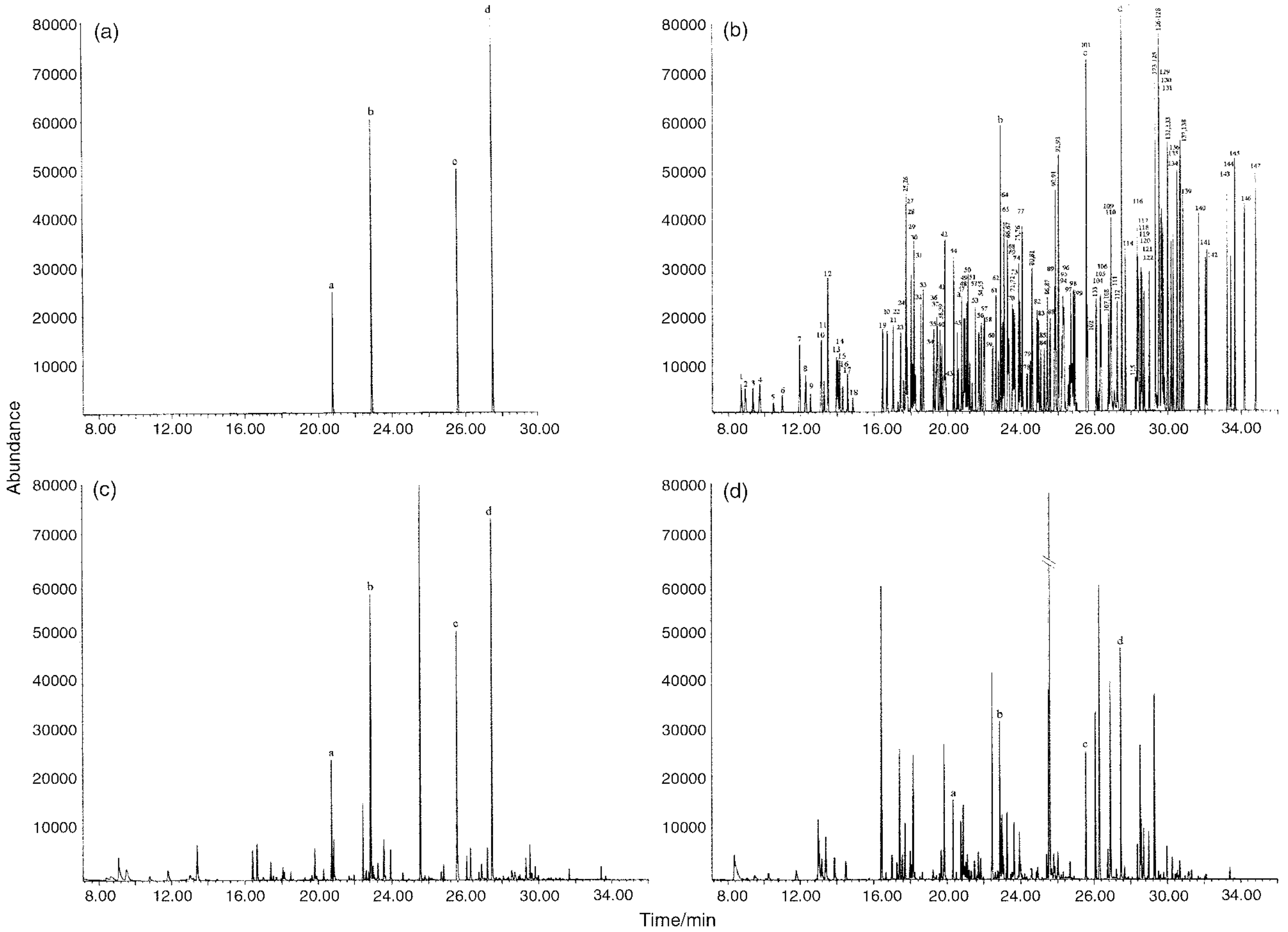

Fig. 2 Total ion chromatograms (TIC) of (a) 1 ppmv internal standards (a, chlorobromomethane, b, 1,4-difluorobenzene, c, chlorobenzene-d_5; and d, bromo-4-fluorobenzene) in 500 mL zero air, (b) 0.2–0.9 μg m^{-3} of working standard solutions and (c) and (d) samples collected at outdoor and semi-confined environment respectively.

Table 3 Stability of VOC standards in canisters at various time intervals and comparison of mean VOC concentrations ($n = 5$) collected inside and outside a semi-confined car park during 10–14 July 2000[a]

No.	VOC	Initial mean concentration/μg m^{-3}	I		II		III		VI		V		Outside car park/μg m^{-3}		Inside car park/μg m^{-3}	
													Day 1	Day 2	Day 1	Day 2
1	Propylene	4.51	4.32	(4.2)	4.23	(6.2)	4.19	(7.2)	4.14	(8.3)	4.08	(9.5)	0.62	0.48	2.6	11
2	Propane	4.39	4.21	(4.1)	4.12	(6.2)	3.99	(9.1)	3.94	(10.3)	3.88	(11.5)	1.7	1.0	1.2	1.0
3	Freon 22	2.24	2.19	(2.3)	2.23	(0.6)	2.17	(3.2)	2.12	(5.2)	2.11	(5.9)	1.7	1.8	2.4	1.4
4	Freon 12	1.79	1.72	(4.2)	1.72	(4.1)	1.70	(5.1)	1.68	(6.2)	1.57	(12.3)	3.4	3.1	3.9	3.5
5	Prop-1-yne	1.83	1.72	(6.1)	1.68	(8.1)	1.64	(10.2)	1.63	(10.9)	1.59	(12.9)	0.04	BDL	0.14	2.3
6	Chloromethane	2.35	2.28	(3.1)	2.31	(1.6)	2.25	(4.1)	2.23	(4.9)	2.20	(6.3)	1.0	0.92	1.0	1.2
7	Isobutane	4.49	4.30	(4.2)	4.22	(6.1)	4.20	(6.5)	4.17	(7.1)	4.14	(7.7)	1.0	0.58	4.0	3.3
8	Freon 114	1.45	1.38	(4.8)	1.36	(6.1)	1.33	(8.1)	1.32	(9.1)	1.30	(10.5)	BDL	BDL	BDL	BDL
9	Chloroethene	1.92	1.84	(4.2)	1.86	(2.9)	1.86	(3.1)	1.80	(6.5)	1.75	(9.0)	BDL	BDL	BDL	BDL
10	But-1-ene/isobutene	7.43	6.37	(14.2)	6.00	(19.2)	5.66	(23.8)	5.51	(25.8)	5.68	(23.6)	0.62	0.53	7.8	23
11	Buta-1,3-diene	2.26	2.25	(0.3)	2.19	(3.1)	2.15	(4.8)	2.14	(5.2)	2.10	(7.0)	0.17	0.12	0.94	5.7
12	Butane	6.57	6.29	(4.2)	6.20	(5.7)	6.05	(8.0)	6.03	(8.2)	5.96	(9.2)	2.7	1.5	12	10
13	*t*-But-2-ene	2.16	2.09	(3.0)	2.15	(0.7)	2.09	(3.5)	2.08	(3.6)	2.08	(3.8)	0.10	0.08	3.8	4.5
14	2,2-Dimethylpropane	2.48	2.45	(1.1)	2.45	(1.3)	2.45	(1.2)	2.43	(1.9)	2.39	(3.5)	BDL	BDL	0.21	0.17
15	Bromomethane	3.64	3.48	(4.5)	3.59	(1.3)	3.37	(7.5)	3.31	(9.0)	3.22	(11.5)	0.16	0.08	BDL	BDL
16	Buty-1-ne	2.48	2.35	(5.1)	2.23	(10.3)	2.28	(8.1)	2.08	(16.2)	2.03	(18.3)	BDL	BDL	BDL	0.2
17	*c*-But-2-ene	2.30	2.23	(3.1)	2.16	(6.1)	2.16	(5.9)	2.13	(7.5)	2.11	(8.2)	0.10	0.08	3.7	4.5
18	Chloroethane	1.47	1.42	(3.1)	1.46	(0.9)	1.45	(1.4)	1.41	(4.3)	1.37	(7.1)	BDL	BDL	BDL	BDL
19	2-Methylbutane	3.84	3.76	(2.0)	3.78	(1.5)	3.68	(4.1)	3.68	(4.2)	3.64	(5.2)	2.2	1.6	56	60
20	Freon 11	1.96	1.75	(10.9)	1.68	(14.1)	1.64	(16.1)	1.61	(18.1)	1.55	(20.8)	2.9	3.1	1.4	1.8
21	Pent-1-ene	4.20	3.57	(15.1)	3.40	(19.1)	3.31	(21.1)	3.15	(25.1)	3.16	(24.8)	0.19	0.16	3.1	4.2
22	2-Methylbut-1-ene	1.74	1.43	(17.6)	1.42	(18.5)	1.35	(22.7)	1.33	(23.5)	1.32	(24.2)	0.11	0.10	4.9	11
23	Pentane	2.36	2.31	(1.9)	2.29	(2.9)	2.30	(2.5)	2.29	(3.1)	2.26	(4.3)	0.91	0.72	18	17
24	Isoprene	3.25	2.23	(31.3)	2.10	(35.3)	2.01	(38.2)	1.87	(42.3)	1.60	(50.7)	0.25	0.28	0.18	0.22
25	Bromoethane	1.86	1.80	(3.1)	1.75	(6.1)	1.78	(4.2)	1.69	(9.1)	1.68	(9.7)	BDL	BDL	BDL	BDL
26	*t*-Pent-2-ene	1.58	1.29	(18.2)	1.25	(20.9)	1.24	(21.3)	1.22	(22.6)	1.21	(23.5)	0.10	0.08	5.8	6.7
27	1,1-Dichloroethene	2.17	2.08	(4.1)	2.06	(5.1)	2.04	(6.1)	2.03	(6.3)	2.01	(7.2)	BDL	BDL	BDL	BDL
28	*c*-Pent-2-ene	9.03	7.50	(16.9)	7.38	(18.3)	7.19	(20.3)	6.75	(25.3)	6.90	(23.6)	0.10	0.07	4.1	5.5
29	Methylene chloride	2.08	2.05	(1.2)	2.05	(1.3)	2.05	(1.5)	2.00	(3.8)	1.97	(5.1)	0.98	1.3	1.3	1.5
30	2-Methylbut-2-ene	4.66	4.50	(3.5)	4.47	(4.1)	4.56	(2.1)	4.37	(6.3)	4.31	(7.6)	0.23	0.16	13	14
31	3-Chloropropene	1.63	1.58	(3.1)	1.62	(0.7)	1.60	(1.8)	1.55	(4.9)	1.54	(5.6)	BDL	BDL	0.20	0.08
32	Freon 113	1.97	1.88	(4.6)	1.81	(8.1)	1.78	(9.8)	1.75	(11.0)	1.75	(11.3)	0.60	0.61	0.60	0.72
33	2,2-Dimethylbutane	3.96	3.84	(3.2)	3.80	(3.9)	3.90	(1.5)	3.84	(3.0)	3.78	(4.5)	0.09	BDL	0.58	1.6
34	Cyclopentene	2.54	2.31	(9.0)	2.13	(16.2)	2.06	(18.9)	2.01	(20.9)	1.98	(21.9)	BDL	BDL	0.63	1.4
35	*t*-1,2-Dichloroethene	1.59	1.51	(4.8)	1.58	(0.8)	1.50	(5.5)	1.54	(3.2)	1.50	(5.7)	BDL	BDL	BDL	0.09
36	*t*-4-Methylpent-1-ene	3.38	2.84	(16.1)	2.65	(21.5)	2.59	(23.5)	2.49	(26.4)	2.55	(24.6)	BDL	BDL	0.24	0.56
37	3-Methylpent-1-ene	4.62	3.82	(17.3)	3.74	(19.2)	3.65	(21.0)	3.61	(21.9)	3.59	(22.3)	BDL	BDL	0.30	0.67
38	1,1-Dichloroethane	2.24	2.16	(3.4)	2.14	(4.3)	2.20	(1.8)	2.17	(3.2)	2.11	(5.8)	BDL	BDL	BDL	BDL
39	Cyclopentane	1.81	1.72	(4.9)	1.71	(5.3)	1.68	(7.2)	1.73	(4.2)	1.67	(7.8)	0.13	0.10	0.73	1.2
40	2,3-Dimethylbutane	1.67	1.45	(13.5)	1.43	(14.5)	1.40	(15.9)	1.40	(16.4)	1.38	(17.6)	0.23	0.16	2.2	4.6
41	*t*-4-Methylpent-2-ene	2.61	2.01	(23.1)	1.95	(25.3)	1.89	(27.5)	1.86	(28.5)	1.84	(29.5)	BDL	BDL	0.13	0.30
42	2-Methylpentane	4.22	4.00	(5.2)	4.05	(4.0)	4.18	(1.0)	4.07	(3.5)	3.97	(5.9)	2.1	1.7	13	20
43	*c*-4-Methylpent-2-ene	1.10	0.81	(26.6)	0.79	(28.5)	0.78	(29.1)	0.75	(31.6)	0.74	(32.9)	BDL	BDL	1.0	1.5
44	3-Methylpentane	3.82	3.77	(1.2)	3.76	(1.5)	3.75	(1.8)	3.66	(4.3)	3.52	(7.8)	0.5	0.30	7.2	13
45	*c*-1,2-Dichloroethene	1.89	1.85	(2.0)	1.88	(0.6)	1.86	(1.6)	1.83	(3.1)	1.80	(4.9)	BDL	BDL	BDL	BDL
47	Hexane	2.29	2.16	(5.5)	2.27	(0.7)	2.17	(5.1)	2.23	(2.7)	2.16	(5.7)	1.9	1.3	8.4	13
48	Chloroform	1.87	1.76	(6.0)	1.72	(8.1)	1.82	(2.7)	1.78	(4.8)	1.68	(10.3)	0.32	0.28	0.22	0.19
49	*t*-Hex-2-ene	1.73	1.47	(15.2)	1.34	(22.3)	1.29	(25.4)	1.31	(24.2)	1.30	(24.8)	BDL	BDL	2.1	2.7
50	2-Ethylbut-1-ene	0.78	0.62	(21.1)	0.62	(20.1)	0.60	(23.5)	0.58	(25.7)	0.56	(28.2)	BDL	BDL	1.4	1.8
51	*t*-3-Methylpent-2-ene	1.43	1.28	(10.3)	1.34	(6.1)	1.24	(13.1)	1.30	(9.0)	1.22	(14.5)	BDL	BDL	1.7	2.9
52	*c*-Hex-2-ene	1.10	1.03	(6.1)	1.09	(1.2)	1.06	(3.9)	1.03	(6.2)	1.00	(9.5)	BDL	BDL	1.6	2.2
53	*c*-3-Methylpent-2-ene	1.71	1.25	(27.1)	1.28	(25.4)	1.22	(28.6)	1.19	(30.4)	1.13	(33.9)	BDL	BDL	2.3	3.5
54	1,2-Dichloroethane	2.17	1.94	(10.8)	2.00	(7.9)	2.11	(2.8)	2.00	(7.9)	1.95	(10.2)	BDL	0.08	0.15	0.11
55	Methylcyclopentane	1.89	1.83	(3.1)	1.82	(3.8)	1.87	(0.8)	1.86	(1.5)	1.82	(3.5)	0.33	0.25	3.8	6.7
56	2,4-Dimethylpentane	1.94	1.88	(3.1)	1.86	(4.2)	1.91	(1.3)	1.88	(2.9)	1.85	(4.6)	0.09	BDL	1.3	3.3
57	1,1,1-Trichloroethane	2.10	1.96	(6.6)	1.91	(9.0)	2.02	(4.0)	1.95	(7.2)	1.87	(11.1)	0.42	0.33	0.31	0.41
58	2,2,3-Trimethylbutane	1.95	1.91	(2.2)	1.86	(4.5)	1.93	(0.8)	1.91	(2.2)	1.86	(4.8)	BDL	BDL	BDL	0.19
59	1-Methylcyclopentene	2.63	2.47	(5.9)	2.58	(1.8)	2.57	(2.4)	2.47	(6.2)	2.39	(9.1)	BDL	BDL	BDL	2.9
60	Benzene	1.98	1.90	(3.8)	1.86	(6.1)	1.88	(5.1)	1.90	(4.1)	1.84	(6.9)	3.5	3.4	16	33
61	Tetrachloromethane	2.13	2.00	(6.1)	1.96	(8.2)	2.00	(6.3)	1.87	(12.1)	1.82	(14.7)	0.68	0.67	0.77	0.75
62	Cyclohexane	1.85	1.82	(1.5)	1.84	(0.4)	1.83	(1.1)	1.81	(2.1)	1.78	(3.8)	0.45	0.43	1.7	1.9
64	2-Methylhexane	1.88	1.86	(1.1)	1.78	(5.1)	1.74	(7.5)	1.68	(10.5)	1.69	(10.0)	0.80	0.54	5.2	12
65	2,3-Dimethylpentane	3.96	3.94	(0.5)	3.90	(1.5)	3.72	(6.0)	3.77	(4.9)	3.63	(8.2)	0.25	0.16	1.6	3.8
66	Cyclohexene	2.77	2.74	(1.3)	2.47	(10.9)	2.66	(4.1)	2.58	(6.9)	2.41	(13.1)	BDL	BDL	0.43	0.58
67	3-Methylhexane	2.08	2.00	(4.1)	2.00	(3.9)	1.95	(6.1)	2.00	(3.6)	1.94	(6.5)	0.81	0.49	5.0	11
68	Dibromomethane	2.23	2.15	(3.5)	2.20	(1.2)	2.16	(3.3)	2.12	(5.1)	2.04	(8.7)	BDL	BDL	BDL	BDL
69	1,2-Dichloropropane	2.14	2.10	(1.9)	2.13	(0.3)	2.13	(0.6)	2.11	(1.5)	2.08	(2.6)	BDL	BDL	BDL	BDL
70	Bromodichloromethane	3.49	2.96	(15.2)	2.93	(16.1)	2.86	(18.1)	2.79	(20.1)	2.64	(24.3)	BDL	BDL	BDL	0.29
71	Trichloroethene	2.22	2.17	(2.1)	2.13	(4.2)	2.17	(2.3)	2.12	(4.6)	2.05	(7.6)	0.23	0.25	0.13	BDL
72	Hept-1-ene	4.73	3.69	(22.1)	3.59	(24.0)	3.45	(27.1)	3.30	(30.2)	3.21	(32.1)	0.46	0.34	0.61	2.1
73	2,2,4-Trimethylpentane	2.42	2.32	(4.1)	2.39	(1.2)	2.32	(4.3)	2.30	(5.1)	2.20	(9.1)	0.22	0.17	3.3	9.5

Table 3 continued on next page—

Table 3 *Continued—*

No.	VOC	Initial mean concentration/µg m^{-3}	I		II		III		VI		V		Outside car park/µg m^{-3}		Inside car park/µg m^{-3}	
													Day 1	Day 2	Day 1	Day 2
74	*t*-Hept-3-ene	0.18	0.15	(15.1)	0.14	(22.2)	0.14	(22.2)	0.14	(22.2)	0.13	(27.8)	BDL	BDL	BDL	BDL
75	Heptane	2.37	2.22	(6.2)	2.22	(6.2)	2.17	(8.5)	2.14	(9.5)	2.10	(11.5)	1.4	0.84	4.0	7.8
76	*c*-Hept-3-ene	1.74	1.42	(18.2)	1.42	(18.5)	1.37	(21.5)	1.33	(23.6)	1.32	(24.2)	0.35	0.23	14	21
77	*t*-Hept-2-ene	2.69	2.61	(3.2)	2.51	(6.5)	2.41	(10.3)	2.37	(11.9)	2.33	(13.4)	BDL	BDL	0.42	0.66
78	*c*-Hept-2-ene	3.65	3.25	(11.1)	3.27	(10.5)	3.10	(15.1)	2.99	(18.0)	2.93	(19.8)	BDL	BDL	0.35	0.76
79	*c*-1,3-Dichloropropene	2.30	2.29	(0.6)	2.23	(3.1)	2.22	(3.6)	2.23	(3.2)	2.19	(4.8)	BDL	BDL	BDL	BDL
80	2,2-Dimethylhexane	1.91	1.87	(1.9)	1.90	(0.5)	1.89	(1.1)	1.87	(2.3)	1.84	(3.6)	BDL	BDL	BDL	0.25
81	Methylcyclohexane	1.97	1.91	(2.8)	1.95	(1.1)	1.91	(3.1)	1.88	(4.7)	1.80	(8.6)	0.41	0.22	0.91	1.8
82	2,5-Dimethylhexane	1.98	1.77	(10.5)	1.68	(15.1)	1.78	(10.3)	1.67	(15.8)	1.63	(17.5)	BDL	BDL	0.42	1.3
83	2,4-Dimethylhexane	1.89	1.85	(2.3)	1.64	(13.2)	1.55	(18.1)	1.48	(21.9)	1.51	(20.2)	0.12	BDL	0.67	2.1
84	*t*-1,3-Dichloropropene	2.43	2.33	(4.1)	2.21	(9.1)	2.11	(13.1)	2.19	(10.1)	2.09	(14.1)	BDL	BDL	BDL	BDL
85	1,1,2-Trichloroethane	1.80	1.76	(2.1)	1.79	(0.6)	1.77	(1.5)	1.75	(3.1)	1.72	(4.5)	BDL	BDL	BDL	BDL
86	Bromotrichloromethane	2.19	1.63	(25.4)	1.19	(45.7)	0.93	(57.5)	0.68	(68.8)	0.76	(65.4)	BDL	BDL	BDL	BDL
87	2,3,4-Trimethylpentane	1.92	1.81	(5.9)	1.77	(7.9)	1.88	(2.1)	1.84	(4.1)	1.78	(7.3)	BDL	BDL	1.0	3.7
88	Toluene	2.04	1.94	(4.7)	2.00	(1.8)	1.99	(2.6)	1.94	(4.8)	1.87	(8.2)	18	8.0	310	400
89	2-Methylheptane	2.41	2.27	(5.9)	2.15	(10.6)	2.24	(7.2)	2.19	(9.2)	2.09	(13.2)	0.16	BDL	1.5	3.1
90	1-Methylcyclohexene	2.92	2.74	(6.2)	2.77	(5.2)	2.65	(9.1)	2.59	(11.3)	2.46	(15.7)	BDL	BDL	0.39	0.54
91	4-Methylheptane	1.99	1.69	(14.9)	1.81	(9.0)	1.73	(13.1)	1.68	(15.5)	1.62	(18.6)	BDL	BDL	0.49	1.0
92	3-Methylheptane	1.93	1.83	(5.1)	1.90	(1.3)	1.89	(2.1)	1.87	(3.3)	1.79	(7.4)	0.14	BDL	1.6	0.26
93	Dibromochloromethane	2.67	2.54	(4.9)	2.45	(8.2)	2.59	(3.0)	2.48	(7.0)	2.42	(9.2)	BDL	BDL	BDL	BDL
94	1,2-Dibromoethane	2.17	2.13	(2.0)	2.08	(3.9)	2.13	(1.8)	2.04	(6.2)	2.02	(7.1)	BDL	BDL	BDL	BDL
95	2,2,5-Trimethylhexane	1.30	1.23	(5.1)	1.22	(6.0)	1.25	(3.6)	1.26	(2.7)	1.24	(4.8)	BDL	BDL	0.21	0.92
96	1-Octene	6.85	5.81	(15.2)	5.32	(22.4)	4.76	(30.5)	4.63	(32.5)	4.40	(35.7)	BDL	BDL	0.16	0.33
97	Octane	2.05	1.96	(4.5)	1.92	(6.2)	2.01	(2.1)	1.95	(4.8)	1.88	(8.4)	0.34	0.10	1.4	2.4
98	*t*-1,2-Dimetylcyclohexane	1.10	1.08	(2.1)	1.09	(0.6)	1.09	(0.9)	1.08	(2.0)	1.07	(3.0)	BDL	BDL	0.26	0.31
99	Tetrachloroethene	2.27	2.20	(3.1)	2.25	(0.9)	2.23	(1.8)	2.17	(4.2)	2.11	(6.9)	1.0	0.38	0.28	0.31
101	*c*-1,2-Dimethylcyclohexane	3.24	3.10	(4.2)	3.21	(0.8)	3.18	(1.9)	3.14	(3.0)	3.04	(6.0)	BDL	BDL	0.25	0.30
102	Chlorobenzene	2.25	2.14	(5.1)	2.23	(0.9)	2.20	(2.2)	2.16	(4.1)	2.09	(7.2)	1.2	1.1	0.14	BDL
103	Ethylbenzene	2.05	1.93	(6.1)	2.03	(1.2)	1.99	(2.8)	1.94	(5.2)	1.85	(9.6)	1.6	1.2	23	24
104	1,2,4-Trimethylcyclohexane	2.22	2.13	(4.2)	2.08	(6.2)	2.15	(3.2)	2.06	(7.2)	2.07	(6.6)	0.22	BDL	1.3	1.1
105	*m*-,*p*-Xylene	4.59	4.40	(4.1)	4.22	(8.1)	4.40	(4.2)	4.23	(7.8)	4.03	(12.2)	2.5	2.3	58	56
106	Bromoform	2.52	2.29	(9.0)	2.24	(11.1)	2.17	(13.9)	2.14	(14.9)	2.17	(13.9)	BDL	BDL	BDL	BDL
107	1,4-Dichlorobutane	2.57	2.41	(6.2)	2.36	(8.2)	2.36	(8.1)	2.29	(10.9)	2.26	(12.0)	BDL	BDL	BDL	BDL
108	Styrene	6.22	5.45	(12.4)	4.90	(21.3)	4.57	(26.5)	4.08	(34.3)	3.57	(42.5)	0.67	0.23	1.2	6.7
109	1,1,2,2-Tetrachloroethane	2.58	2.26	(12.5)	2.14	(17.0)	1.98	(23.2)	2.00	(22.3)	1.94	(24.9)	BDL	BDL	BDL	BDL
110	*o*-Xylene	2.32	2.25	(2.9)	2.20	(5.2)	2.27	(2.1)	2.25	(3.1)	2.16	(6.8)	0.78	0.47	23	20
111	1-Nonene	6.77	6.16	(9.1)	5.81	(14.2)	5.61	(17.2)	5.34	(21.1)	5.21	(23.0)	0.29	0.14	1.4	1.7
112	Nonane	2.25	2.20	(2.1)	2.23	(0.9)	2.20	(2.3)	2.15	(4.5)	2.09	(6.9)	1.4	0.32	1.7	1.5
114	Isopropylbenzene	2.24	2.14	(4.5)	2.05	(8.5)	2.17	(3.3)	2.09	(6.5)	1.99	(11.3)	BDL	BDL	0.64	1.16
115	3,6-Dimethyloctane	1.35	1.31	(3.0)	1.27	(6.1)	1.28	(5.2)	1.21	(10.6)	1.18	(12.4)	BDL	BDL	0.14	0.16
116	*m*-/*p*-Chlorotoluene	4.30	4.17	(3.0)	4.08	(5.1)	4.08	(5.2)	4.00	(7.0)	3.93	(8.6)	BDL	BDL	BDL	5.8
117	Propylbenzene	2.13	2.11	(0.9)	2.08	(2.3)	2.06	(3.5)	1.98	(7.2)	1.84	(13.5)	0.12	BDL	2.2	3.4
118	*o*-Chlorotoluene	2.36	2.29	(3.0)	2.26	(4.1)	2.17	(8.1)	2.12	(10.1)	2.14	(9.3)	BDL	BDL	BDL	BDL
119	3-Ethyltoluene	2.16	2.05	(5.0)	1.99	(8.1)	1.88	(13.0)	1.90	(12.1)	1.82	(15.7)	0.42	0.15	9.5	15
120	4-Ethyltoluene	2.16	2.07	(4.1)	1.94	(10.1)	1.90	(12.1)	1.90	(12.0)	1.84	(14.6)	0.24	BDL	4.5	6.3
121	1,3,5-Trimethylbenzene	2.15	2.04	(5.0)	1.92	(10.9)	1.89	(12.1)	1.85	(14.1)	1.82	(15.2)	0.25	BDL	3.7	6.1
122	2-Ethyltoluene	2.23	2.12	(5.1)	2.03	(9.0)	1.94	(13.2)	1.89	(15.2)	1.87	(16.1)	0.23	BDL	3.2	5.1
123	Tertbutylbenzene	2.46	2.14	(13.0)	2.01	(18.2)	1.91	(22.3)	1.92	(21.8)	1.88	(23.5)	BDL	BDL	BDL	BDL
124	1,2,4-Trimethylbenzene	2.57	2.41	(6.1)	2.30	(10.4)	2.27	(11.5)	2.18	(15.1)	2.12	(17.3)	0.75	0.29	13	18
125	Dec-1-ene	0.66	0.54	(18.2)	0.53	(19.2)	0.51	(23.2)	0.49	(25.1)	0.48	(27.6)	0.13	BDL	0.71	0.63
126	Benzyl-chloride	2.41	1.95	(19.0)	1.50	(37.9)	1.44	(40.4)	1.29	(46.6)	1.21	(49.7)	BDL	BDL	BDL	BDL
127	Decane	2.25	2.11	(6.1)	1.96	(13.1)	1.91	(15.0)	1.86	(17.1)	1.89	(16.2)	1.4	0.48	1.7	0.86
128	1,3-Dichlorobenzene	2.52	2.44	(3.2)	2.36	(6.2)	2.31	(8.2)	2.40	(4.8)	2.25	(10.5)	BDL	BDL	BDL	BDL
129	1,4-Dichlorobenzene	2.63	2.49	(5.2)	2.30	(12.4)	2.39	(9.1)	2.22	(15.5)	2.24	(15.0)	0.32	0.25	0.70	0.59
130	Isobutylbenzene	2.28	2.19	(4.1)	2.12	(7.2)	1.96	(14.2)	1.95	(14.5)	1.92	(16.0)	BDL	BDL	BDL	BDL
131	*sec*-Butylbenzene	2.40	2.03	(15.6)	1.96	(18.2)	1.89	(21.3)	1.82	(24.3)	1.83	(23.8)	BDL	BDL	BDL	BDL
132	1,2,3-Trimethylbenzene	2.15	2.04	(5.1)	1.89	(12.2)	1.87	(13.1)	1.79	(16.9)	1.83	(15.0)	0.17	BDL	2.3	2.9
133	4-isopropyltoluene	2.30	2.04	(11.2)	1.95	(15.3)	1.91	(17.2)	1.87	(18.5)	1.83	(20.6)	BDL	BDL	BDL	BDL
134	1,2-Dichlorobenzene	2.61	2.56	(2.0)	2.50	(4.1)	2.42	(7.1)	2.37	(9.0)	2.31	(11.5)	BDL	BDL	BDL	BDL
135	Indan	2.31	2.19	(5.2)	2.05	(11.5)	1.96	(15.2)	1.96	(15.2)	1.92	(16.7)	BDL	BDL	1.5	1.9
136	1,3-Diethylbenzene	2.31	2.12	(8.2)	2.07	(10.5)	2.05	(13.1)	1.90	(17.8)	1.97	(14.6)	BDL	BDL	0.20	0.43
137	1,4-Diethylbenzene	2.39	2.12	(11.2)	2.14	(10.3)	1.98	(17.2)	1.96	(18.2)	1.91	(19.9)	BDL	BDL	0.50	1.1
138	Butylbenzene	2.35	2.20	(6.4)	2.05	(12.8)	2.01	(14.4)	2.03	(13.7)	1.95	(16.9)	BDL	BDL	0.18	0.25
139	1,2-Diethylbenzene	2.38	2.06	(13.5)	1.99	(16.2)	1.90	(20.3)	1.79	(24.6)	1.85	(22.3)	BDL	BDL	BDL	BDL
140	Undecane	2.33	2.23	(4.5)	2.19	(6.1)	2.08	(10.5)	1.97	(15.5)	1.99	(14.6)	0.55	0.20	1.0	0.41
141	1,2,3,5-Tetramethylbenzene	2.42	2.22	(8.1)	2.12	(12.2)	2.17	(10.5)	1.99	(17.7)	2.06	(15.0)	BDL	BDL	0.36	0.48
142	1,2,4,5-Tetramethylbenzene	1.53	1.41	(8.0)	1.46	(4.6)	1.39	(9.2)	1.25	(18.4)	1.30	(14.8)	BDL	BDL	0.32	0.41
143	1,2,4-Trichlorobenzene	2.76	2.54	(8.1)	2.29	(17.2)	2.29	(17.2)	2.26	(18.3)	2.19	(20.6)	BDL	BDL	BDL	BDL
144	Naphthalene	1.85	1.57	(15.0)	1.44	(22.3)	1.41	(23.5)	1.42	(23.2)	1.45	(21.6)	0.60	0.39	2.9	1.3
145	Dodecane	2.83	2.71	(4.2)	2.60	(8.0)	2.42	(14.6)	2.34	(17.2)	2.40	(15.1)	0.23	BDL	0.57	0.17

Table 3 continued on next page—

Table 3 *Continued—*

No.	VOC	Initial mean concentration/μg m^{-3}	I		II		III		VI		V		Outside car park/μg m^{-3}		Inside car park/μg m^{-3}	
													Day 1	Day 2	Day 1	Day 2
146	Hexachlorobutadiene	3.16	2.73	(13.7)	2.59	(18.2)	2.46	(22.2)	2.52	(20.2)	2.48	(21.5)	BDL	BDL	BDL	BDL
147	Hexylbenzene	1.85	1.66	(10.3)	1.56	(15.6)	1.58	(14.8)	1.51	(18.6)	1.51	(18.2)	BDL	BDL	BDL	BDL
	No. of VOCs detected												73	60	104	109
	Total VOCs/μg m^{-3}												71.4	46.8	730	989
	Alkanes (%)												32.2	28.2	22.5	22.7
	Alkenes (%)												5.4	6.1	11.0	14.4
	Aromatics (%)												41.3	35.1	64.7	61.3
	Halohydrocarbons (%)												21.2	30.7	2.0	2.3

[a] I, II, III, VI and V represent the average of two concentrations measured in μg m^{-3} at 1, 2 and 4 weeks and 2 and 4 months, respectively, after preparation of standards. Differences (%) in the concentration compared with initial mean concentration are given in parentheses. BDL denotes concentration below method detection limits. Coversion equation of μg m^{-3} to ppbv at 25 °C: concentration/μg m^{-3} = (ppbv × molecular weight)/24.45.

reported that the enriched C_4–C_6 alkenes were formed by the structural rearrangement of other alkene analogues on a Nafion® dryer during the regeneration cycle.[32] Obviously, large discrepancies exist amongst literature data on the stability of VOCs. The disagreements were possibly caused by variables such as the quality of canisters, sample storage conditions, storage temperature, canister cleaning method, canister pressure, different reactivities in air matrices and other unknown factors. Although we are unable to identify specifically any of the above loss mechanisms, it is comprehensible from our recovery statistics that non-polar VOCs such as alkanes are more stable than comparatively polar VOCs such as alkenes in canisters. As a consequence, it is recommended that the VOCs analysis is commenced promptly as the concentrations of these compounds decreased fairly rapidly, *e.g.*, isoprene lost 31% after 1 week of storage in canisters at room temperature.

All the stability data obtained in this study were obtained using VOC standards in humidified zero air above atmospheric pressure and this might not reflect perfectly the situation in 'real' samples. Although statistical analysis revealed insignificant differences in the VOC stability when stored at ambient and at elevated pressure,[29] the presence of other chemical species in 'real' samples, *e.g.*, NO_X, ozone and unknown VOCs, might have unpredictable effects towards some of the VOCs within canisters and reduce the stability of these compounds. Therefore, additional investigations are recommended and the results of the present study could provide a useful reference for the confirmation of reaction loss, if any, in complex air matrices in future studies.

Field measurements

The method was used in measuring two sets of field samples collected outside and inside a semi-confined car park environment during the period 10–14 July 2000. As shown in Table 3, the number and total concentrations of VOCs detected inside the car park were correspondingly much higher than the outdoors figures. The percentage compositions of individual classes of VOCs at the two sampling sites were also different: alkanes were 28.2–32.2 and 22.5–22.7%, alkenes were 5.4–6.1 and 11.0–14.4%, aromatics were 35.1–41.3 and 61.3–64.7% and halohydrocarbons were 21.2–30.7 and 2.0–2.3% for outdoor and indoor measurements, respectively. The presence

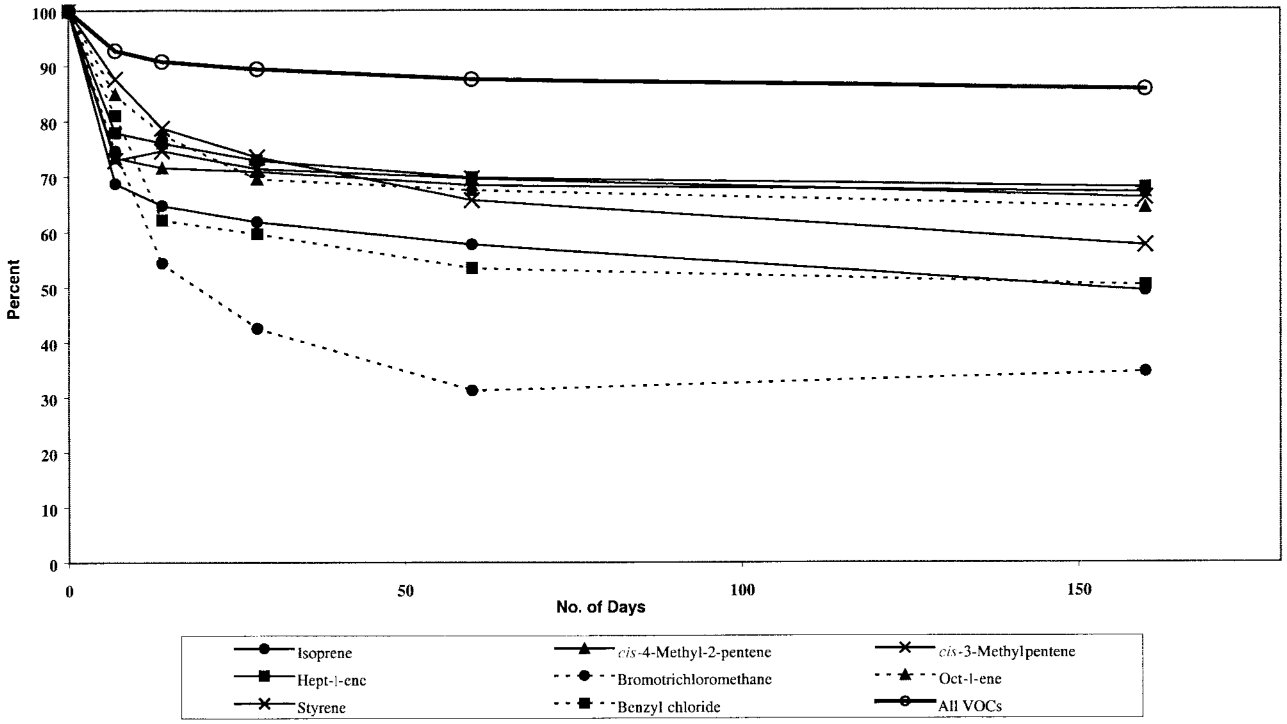

Fig. 3 Recovery of eight unstable VOCs and the mean recovery of 143 VOCs during 4 months of storage in canisters.

of small amounts of halohydrocarbons in the car park showed that vehicular emission is the characteristic source. The total VOC concentration in the outside area was found to be 46.8 and 71.4 $\mu g\ m^{-3}$, which lie within the annual VOC concentration range (24.4–169 $\mu g\ m^{-3}$) and close to the annual average of 61.0 $\mu g\ m^{-3}$ at urban sites in Hong Kong during 1999–2000.[33] The results also agreed with recent findings[34] that alkanes and aromatics are the two largest groups of ambient VOCs. No significant difference ($p \leqslant 0.05$) was found between the total VOC concentration of the urban sites and outside the car park area, indicating that the VOC composition outside the car park resembled the ambient VOCs at urban sites. On the other hand, the total VOCs detected in the car park was substantially different, with concentrations at 730 and 989 $\mu g\ m^{-3}$, respectively, in the two samples. The extremely high VOC concentration was due to the mobile exhaust and evaporative unburned fuel in a confined environment that could not be efficiently removed by the existing ventilation system. As some of the VOCs such as benzene are potential carcinogens, the amounts present are likely to induce hazards to human health with long-term exposure in the indoor car park. To understand better the VOC profiles in different environments, further investigations of the VOC levels in various environmental settings will be conducted based upon the present methodology.

We conclude that the overall satisfactory stability of VOCs in canisters and the successful application of the method to field samples illustrate that the present technique is amenable to the measurement of the 143 VOCs, with due regard to its limitations, under different environmental conditions.

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References

1 *Scientific Assessment of Ozone Depletion: 1994*, Report No. 37, World Meteorological Organization, Geneva, 1995.
2 A. Guenther, C. N. Hewitt, D. Erickson, R. Fall, C. Geron, T. Graedel, P. Harley, L. Klinger, M. Lerdau, W. A. McKay, T. Pierce, B. Scholes, R. Steinbrecher, R. Tallamraju, J. Taylor and P. Zimmermann, *J. Geophys. Res.*, 1995, **100**, 8873.
3 R. T. Burnett, R. E. Dales, M. E. Raizene, D. Krewski, P. W. Summers, G. R. Roberts, M. Raad-Young, T. Dann and J. Brook, *Environ. Res.*, 1994, **65**, 172.
4 R. G. Derwent, M. E. Jenkin and S. M. Saunders, *Atmos. Environ.*, 1996, **30**, 181.
5 R. Atkinson, *Atmos. Environ.*, 2000, **34**, 2063.
6 P. G. Simmonds, R. G. Derwent, A. McCulloch, S. O'Doherty and A. Gaudry, *Atmos. Environ.*, 1996, **30**, 4041.
7 M. A. K. Khalil and R. A. Rasmussen, *Atmos. Environ.*, 1999, **33**, 1151.
8 V. Camel and M. Claude, *J. Chromatogr.*, 1995, **710**, 3.
9 J. P. Greenberg, P. R. Zimmerman, W. F. Pollock, R. A. Lueb and L. E. Heidt, *J. Geophys. Res.*, 1992, **97**, 10395.
10 D. R. Blake, T. W. Smith, Jr., T.-Y. Chen, W. J. Whipple and F. S. Rowland, *J. Geophys. Res.*, 1994, **99**, 1699.
11 *Compendium Method TO-17*, United States Environmental Protection Agency, Cincinnati, OH, 1997.
12 *Compendium Method TO-14A*, United States Environmental Protection Agency, Cincinnati, OH, 1997.
13 D. Helmig, *J. Chromatogr.*, 1996, **732**, 414.
14 X.-L. Cao and C. N. Hewitt, *J. Chromatogr.*, 1994, **688**, 368.
15 C.-Y. Peng and S. Batterman, *J. Environ. Monit.*, 2000, **2**, 313.
16 S. A. Batterman, G.-Z. Zhang and M. Batterman, *Atmos. Environ.*, 1998, **32**, 1647.
17 K. D. Oliver, J. D. Pleil and W. A. McClenny, *Atmos. Environ.*, 1986, **20**, 1403.
18 A. R. Gholson, R. K. M. Jayanty and J. F. Storm, *Anal. Chem.*, 1990, **62**, 1899.
19 J. P. Hsu, G. Miller and V. Moran, *J. Chromatogr. Sci.*, 1991, **29**, 83.
20 J. T. Kelly and M. W. Holdren, *Atmos. Environ.*, 1995, **29**, 2595.
21 J. F. Pankow, W. Luo, L. M. Isabelle, D. A. Bender and R. J. Baker, *Anal. Chem.*, 1998, **70**, 5213.
22 *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, Washington, DC, 17th edn., 1989.
23 K. D. Oliver, W. A. McClenny, M. J. Yoong, M. A. Pardee, E. B. Almasi and N. A. Kirshen, *Environ. Sci. Technol.*, 1996, **30**, 1939.
24 S. M. Boswell and D. Smythe-Wright, *Analyst*, 1996, **121**, 505.
25 *Handling of Test Samples*, Document No. AC/SWM/1, Issue No. 3, Analytical and Advisory Services Division, Hong Kong Government Laboratory, Hong Kong, 1999.
26 G. F. Evans, T. A. Lumpkin, D. L. Smith and M. C. Somerville, *J. Air Waste Manage. Assoc.*, 1992, **42**, 1319.
27 M. P. Fraser, G. R. Cass and B. R. T. Simoneit, *Environ. Sci. Technol.*, 1998, **32**, 2051.
28 E. Grosjean, R. A. Rasmussen and D. Grosjean, *Environ. Sci. Technol.*, 1999, **33**, 1970.
29 D. A. Brymer, L. D. Ogle, C. J. Jones and D. L. Lewis, *Environ. Sci. Technol.*, 1996, **30**, 188.
30 D. W. M. Sin, Y. C. Wong and P. K. K. Louie, *Indoor Built Environ.*, 2000, **9**, 216.
31 B. Zielinska, J. C. Sagebiel, G. Harshfield, A. W. Gertler and W. R. Pierson, *Atmos. Environ.*, 1996, **30**, 2269.
32 Q. Gong and K. L. Demerjian, *J. Air Waste Manage. Assoc.*, 1995, **45**, 490.
33 VOCs Monitoring Work at Urban and Rural Sites in Hong Kong, Unpublished material.
34 R. G. Derwent, T. J. Davies, M. Delaney, G. J. Dollard, R. A. Field, P. Dumitrean, P. D. Nason, B. M. R. Jones and S. A. Pepler, *Atmos. Environ.*, 2000, **34**, 297.