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Measurement of volatile organic compounds by the US Environmental Protection Agency Compendium Method TO-17 Evaluation of performance criteria

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Abstract

An evaluation of performance criteria for US Environmental Protection Agency Compendium Method TO-17 for monitoring volatile organic compounds (VOCs) in air has been accomplished. The method is a solid adsorbent-based sampling and analytical procedure including performance criteria for four merit parameters. These are: (1) the method detection limit (MDL); (2) the method precision; (3) the agreement between two samples taken at different flow-rates over the same time period [a distributed volume pair (DVP)]; and (4) audit accuracy. A two-adsorbent tube packing of Carbotrap and Carboxen 1000 (Supelco) was tested. Synthetic mixtures containing 41 compounds at concentrations of 10 ppb (v/v) or 2 ppb (v/v) each in humidified zero air, and indoor air from a personal residence, were sampled for 1-h periods during which 1-1 and 4-1 samples were obtained simultaneously. For synthetic samples, the MDL was determined to be ≤ 0.5 ppb (v/v) for 29 of the 41 compounds examined for samples at 47% relative humidity (RH), and for 27 of 41 compounds at 85% RH. The method precision at both 2 and 10 ppb (v/v) was $\leq 20\%$ for 90+% of the samples using five sampling runs and the DVP samples were within 25% for 80% of the samples. For the indoor samples, 26 target compounds were tentatively identified and 12 unknowns were detected; all but 10% of these compounds met the DVP criteria. Published by Elsevier Science B.V.

Keywords: Air analysis; Environmental analysis; Adsorbents; Volatile organic compounds

1. Introduction

The US Environmental Protection Agency (EPA) Compendium of Methods for the Determination of Toxic Volatile Organic Compounds in Ambient Air [1] has recently been supplemented with the Method TO-17 entitled "Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes" [2]. The document describes a sorbent tube–thermal desorption–gas chromatographic-based monitoring method for volatile organic

compounds (VOCs) in air at 0.5 to 25 parts per billion by volume (ppbv). The development of this method was motivated by interest in the use of a new generation of thermal desorption systems as well as the newest solid adsorbents that are available commercially [3]. The sorbents are used singly or in multisorbent beds. The sorbents in multisorbent tubes were placed in order of increasing sorbent strength. This facilitates quantitative retention and ease of desorption of VOCs over a wide volatility range. Ideally, the higher-molecular-mass compounds are retained on the front, less retentive sorbent; the more volatile compounds are retained

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farther into the packing on a stronger sorbent. The higher-molecular-mass compounds never encounter the stronger sorbents, thereby improving the efficiency of the thermal desorption process. The amount of each adsorbent in a multibed packing is typically based on the adsorption strengths of the sorbents (as indicated, for example, by their safe sampling volumes for the target compounds), and the sample volume.

Considerable information about solid adsorbents is available in the open literature. Brown and co-workers at the Health and Safety Laboratory, Health and Safety Executive (HSE), Sheffield, UK originated numerous methods employing solid sorbents, for example see Ref. [4]. Bruner et al. [5] investigated critical parameters including the breakthrough volume associated with sampling with adsorbent packings of Carbo-pack B. Ciccio-li and co-workers used Carbo-pack B adsorbent for sampling of C_6 – C_{10} hydrocarbons [6] and used multisorbent packings of the carbon-based adsorbents Carbotrap C, Carbotrap and Carbosieve S III for sampling of polar and non-polar C_4 – C_{14} hydrocarbons in ambient air [7]. Harper [8,9] has documented the methods for characterizing sorbents for air sampling and has examined the effects of vapor concentration, temperature, humidity, interferences, flow-rate and sorbent bed geometry on breakthrough. Betz and Lambiase [10] used gas–solid chromatography studies to derive breakthrough volumes for carbon molecular sieves and O'Doherty et al. [11] investigated the adsorption characteristics of the four-carbon molecular sieve type materials (Carboxens). Bishop and Valis [12] evaluated recoveries of multisorbent tubes as a function of sampling volume, storage time, and humidity; in their studies, clean sample air was passed through sorbent tubes after the tubes were spiked with a mixture of solvent gases.

The TO-17 procedure involves pulling a volume of air through a sorbent bed to collect VOCs, followed by a thermal desorption of VOCs from the tube into a capillary column that leads to either specific detectors (flame ionization, electron-capture, photoionization, etc.) or a mass spectrometer, or both. The choice of sorbents is critical to obtain an acceptable performance since such factors as retention of water vapor can be critical in avoiding response variability on water-sensitive detection

systems, especially bench-top gas chromatography–mass spectrometry (GC–MS) systems.

The history of solid sorbent work at EPA with Tenax-GC [13,14], indicates the wisdom of an inherent quality assurance check to insure the linearity of the analytical response with the sample loading. In the past, this type of quality assurance was achieved using the distributed air volume (DAV) sampling approach in which samples were taken through four tubes at once, each with a different sampling rate. To incorporate the idea of DAV sampling in its simplest form, the Method TO-17 specifies the use of a distributed volume pair (DVP), i.e., simultaneous air sampling through two tubes at different flow-rates from the same air volume. If the results of analyses show that the difference in the amount of compound collected divided by the average amount collected is 25% or less and other performance criteria are met, then the value obtained is acceptable. Otherwise, the analysis is repeated. Continued large differences are investigated by use of a full DAV set or by comparison with other techniques; i.e., canister-based analysis [15] or automated GC analysis [16]. The other performance criteria of the Method TO-17 are that the method detection limit be 0.5 ppbv or less, that the duplicate precision be 20% or less, and that the audit accuracy be 30% or less.

This paper reports the application of Method TO-17 to the Method TO-14 target compound list of toxic VOCs, using a sorbent bed comprised of Carbotrap and Carboxen 1000 and sampling for 1-h periods. This combination of sorbents was chosen initially because it was commercially available and widely used for collection of volatile organic gases in the C_4 – C_{10} range. Water retention is low and the organic gases can be thermally desorbed for analysis. Loaded in series in a tube holder, the graphitic carbon sorbent Carbotrap captures heavier gaseous organic compounds as the first sorbent and the carbon molecular sieve Carboxen 1000 captures the lighter compounds that break through the Carbotrap packing. Sampling and analysis of synthetic mixtures of the target compounds in humidified zero air was used to establish the method detection limit (MDL), the duplicate precision, and the agreement of DVPs. After establishing the capability of the sampling and analytical systems to meet the TO-17 criteria in the

laboratory, indoor air samples were taken from a private residence using hardware that was specifically chosen to allow the convenient implementation of TO-17. For this application, examination of the analytical results for DVPs was used to indicate valid data. Target compounds were identified based on GC retention time and unknown compounds of highest concentrations were associated with a retention time only.

2. Experimental

The tubes were glass tubes (90 mm×4.0 mm I.D.) packed with 160 mg (35 mm bed length in tube) of Carbotrap graphitized carbon black (20–40 mesh) followed by a second sorbent bed of 70 mg (10 mm bed length) of Carboxen 1000 carbon molecular sieve (60–80 mesh). The sorbents were manufactured at Supelco (Supelco Park, Bellefonte, PA, USA) and the packed tubes were obtained from Perkin-Elmer (Wilton, CT, USA). Sorbents were separated and retained in the tube with 3-mm quartz wool sections. Tubes were initially conditioned by flushing with He for a period of 30 min at 350°C at a flow-rate of 30 ml/min. They were then sealed with Swagelock fittings and PTFE ferrules to prevent contamination prior to use. The tubes were analyzed within one day of sampling. After any subsequent thermal desorptions, the tubes were considered ready for use and were resealed. The tube conditioning and desorption device was a Perkin-Elmer automatic thermal desorption system (ATD 400) equipped with a temperature-regulated multisorbent trap for refocusing of VOCs after thermal desorption from the sample tube. The sorbents in the sorbent trap of the ATD 400 were identical to the sorbents in the tube.

For the tube analysis, the sorbent tube was heated to 250°C and flushed with helium to transfer the sample to the ATD 400 sorbent trap. The trap was set at 27°C during transfer and then rapidly heated at a rate of 40°C/s to 280°C and held at this temperature for 15 min. The ATD 400 was interfaced through a deactivated fused-silica column (held at 200°C) to a Perkin-Elmer gas chromatograph (AutoSystem GC). This column was attached to the analytical column (a high-resolution, fused-silica capillary column, 50 m×0.32 mm, 5.0 μm di-

methylpolysiloxane). The analytical column was connected to a flame ionization detection (FID) system. The GC temperature program, with a total time of 47.0 min, consisted of an initial temperature of 40°C held for 8 min followed by a temperature increase of 5°C/min for 30 min and finally a rate of 15°C/min for 2.7 min to reach a temperature of 230°C. The program was set to hold the final temperature of 230°C for 6.3 min.

The equipment for sampling from a gas manifold consisted of two Tylan (Torrance, CA, USA) Model F-260 electronic flow controllers and a metal bellows air pump, Model MB-151 manufactured by Metal Bellows (Sharon, MA, USA). The sampling tubes were mounted between the gas manifold and the flow controller during sampling. Known concentrations of TO-14 target gas mixtures (41 VOCs) in humidified zero air were prepared by blending gases dynamically in a glass calibration manifold and allowing the system to stabilize overnight. The TO-14 gas mixture was prepared by Alphagaz (Walnut Creek, CA, USA) as 1 ppmv in nitrogen and was blended by addition of high purity zero air to nominal concentrations of 10 ppbv or 2 ppbv. Two pairs of compounds coeluted from the GC column, *o*-xylene and tetrachloroethane, and benzyl chloride and *m*-dichlorobenzene, so that the number of peaks detected from the TO-14 gas mixture was 39 instead of 41. Different levels of relative humidity (RH) were obtained by bubbling zero air through deionized, doubly distilled water. The final blend in the manifold was checked using a HYCAL (El Monte, CA, USA) integrated circuit humidity sensor for recording RH and a thermistor imbedded in the circuit for recording temperature. Accuracy of %RH measurement was determined by using the headspace equilibrium above saturated salt solutions in water for reference; at a nominal 93.6% RH (for KNO₃) a ±2% RH was indicated and at 43.2% RH (for K₂CO₃) a ±3% RH was indicated.

The equipment for sampling in the indoor air environment consisted of the AirPro Surveyer II made by Bios International (Pompton Plains, NJ, USA). This unit was designed with two independently controlled sampling channels [17]. It contains flow regulation mechanisms that compensate for changes in pressure drop across the sampling tubes as sampling occurs. The unit is operated with rechargeable

batteries and is lightweight and compact. The Bios DryCal DC-1 was used for establishing flow-rates; these units carry a certification of NIST traceability.

For indoor air sampling, the two sampling channels of the unit were set at 16.7 ml/min and 66.7 ml/min while sampling for 1.0 h. Previous experience indicated that the flow-rate was highly reproducible over short times (minutes) but drifted slightly, e.g., by 1–3 ml/min over several hours at both low and high flow-rates. To account for any flow drift, the flow-rate was measured before and after loading and averaged.

3. Results and discussion

3.1. Performance criteria

The performance criteria for TO-17 are the following: (1) a MDL of ≤ 0.5 ppbv where the MDL is equal to the standard deviation of seven duplicate sample analyses $\times 3.14$ (Student's *t*-test value for 99% confidence). (2) Duplicate precision must be such that the difference between duplicate tube analyses divided by their average analysis value is less than or equal to 0.20, i.e., that $(\text{difference}/\text{average}) \times 100\% \leq 20\%$. (3) DVPs must be such that the difference in their analyses divided by their average analysis value is less or equal to 0.25, i.e., that $(\text{difference}/\text{average}) \times 100\% \leq 25\%$. (4) Audit accuracy must be within 30% for concentrations normally expected in contaminated ambient air (0.5 to 25 ppbv), i.e., $[(\text{tube} - \text{audit})/\text{audit}] \times 100\% \leq 30\%$.

The results of testing for criteria 1–3 will be considered in this paper; item 4 is best considered as part of specific quality assurance programs since our experiment cannot duplicate the quantitation standard that would be used in other experiments. Criteria 1–3 were examined using synthetic samples at both 2 ppbv (4-1 samples only) and 10 ppbv (both 1-1 and 4-1 samples). Two humidity levels were prepared, 47% RH and 85% RH for 10 ppbv tests and 40% and 87% RH for 2 ppbv tests. Laboratory temperature range was $23 \pm 3^\circ\text{C}$. After the criteria for the MDL and analytical precision were met using synthetic samples, the assumption was made that the sampling and analytical procedure would also meet these criteria for unknown samples in routine monitoring.

Hence, indoor air samples were taken and the criterion for distributed volume pairs was used as the sole determinant of acceptability for monitoring results.

3.2. Method detection limit

The MDL was determined by analyzing seven individual samples. The FID responses were processed to obtain a standard deviation which was multiplied by the value 3.14 (the Student's *t* value for 99% confidence for seven values) in order to obtain the MDL as defined in the US Code of Federal Regulations (40CFR136 Appendix B). The MDL determination must result in a value that is within a factor of five of the challenge concentration to be appropriate.

The challenge concentration was chosen as 2 ppbv and seven 4-1 identical samples were taken at each of the two relative humidities. The sampling time was 1 h and the sampling rate was 67 ml/min. Results are shown in Table 1. Of the 41 TO-14 compounds, 29 compounds (71%) satisfied the TO-17 criterion at 40% RH, while five (12%) had MDLs between 0.5 and 1.0 ppbv and five (12%) had MDLs between 1.0 and 1.5 ppbv. Freon 12 and Freon 11 showed high variability with MDLs of 2.78 and 3.15 ppbv, respectively. For 87% RH, 28 compounds (68%) met the criterion, 11 (27%) had MDLs between 0.5 and 1.0 ppbv, and only Freon 12 and Freon 113 at 3.50 and 2.37 ppbv, respectively, were highly variable.

3.3. Duplicate precision

To obtain the duplicate precision, GC-FID analyses were considered separately for 1-1 samples and for 4-1 samples taken over 1-h sampling periods at sampling rates of 16.7 and 66.7 ml/min, respectively. Duplicate precision was obtained for each of the possible compound pairs using five individual samples. The results are shown in Table 2 for the specific example of a 4-1, 10 ppbv sample at 85% RH; only four samples (instead of five for other sets) were taken in this set because of instrument problems. Individual sampling combinations that were below the target analytical precision of 20% are shown in italics. For several of the compound pairs, the use of integration limits for automated peak

Table 1
Minimum detection limits for 2.0 ppbv TO-14 mixture in humidified zero air at 40% and 87% RH, 23±3°C samples

Target compound list	MDL	
	40%	87%
Freon 12	2.93	3.50
Chloromethane	0.20	0.07
Freon 114	0.89	0.29
Chloroethane	1.09	0.34
Bromomethane	0.30	0.20
Chloroethane	0.69	0.40
Freon 11	3.15	0.42
1,1-Dichloroethane	1.32	0.39
Dichloromethane	0.30	0.46
3-Chloropropene	1.19	0.36
Freon 113	0.30	2.37
1,1-Dichloroethane	1.08	0.54
<i>cis</i> -1,2-Dichloroethane	0.28	0.71
Trichloromethane	0.90	0.65
1,2-Dichloroethane	0.90	0.88
1,1,1-Trichloroethane	1.28	0.58
Benzene	0.28	0.43
Carbon tetrachloride	0.76	0.47
1,2-Dichloropropene	0.09	0.34
Trichloropropene	0.11	0.72
<i>cis</i> -1,3-Dichloropropene	0.30	0.16
<i>trans</i> -1,2-Dichloropropene	0.32	0.14
1,1,2-Trichloroethane	0.14	0.37
Toluene	0.06	0.24
1,2-Dibromoethane	0.23	0.40
Tetrachloroethane	0.13	0.20
Chlorobenzene	0.21	0.56
Ethylbenzene	0.13	0.25
<i>m,p</i> -Xylene	0.31	0.51
Styrene	0.06	0.07
Tetrachloroethane/ <i>o</i> -xylene	0.19	0.59
4-Ethyltoluene	0.10	0.25
1,3,5-Trimethylbenzene	0.08	0.20
1,2,4-Trimethylbenzene	0.07	0.52
<i>m</i> -Dichlorobenzene/benzyl chloride	0.16	0.33
<i>p</i> -Dichlorobenzene	0.12	0.12
<i>o</i> -Dichlorobenzene	0.11	0.28
1,2,4-Trichlorobenzene	0.05	0.60
Hexachlorobutadiene	0.09	0.19

Note: Italics indicates a MDL of >0.5 ppbv.

integration was critical to the result and the two available options (valley to valley or baseline to baseline integration) were both tried with the best result being chosen. The compounds for which baseline to baseline integration was the better are indicated as reintegrated values. Better results are likely with manually-chosen integration limits. Sum

of column and sum of row entries in the Table 2 indicate the comparability of precision by tube pair over all compounds and by compound over all tubes, respectively. From the results of tube pairs, tube 1 is seen to be associated with the poorest average precision values when paired with other tubes, and appears to be somewhat of an anomaly. Table 2 shows that *p*-dichlorobenzene and Freon 113 easily pass the criterion for analytical precision for all but the tube pairs containing tube 1. The corresponding tube taken at the same time from the gas manifold for the 1-l sample showed good analytical precision for both compounds. Inspection of the chromatogram corresponding to this tube showed interferences for *p*-dichlorobenzene and Freon 113 which were not present for other analyses, and, because of the use of a non-specific GC detector, the target compound and interference were not adequately separated during peak integration. Similarly, the analytical precision for 3-chloropropene was low for tube pairs containing tube 3 (note: tube combination 1,3 gave a better result with the alternate baseline integration but otherwise would not have passed the criterion). The remaining instances of low analytical precision involved pairings of the tubes 1,2 with 4,5 and occurred for the lighter compounds, Freon 12, chloroethane and bromomethane. Since all target compounds were diluted from a single gas cylinder and since all but the lighter compounds showed good precision, variability of manifold concentrations for the lighter compounds was not indicated.

The results of similar comparisons for all four combinations of relative humidity and sample volume are summarized in Table 3. These results indicate that: for 47% RH and 1.0-l samples, the percentage of those passing was 81% (84.5% excluding missing values); for 47% RH and 4.0-l samples, it was 93%. For the tests with 85% RH and 1.0-l and 4.0-l samples the percentages were 91% and 92%, respectively. Separate but similar tests using seven samples with a 2 ppbv mixture, 4-l sample volume and both 87% RH and 40% RH gave the percentage of passing as 85.8% and 83.0%, respectively, while the last five of this set gave 90% and 91%, respectively, i.e., almost identical to the 10 ppbv runs. Patterns in the data were again evident and were similar to the cases of *p*-dichlorobenzene mentioned in the last paragraph.

Table 2

Database for the determination of analytical precision of 4-1, 85% RH, 23±3°C samples of a 10 ppvb, TO-14 compound mixture in humidified zero air (difference/sum·100%)

Target compound list	Results for paired tubes using all combinations of sample tubes (%)						
	1,2	1,3	1,4	2,3	2,4	3,4	Compound sum
1 Freon 12	8.17	<i>38.37</i>	<i>32.70</i>	<i>82.47</i>	<i>72.68</i>	5.86	244
2 Chloromethane	10.66	14.37	13.55	3.72	2.90	0.83	46
3 Freon 114	0.53	4.86	4.26	4.33	3.72	0.61	18
4 Chloroethane	5.37	19.49	<i>24.69</i>	<i>24.80</i>	<i>29.96</i>	5.26	110
5 Bromomethane	9.69	<i>30.45</i>	<i>36.92</i>	<i>39.85</i>	<i>46.19</i>	6.65	170
6 Chloroethane	3.47	12.90	14.59	9.44	11.13	1.69	53
7 Freon 11	3.73	3.89	2.32	7.62	6.05	1.57	25
8 1,1-Dichloroethane	1.10	2.66	2.17	1.57	1.07	0.50	9
9 Dichloromethane	4.32 ^a	0.86	5.67	5.18 ^a	19.76 ^a	6.09	13
10 3-Chloropropene	9.28	7.38 ^a	19.89	<i>40.49</i>	10.66	<i>28.93</i>	109
11 Freon 113	<i>41.00</i>	<i>46.43</i>	<i>54.81</i>	5.20	4.05	8.48	160
12 1,1-Dichloroethane	3.30	1.93	4.21	0.05	0.39	0.44	10
13 <i>cis</i> -1,2-Dichloroethane	6.10	0.91	1.50	4.55	4.60	0.59	18
14 Trichloromethane	12.18	4.52	2.71	7.68	9.49	1.81	38
15 1,2-Dichloroethane	13.13	4.79	5.50	7.90	7.64	0.26	39
16 1,1,1-Trichloroethane	1.96	5.62	5.59	3.66	3.63	0.04	20
17 Benzene	0.39	4.94	5.45	4.55	5.06	0.51	21
18 Carbon tetrachloride	1.15	5.53	5.46	3.19	3.75	0.06	19
19 1,2-Dichloropropene	1.61	5.86	5.92	4.25	4.97	0.72	23
20 Trichloropropene	1.78	6.10	0.30	5.75	0.23	5.98	20
21 <i>cis</i> -1,3-Dichloropropene	0.73	5.37	6.28	5.39	5.55	0.16	23
22 <i>trans</i> -1,2-Dichloropropene	1.64	3.05	5.96	5.22	7.60	0.64	24
23 1,1,2-Trichloroethane	1.37	4.91	6.87	3.75	5.50	0.92	23
24 Toluene	1.24	1.15	0.29	0.09	1.52	1.44	6
25 1,2-Dibromoethane	0.16	3.72	5.59	3.56	5.44	1.87	20
26 Tetrachloroethane	2.18	1.11	1.63	1.07	3.81	2.74	13
27 Chlorobenzene	0.38	1.71	4.53	0.59	4.15	2.53	14
28 Ethylbenzene	0.56	0.06	2.01	0.04	2.57	2.08	7
29 <i>m,p</i> -Xylene	0.16	1.04	2.77	1.07	2.94	1.73	10
30 Styrene	2.30	0.67	0.23	1.63	1.00	0.63	6
31 Tetrachloroethane/ <i>o</i> -xylene	0.32	3.42	4.32	3.75	4.64	0.89	17
32 4-Ethyltoluene	2.02	0.99	3.50	0.93	0.92	1.24	10
33 1,3,5-Trimethylbenzene	2.69	1.49	1.51	3.73	1.96	1.34	13
34 1,2,4-Trimethylbenzene	0.34	1.71	0.19	2.04	0.15	1.89	6
35 <i>m</i> -Dichlorobenzene/benzyl chloride	15.20	9.48	9.97	5.74	5.25	0.49	46
36 <i>p</i> -Dichlorobenzene	<i>48.67</i>	<i>49.95</i>	<i>48.33</i>	1.36	0.36	0.48	149
37 <i>o</i> -Dichlorobenzene	3.84	0.83	5.34	3.00	1.50	4.50	19
38 1,2,4-Trichlorobenzene	1.65	1.53	16.36	9.14	14.72	5.60	49
39 Hexachlorobutadiene	3.46	1.40	0.01	3.40	7.44	1.39	17
Sum of column	181	180	374	143	131	109	

Note: Italics indicate the analytical precision was >20%.

^a Reintegration using baseline-to-baseline integration gives better values.

Based on all observations, there appeared to be infrequent tube-specific interferences with target compound peak integration which limited the preci-

sion for this GC-FID system. For 2 ppbv samples (4-1 samples only), the criterion was achieved in 90+% of comparisons for a subset of five samples

Table 3
Success percentage for TO-17 criteria with Carbotrap/Carboxen 1000 tube packing

10 ppbv							
40% RH			85% RH				
Analytical precision (%)		Distributed volume pairs (%)	MDL ≤ 0.5 ppbv (%)	Analytical precision (%)		Distributed volume pairs (%)	MDL ≤ 0.5 ppbv (%)
1 L	4 L	4 L/1 L		1 L	4 L	4 L/1 L	
86	93	98	–	91	92	83	–
2 ppbv							
47% RH			87% RH				
–	86 (90) ^a	–	71	–	83 (91) ^a	–	68

^a Percentage if first two of seven replicate values are excluded.

(last five analyzed) out of seven total samples. For the full set of seven samples, the “pass” percentage dropped about 5%.

3.4. Distributed volume pair

3.4.1. Synthetic samples

The performance criterion for DVPs, where one sample is taken at four times the flow-rate of the

other, is equivalent to requiring that the ratio of the higher volume sample to the lower volume sample be between 3.1 and 5.1 with the ideal value being the ratio of sample volumes or 4.0. The results of dividing area counts resulting from the 4.0-1 sample by the area counts for the corresponding 1.0-1 sample for the cases of 47% RH and of 85% RH are given in Figs. 1 and 2, respectively. Each figure shows the data points for all five sampling runs (four for the

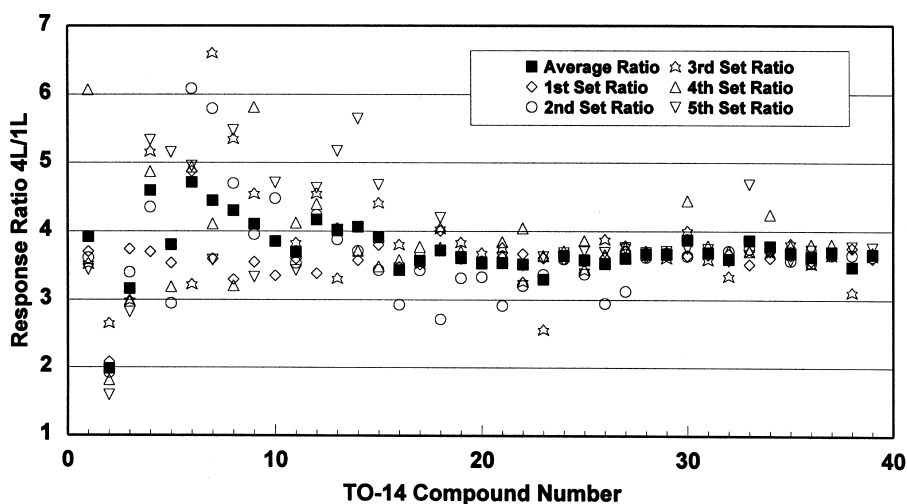


Fig. 1. The response ratio for a DVP of 10 ppbv samples taken at 47% RH, $23 \pm 3^\circ\text{C}$.

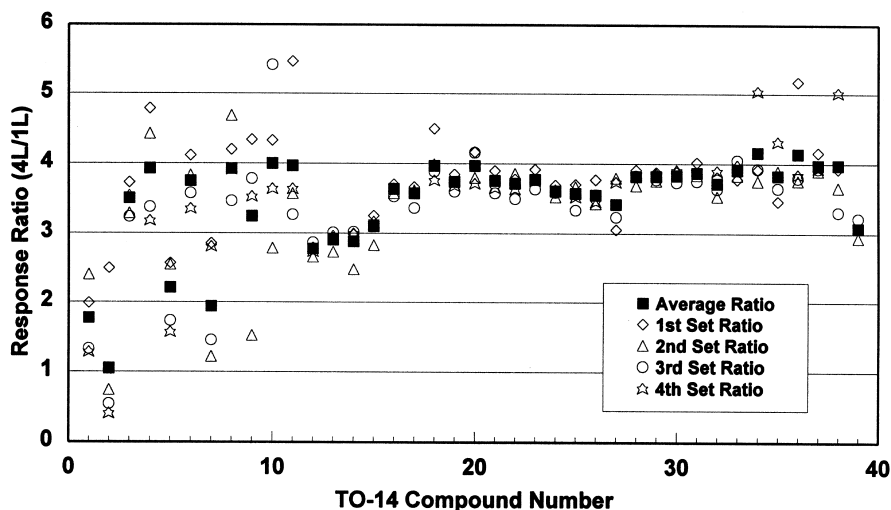


Fig. 2. The response ratio for a DVP of 10 ppbv samples taken at 85% RH, $23 \pm 3^\circ\text{C}$.

85% RH, 4-1 runs) as well as the average ratio. For the 47% RH example, the higher boiling compounds easily met the performance criterion with very little scatter in the data. For more volatile compounds, the average value of the ratio for lighter compounds fell in the acceptable range except for chloromethane. The lack of precision of the ratio for TO-14 compounds numbered 1–15 was significant and, although the average of the five runs often met the TO-17 criteria, individual runs sometimes did not. For compounds 16–39, the precision of the measurement was much better so that the criterion was met by almost every one of the individual runs. Several instances of a high ratio indicate that the area counts corresponding to the 1-1 sample were low, possibly because of a lack of recovery of the light compounds from the most retentive sorbent.

For the 85% RH sample, a pronounced dip in the ratio was present while the scatter in the lower numbered compounds was less pronounced (only compounds 1–11 have significant scatter). Seven compounds did not meet the DVP criterion and loss of the more volatile compounds by breakthrough is a likely explanation. The average ratio of response for compounds 16–38 served as a check on the actual sample volume ratio and in this case indicated that the ratio of sample volumes was probably less than 4.0. Based on boiling point, the compounds can be

imagined to be distributed along the abscissa of the figures, with the most retentive sorbent to the left. Lower variability for more compounds in the 85% RH runs could be due to the fact that water vapor is occupying more of the most active adsorption sites and the sorbent is therefore more readily releasing the lighter compounds. To investigate the reason for the dip in Fig. 2, the two sorbents were each packed in separate tubes and placed in series. The Carbotrap trapped compounds beginning with 1,1,1-trichloroethane (compound 16) completely while compounds ≤ 15 were generally trapped on both sorbents. This suggests that the variability for the lower-numbered compounds may be associated with retrieving them from both sorbents.

3.4.2. Indoor air samples

Indoor air samples were taken at a private home at two locations, one in a den on the ground floor, and one in a downstairs (basement) den. The house had a central air conditioning system and the fan for this system was operated continuously. The duration and procedures for sampling were the same as in the laboratory setting except the BIOS AirSurveyer II, battery-operated sampler, was used. Given that a prior examination of the performance criteria 1 and 2 had been performed for the system in use, only the DVP criterion was tested. The results of applying

this criterion for distributed volume pairs for the target list is shown in Table 4. Forty-five out of 50 ratios or 90% were acceptable for the target compound list. Only those unknown compounds having the highest response and being above compound 15 on the TO-14 list were considered; 24 out of 25 DVP ratios or 96% of recorded unknown compounds were acceptable. A detailed inspection of the chromatograms was necessary to avoid interferences and problems associated with very low area counts. Although quantitation of compound concentrations is not the focus of this paper, the estimated concentrations of the restricted list of target compounds and some unknowns (identified by retention time only) are shown in Table 5. These concentrations varied from 0.23 ppbv to 8.78 ppbv assuming a response factor for each component equal to that of benzene.

4. Conclusions

Based on the results presented here, the TO-17 criteria are shown to be achievable for the majority of the TO-14 VOCs for both high and low humidities although the Freons are an exception. For compound numbers above 15 on the Method TO-14 target compound list of 41, all criteria were almost always met. A summary of results of applying the Method TO-17 performance criteria to synthetic samples containing the TO-14 target compounds is given in Table 3. MDL values exceeded 1.0 ppbv only for the Freons. For the duplicate precision criterion, systematic patterns in the data indicated that the 10% of samples that did not pass this criterion appear to have tube-specific, compound-specific interferences caused by contamination. Although this problem

Table 4
Distributed volume pair ratios for target compounds and unknowns in residential indoor air

Target compounds Name	Target compounds		Unknown compounds		
	Upstairs	Downstairs	Retention time (min)	Upstairs	Downstairs
Freon 12	3.82	3.24	8.393	4.64	4.39
Freon 114	3.59	3.52	5.388	4.68	4.32
Bromomethane	3.61	3.55	9.958	4.47	4.43
Chloroethane	4.87	4.43	14.312	4.41	4.27
Freon 11	4.52	3.20	15.203	4.51	4.28
1,1-Dichloroethene	4.77	NV	19.945	4.49	4.45
<i>cis</i> -1,2-Dichloroethene	NV	3.18	20.427	4.28	4.22
Trichloromethane	4.68	4.28	21.605	4.61	4.31
1,2-Dichloroethane	4.48	4.31	32.188	3.21	2.39
1,1,1-Trichloroethane	3.80	3.38	33.458	4.54	4.73
Benzene	3.87	3.46	38.107	4.52	4.06
Carbon tetrachloride	4.41	3.99	41.798	3.05	3.15
Trichloroethene	4.06	3.82			
<i>trans</i> -1,3-Dichloropropene	3.26	3.32			
Toluene	4.09	4.01			
1,2-Dibromoethane	1.27	4.53			
Tetrachloroethene	NV	2.61			
Chlorobenzene	1.68	1.76			
Ethylbenzene	4.41	4.32			
<i>m,p</i> -Xylene	4.22	4.15			
Styrene	3.00	2.37			
Tetrachloroethane/ <i>o</i> -xylene	4.52	4.45			
4-Ethyltoluene	4.63	3.79			
1,3,5-Trimethylbenzene	4.88	4.52			
1,2,4-Trimethylbenzene	4.41	4.25			
<i>p</i> -Dichlorobenzene	NV	4.41			
<i>o</i> -Dichlorobenzene	4.43	4.33			

NV=No value (no peak detection).

Table 5

Estimated concentration for target compounds and unknowns in residential indoor air

Target compounds (ppbv)			Unknown compounds – benzene equivalent (ppbv)		
	Upstairs	Downstairs	Retention time (min)	Upstairs	Downstairs
1,1,1-Trichloroethane	1.09	0.72	19.945	4.25	3.66
Benzene	2.79	2.48	20.427	3.84	3.32
Carbon tetrachloride	0.61	0.56	21.605	3.46	3.00
Trichloroethene	6.34	5.68	32.188	4.63	4.96
<i>trans</i> -1,3-Dichloropropene	1.17	1.02	33.458	4.04	2.70
Toluene	8.78	7.72	38.107	2.70	3.14
1,2-Dibromoethane	0.58	0.97	41.798	2.00	1.21
Tetrachloroethene	NV	0.61			
Chlorobenzene	0.57	0.60			
Ethylbenzene	1.22	1.08			
<i>m,p</i> -Xylene	4.77	4.18			
Styrene	0.34	0.35			
Tetrachloroethane/ <i>o</i> -xylene	2.60	2.33			
4-Ethyltoluene	0.66	1.53			
1,3,5-Trimethylbenzene	0.90	0.84			
1,2,4-Trimethylbenzene	2.71	2.56			
<i>p</i> -Dichlorobenzene	NV	0.23			
<i>o</i> -Dichlorobenzene	2.28	2.27			

NV=No value (no peak detection).

should be approachable through better cleaning and handling procedures, the use of a GC–MS analytical system should also eliminate many of the interferences by selecting specific target compounds ions for identification and quantitation. A mass spectrometer detector is preferred for this method as noted in the text of TO-17. A dip in the DVP ratio for high humidity samples remains unexplained. For compound numbers above this dip, all compounds are trapped on the first sorbent. Below the dip, compounds are partitioned between the two sorbents.

For indoor air samples, the criterion for agreement between distributed volume samples was applied with the result that out of 48 tentative identifications of individual target compounds, all but five met the DVP criterion. Twenty-three of the 24 DVP ratios for unknown compounds in the indoor air sample gave acceptable values.

5. Disclaimer

This paper has been reviewed in accordance with the US Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication. Mention of trade names

or commercial products does not constitute endorsement or recommendation for use.

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