

## INTRINSICALLY VALID VOLATILE ORGANIC COMPOUND MEASUREMENTS

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### INTRODUCTION

Active adsorption sampling is a widespread technique for sampling trace volatile organic compounds in ambient atmospheres. Adsorbent samplers, both passive and active, have been used for many years to sample airborne volatile organic compounds (VOC)<sup>1-8</sup>. Useful reviews of active sampling techniques have been published previously<sup>9,10</sup>.

The collection of VOC with an adsorbent trap is only one of the stages in a measurement sequence, but it is perhaps the most important. It imparts selectivity to the analysis, and as such adsorbent selection is based on the chemical nature of the volatile organic compounds to be sampled. However, there are other factors that influence the performance of an adsorbent trap, such as analyte concentration, humidity, temperature, adsorbent conditioning, competitive effects, and the handling and storage of adsorbent traps. Fault tree analysis (Figure 1) reveals seven main stages in the measurement sequence<sup>11</sup>:

1. Adsorbent conditioning
2. Sample hydraulics
3. Adsorption
4. Sample storage
5. Analyte recovery
6. Separation
7. Detection

There are many and varied ways in which errors and faults may arise in such a sequence. What is critical to the usefulness and reliability of data produced by a measurement sequence described in general terms by Figure 1 is that there is no indication from the chromatographic output that the measurement is fault free. Indeed concentration dynamics in the sampled air can introduce changes to the performance of the measurement sequence leading to completely erroneous data arising from a fault-free system<sup>11-17</sup>. Thus an analyst or their client is faced with the dilemma of having no way of proving the validity or otherwise of the measurement.

Unsurprisingly, a variety of validation procedures have been invoked during the design and development of adsorbent based methods for VOC analysis, but the approach is piecemeal and not generally undertaken with the same rigor as liquid based separations. The use of blanks and controls can indicate

contamination or adsorbent deterioration; however such approaches are inferential in nature and prove nothing about an actual sample. Back-up adsorbent traps can be used to demonstrate the absence of breakthrough, but such an approach provides little information about the reliability or efficiency of the thermal desorption procedure or indicate that the sampling pump operated correctly. Back-up traps also increase the cost of the analysis substantially, with the consequence that many organizations rely on the safe sampling volume concept to safeguard their analyses. Recently improvements have been made with the introduction of distributed sample volumes, but this is still an inferential approach.

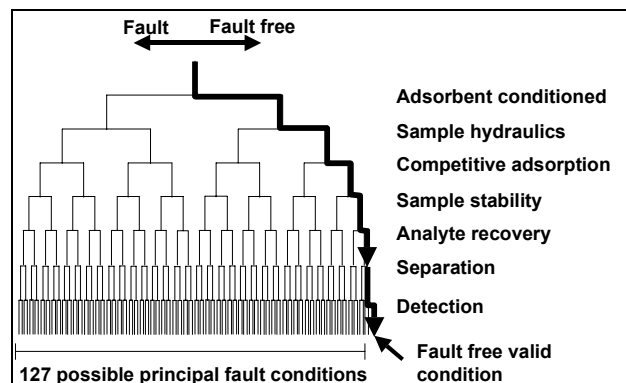


Figure 1. Fault tree showing the principle sources of error in the measurement sequence for the determination of VOC in air with active sampling onto an adsorbent trap followed by recovery with thermal desorption and separation by gas chromatography<sup>11</sup>.

The use of internal standards is established practice in the analysis of liquid mixtures improving both the accuracy and precision of the analysis. The Grob test extends the utility of internal standards even further. The different molecular probes enable the efficiency of separation to be evaluated and provide a mechanism for determining the transfer efficiency of analytes through the separation system. It seems logical to suggest therefore, that the rigorous extension of internal standards to adsorbent based sampling would provide a useful mechanism for validating adsorbent based active sampling methodologies for VOC analysis. The internal standards would necessarily be incorporated into the sampled material as part of the sampling process. Such an addition to the sampling operation would provide a reference against which each sample

could be evaluated, allowing faults in the measurement sequence to be identified. Thus the final chromatogram would contain all the information required to validate the measurement from sampling to transduction. An analysis with these features might be considered as intrinsically valid.

This work seeks to demonstrate the intrinsically valid measurement concept with a sampling system that introduces two internal standards, with different retention characteristics on an adsorbent into sampled air, prior to six identical samples being taken with adsorbent traps. (Six independent adsorbent traps provide sufficient statistical confidence in the analysis).

Comparative studies were run on :

- The precision of data obtained with and without the use of internal standards; and,
- Different modes of failure incorporated into the method. The faults investigated were:
  - Incorrect sampling times;
  - Incorrect pump flow-rates; and,
  - A transient vapor excursion, where a highly concentrated solvent vapor was applied briefly at the sampling system inlet during normal sampling (intended to simulate a plume of volatile material passing across the sampling point).

## MATERIALS

### Vapor Sources.

Permeation type vapor sources were used throughout this work. The permeation sources were placed in a test atmosphere generator consisting of a stainless steel block with eight individual chambers with separate inlets and a shared outlet. The temperature of the test atmosphere generator was maintained to within  $\pm 4^\circ\text{C}$  of  $50^\circ\text{C}$  with a variation in temperature of less than  $\pm 0.5^\circ\text{C}$  using a 50W, 240V cartridge heater and proportional difference type analog temperature controller (RS Components). The permeation rates were determined by mass loss measurements over a period of several weeks.

Analyte vapors were generated by passing clean, dry nitrogen at  $10\text{ cm}^3\text{ min}^{-1}$  over each permeation source, giving a total of  $60\text{ cm}^3\text{ min}^{-1}$  through the test atmosphere generator. To achieve the low concentrations needed, the flow was split, passing through either a needle valve to vent or through a 1 meter long, 0.32 mm I.D. deactivated silica capillary (Alltech) into a diluent nitrogen stream.

### Solvent Vapor Generation.

Dichloromethane (99.9%, Sigma-Aldrich) vapor was introduced by bubbling purified air at  $1\text{ dm}^3\text{ min}^{-1}$  for 30 seconds through a  $500\text{ cm}^3$  impinger bottle containing  $100\text{ cm}^3$  solvent and then passing it directly into the sampling inlet. The resultant vapor concentration within the sampling manifold during the concentration transient was

estimated from the vapor pressure of dichloromethane to be  $580\text{ g m}^{-3}$ .

### Adsorption Traps.

The adsorbent traps were constructed from 5 mm Optic 100 injection liners (Atas Ltd, Cambridge, UK), filled with 100 mg Tenax TA (Supelco), held in place by silanised glass wool. Heating at  $250^\circ\text{C}$  in a stream of  $\text{N}_2$  at  $10\text{ cm}^3\text{ min}^{-1}$  for eight hours conditioned the tubes.

## SAMPLING SYSTEM

### Sampling Manifold

A schematic diagram of the sampling manifold is shown in Figure 2. Dimensions are marked on the diagram (not to scale).

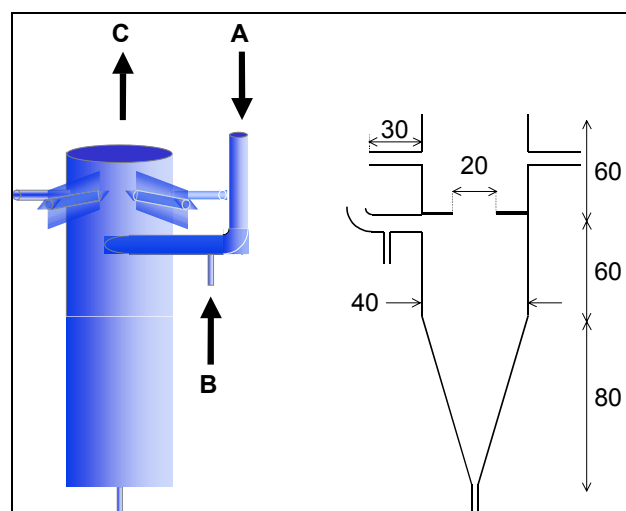


Figure 2. Schematic diagram of the sampling manifold. Air enters the chamber at A and passes through the sample inlet into the manifold. The internal standards are bled into the sampled air at B. Thorough mixing is carried out in the lower cyclone part of the manifold before the air passes into the upper part of the chamber. Adsorbent tubes protrude into the upper part of the manifold and a pump draws air through them. The sampled air passes out through the top of the manifold at C via a length of hose attached to a ventilating fan.

The manifold was constructed from glass, the surfaces of which were treated by first cleaning with Decon 90 (Decon Laboratories Ltd) followed by  $100\text{ cm}^3$  70% nitric acid (Sigma-Aldrich), thoroughly rinsing with de-ionized water, drying, and then treating with  $100\text{ cm}^3$  dichlorodimethylsilane (Sigma-Aldrich) before a final rinse with de-ionized water. Air was drawn into the sampling manifold at a rate of  $2580 \pm 90\text{ cm}^3\text{ min}^{-1}$  (95% confidence limits) through the sampling inlet (a 30 cm tall, 2 cm internal diameter glass tube also treated with dichlorodimethylsilane). The lower, conical cyclone removed entrained particulate debris and, most importantly, efficiently mixed the sampled gases before they passed into the upper section. Adsorbent traps were located in the

upper section of the sampling manifold and extended radially outwards. A single pump was used to draw the sampled air through the adsorbent traps. The sampled air was sucked out of the top of the sampling manifold and passed down 2.5 meters of plastic hose (1.5 cm diameter) to a powerful fan (429 dm<sup>3</sup> min<sup>-1</sup>, 12 V, 60 x 25 mm<sup>2</sup>, RS Components). The whole of the sampling manifold and inlet was heated to 60°C ±2°C with a variation in temperature of less than ±0.5°C using resistive heating, controlled using a 12 V digital temperature controller (RS components).

#### Internal Standards

The internal standard permeation sources were housed in a short length of stainless steel tubing maintained at 50°C ±2°C with a variation in temperature of less than ±0.5°C by a mat heater (15 W, RS Components) and a simple electronic circuit. Air was passed through the permeation source housing at approximately 10 cm<sup>3</sup> min<sup>-1</sup> and carried the internal standards into the sample at the bottom of the sample inlet (Figure 2). The air-flow was maintained by controlling the pressure balance between the two inlets into the sample manifold. The internal standards were selected to:

- Exhibit markedly different breakthrough characteristics on Tenax TA;
- Be easily identified in the chromatogram with baseline resolution from other components;
- Not be found in ambient air; and,

- Have a relatively low toxicity.

1-Fluoropentane and 1-fluorononane conform to these criteria. Various physical characteristics are presented in Table I.

#### Electrical Control

The temperature controllers, heaters, ventilating fan, and sampling pump all require a 12 V power supply, enabling them to be run off a portable power unit for remote sampling. A high performance rechargeable lead-acid battery (RS Components) was selected to ensure a stable supply voltage over the sampling period. The supply voltages to the fan and sampling pumps were adjusted so that they were identical for each sampling campaign. This was found to ensure a high level of reproducibility in sampling flow rates.

#### INSTRUMENTATION

Adsorbent tubes were analyzed by thermal desorption, undertaken with an Optic 100 injector port with a liquid nitrogen cold trap (Ai Cambridge Ltd.). Separation and analysis of the cold trap contents was achieved using a Carlo Erba 8035 Gas Chromatograph and QMD 1000 Mass Spectrometer operating in the selective ion mode. The operating parameters are summarized in Table II.

Table I Physical Properties of the Volatile Organic Compounds Used in this Work<sup>11</sup>

Elution order	Compound	Boiling Point / °C	Retention Time / Minutes
1	1-Fluoropentane	62-63	1.9
2	n-Octane	125-127	2.2
3	Benzene	80	2.6
4	Pentan-2-one	100-101	3.1
5	Toluene	110.6	3.7
6	1-Fluorononane	166-169	4.8
7	1-Xylene	138-139	5.2
8	Propylbenzene	159	5.4

Table II Instrument Conditions for the Analysis of Adsorbent Tubes<sup>11</sup>

Optic 100 Injector	
Initial Temperature	40°C
Temperature Ramp	16° s-1
Desorption Temperature	230°C
Desorption Time	60 seconds
Cold Trap Temperature	< -140 °C
Gas Chromatograph	
Program	40°C for 3 minutes, then 90°C @ 30° min-1 for 1 minute
Column Phase	DB-WAX
Length	30 meters
Internal Diameter	0.25 mm
Film thickness	0.25 µm
Carrier Gas	He
Column Flow	1 cm <sup>3</sup> min <sup>-1</sup>
Split	50 cm <sup>3</sup> min <sup>-1</sup>
Mass Spectrometer	
Mode	Selective ion monitoring
Dwell Time	0.08 second
Delay	0.02 second
Tuned m / z Values	43, 55, 57, 58, 70, 71, 77, 78, 84, 91, 92, 106, 114

## EXPERIMENTAL

### Breakthrough Experiments

The capacity of the trap for 1-fluoropentane was determined through breakthrough experiments with 1-fluoropentane at 138 µg m<sup>-3</sup> and 1-fluorononane at 238 µg m<sup>-3</sup> at 23°C sampled directly onto an adsorbent trap at 50 cm<sup>3</sup> min<sup>-1</sup> for between 5 and 80 minutes. The resultant chromatograms were analyzed and the ratio of the peak areas obtained was defined as  $R_{IS}$ , where:

$$R_{IS} =$$

Peak area 1-fluoropentane / Peak area 1-fluoroname

The value of  $R_{IS}$  was determined for a range of different sampling volumes, leading to an estimate for the breakthrough volume for 1-fluorononane, which was compared through the analysis of backup traps. The determination of the capacity for 1-fluoropentane was important because this feature of its behavior was the controlling factor in the specification of the sampling volume.

### System Blanks

System blanks were obtained by placing a 2 dm<sup>3</sup> Poly(ethylene terephthalate) shroud over the sampling manifold inlet and purging it with purified nitrogen at 5 dm<sup>3</sup> min<sup>-1</sup> for 20 minutes prior to sampling. With the shroud still in place and the nitrogen purge still operating, a normal sampling campaign was then carried out. Table III shows the normal sampling time and trap flow rate. Such a test enabled the condition of the sampling manifold, adsorbents, and instrumentation to be evaluated and ensured that no analyte contamination or carry over occurred between the different experimental campaigns.

### Comparative Studies

A test atmosphere containing six volatile organic compounds was introduced directly into the sample manifold inlet where they were diluted with the sampled nitrogen. Analyte boiling points and retention times on the analytical column are given in Table I. A calibration was undertaken by varying the split in the test atmosphere generator and hence controlling the mass-flux of the six analytes into the sampling manifold. The concentrations are given in Table IV.

### Evaluation of the Sampling System Under Different Modes of Failure

Four experiments were run with different fault sequences imposed on the sampling system. The effectiveness of using the internal standards to identify the faults was evaluated. The various conditions used are shown in Table III.

Table III Experimental Conditions for Normal Sampling and Failure Experiments<sup>11</sup>

Experiment	Sample Flow / cm <sup>3</sup> min <sup>-1</sup>	Sample Time /min	Transient Events	m/z Determined
Normal	45	20	-	see Table II
Low volume, short sample time	45	5	-	see Table II
High volume, long sample time	45	70	-	see Table II
High volume, high sample flow	150	20	-	see Table II
Transient vapor event, Dichloromethane introduced at 10 minutes for 30 seconds	45	20	Concentration in sampling manifold was ca. 580 ng m <sup>-3</sup> for 39 seconds.	Octane, Pentan-2-one (43, 55, 57, 58, 70,71); Benzene (77,78); Others see Table II.

Note: The m/z refers to the masses scanned to prevent the dichloromethane event from interfering with the relevant analytes.

Table IV Vapor Concentration of Compounds in Calibration Experiment  $\mu\text{g m}^{-3}$ <sup>11</sup>

Split Ratio	100	57	19	10
1-Fluoropentane	195	106	34.8	18.3
n-Octane	21.3	11.54	3.80	2.00
Benzene	256	138	45.6	24.1
Pentan-2-one	55.3	30.0	9.87	5.20
Toluene	154	83.6	27.5	14.5
1-Fluorononane	163	88	29.1	15.3
1-Xylene	34.3	18.6	6.12	3.23
Propylbenzene	31.2	16.9	5.56	2.93

Note: The split ratio refers to the percentage of the total mass-flux passing through the restriction and into the sampling system. The remainder passes to vent.

## RESULTS

### Breakthrough

It was found that the breakthrough volume for 1-fluoropentane in air on 100 mg Tenax TA was  $17.4 \text{ dm}^3 \text{ g}^{-1}$  at a concentration of  $138 \text{ } \mu\text{g m}^{-3}$  1-fluoropentane in air on 100 mg Tenax TA.

### System Blanks

It is vital that the sampling system is not allowed to become contaminated with sampled vapors and that blanks be taken before and after sampling campaigns to ensure the absence of such artifacts. Thus a decontamination procedure was devised whereby the temperature of the sampling manifold was increased to  $100^\circ\text{C}$  and baked out for 12 hours between experiments. This cleaned the sampling manifold; no analytes were detected in the resultant blank analyses. The bake out procedure and contamination monitoring through system blanks was incorporated into the operating procedures for the system. No contamination was observed.

### Performance Evaluation

Figure 3 shows a typical selective ion chromatogram with 1-fluoropentane, 1-fluorononane, and the six analytes identified. Satisfactory calibration curves were produced for each of the analytes investigated (Table V).

Using the 1-fluorononane peak as the internal standard to account for day-to-day variations in the operation of the sampling system and instrumentation yielded a general improvement in the precision of the calibration curves.

The improvement in the between-run variance offered by the use of an internal standard was also investigated. The relative standard deviation of each of the analyte responses over the six simultaneously sampled traps was determined with and without the use of 1-fluorononane as an internal standard (Table VI). In this case a significant improvement in precision was achieved for all the analytes apart from 1-xylene. These experiments were also used to estimate the mean internal standard peak area ratio,

$$\bar{R}_{IS} = 4.05 \pm 0.22 \text{ (95\% confidence limit)}$$

It was not possible to deduce the reason or reasons for the 1-xylene anomaly; most likely ionization artifacts in the mass spectrometer source caused it. The levels of 1-xylene were low, almost at the limits of quantitation, and even small changes in the operation of the mass spectrometer introduced large variability into the measurement.

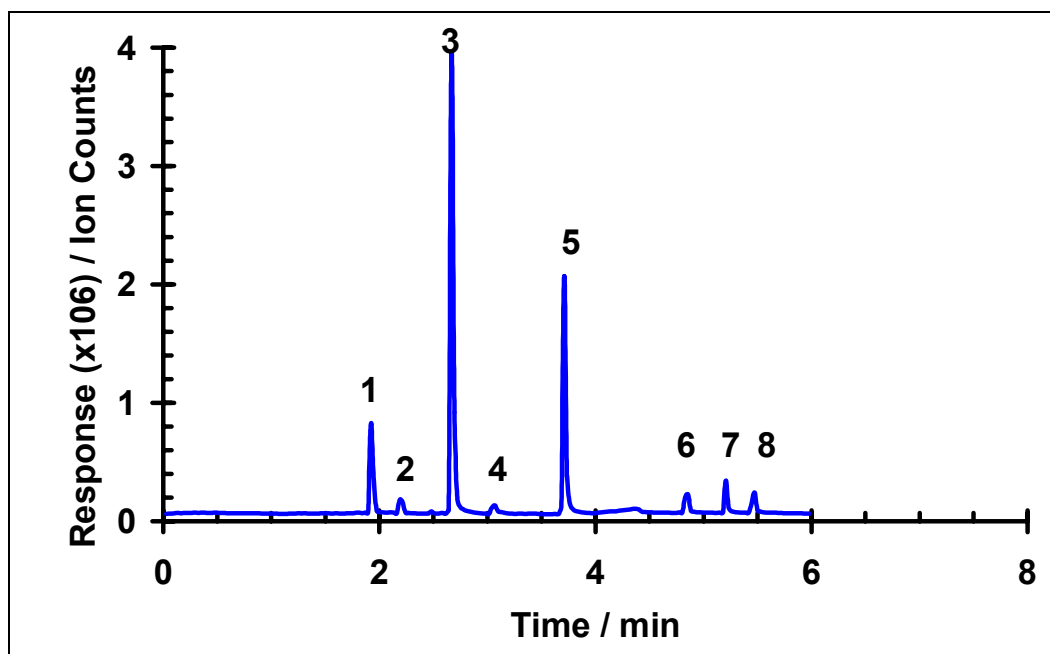


Figure 3. A typical chromatogram collected from the sampling manifold. The six vapors present in the test atmosphere applied to the sampling inlet are all resolved. The two internal standards introduced into the sampled air are also present. See Table I for peak assignments. Note that the tailing seen in the peaks is an artifact of the thermal desorption sequence<sup>11</sup>.

Table V Calibration Curves Obtained for Each Analyte Before and After the Internal Standard is Applied<sup>11</sup>

	Raw Rata	R <sup>2</sup>	After Application of Internal Standard	R <sup>2</sup>
n-Octane	y = 6609x + 4626	0.975	y = 7013x + 17639	0.979
Benzene	y = 13498x - 146062	0.952	y = 14013x + 95074	0.988
Pentan-2-one	y = 1866x + 7103	0.974	y = 1985x + 16494	0.972
Toluene	y = 10840x - 113004	0.921	y = 11481x - 31933	0.977
1-Xylene	y = 6053x - 6629	0.956	y = 6549x + 5770	0.999
Propylbenzene	y = 8184x - 17205	0.933	y = 8929x - 7581	0.987

Note: This accounts for indeterminate variations in the operation of the experimental systems. The least-square analysis results are also given to show the improvement in the precision of the calibration curve after the internal standard has been applied.

Table VI Standard Deviation Between Six Simultaneous Samples for Each Analyte Concentration Determined<sup>11</sup>

	Without Internal Standard	With Internal Standard
n-Octane	22.3	16.9
Benzene	23.5	13.1
Pentan-2-one	29.7	14.3
Toluene	27.3	14.4
1-Xylene	21.8	25.3
Propylbenzene	24.1	14.2

Note: There is a significant reduction in the variance of all the analytes except 1-xylene when the internal standard is applied..

### Evaluation of the Sampling System Under Different Modes of Failure

Figure 4<sup>11</sup> illustrates how the value for  $R_{IS}$  changes during each of the fault sequence experiments. Each axis of the target represents an experiment and expresses the difference in  $R_{IS}$  from  $\bar{R}_{IS} = 4.05$ , (determined over the course of the calibration and blank experiments under normal sampling conditions) as a percentage. Hence the further the result falls from the center of the target, the greater is the deviation in sampling conditions from those expected.

#### Normal Experiment

The normal  $R_{IS}$ , as expected, falls close to the center of the target, within two standard deviations of  $\bar{R}_{IS}$ .

#### Reduced Sampling Time

When the sampling time was reduced to five minutes, the relative areas of both the internal standard peaks were significantly lower than those observed under normal sampling conditions (Table VII). A fault is immediately identified. Without the presence of the internal

standards however, the pump failure would not be apparent and the results would be interpreted as a lower atmospheric concentration of analytes.

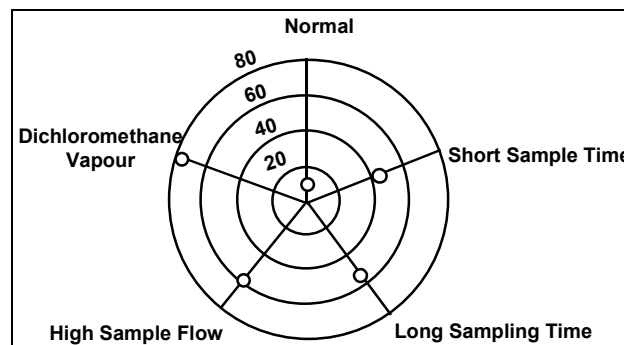


Figure 4. Target diagram showing the % deviation of  $R_{IS}$  in various failure modes compared with that observed under normal sampling conditions. The axes each represent a different set of sampling conditions. The distance along each axis is the extent of deviation of  $R_{IS}$  as a percentage of the normal  $\bar{R}_{IS}$ . Thus the further along the axis, the greater the extent of the change in trap adsorption characteristics<sup>11</sup>.

### Long Sampling Time

Here, the sampling time was increased to 70 minutes. There are two indications that there is a fault present. First, the relative internal standard peak areas are between 6 and 12 times greater than normal. Second, the value for  $R_{IS}$  has decreased significantly compared with that observed under the "normal" condition. In this case, the area of the 1-fluoropentane peak has decreased with respect to that of the 1-fluorononane peak. The change in the peak area ratio in favor of the more strongly retained compound suggests that while at this increased sampling volume the 1-fluorononane is still being quantitatively trapped, the breakthrough volume for 1-fluoropentane has been exceeded and is no longer being quantitatively retained.

### High Pump Flow

The increased sampling flow through the adsorbent traps of  $150 \text{ cm}^3 \text{ min}^{-1}$  results in an 3-fold increase in material passing through the traps within the same sampling time. As expected, the 1-fluoropentane and 1-fluorononane peak areas are observed to increase by 2.1 and 3.6 times respectively, indicating a fault has occurred. The ratio of internal standard peak areas is reduced, suggesting that 1-fluoropentane is no longer being quantitatively retained on the trap and again that a fault has occurred.

### Transient Vapor Event

Table VII shows that sampling was affected significantly by the transient vapor event. Note that the peak areas of n-octane, pentan-2-one and benzene were calculated from a smaller number of ions (Table III). This was to eliminate interference due to the strong dichloromethane response that dominated these chromatograms. The other chromatograms were therefore re-evaluated using the same criteria to obtain comparable results.

The recovery of 1-fluorononane illustrates the effect of the solvent vapor on sampling. One hundred seventy-five (175) ng of 1-fluorononane should be trapped during a normal 20 minute sampling run. At the end of the transient vapor experiment less than 70 ng were recov-

ered. The 1-fluorononane trapped before and during the introduction of the transient vapor into the sampling system has been swept from the adsorbent bed, while the 1-fluorononane passing through the trap after the introduction of the vapor has been not been fully retained. The high concentration solvent vapor has displaced analyte from the surface due to competitive desorption effects. This behavior was observed for all the analytes and was predicted previously when high concentration dichloromethane vapor was observed to effectively desorb material from a Tenax trap<sup>18</sup>.

In the case of the more highly volatile benzene and 1-fluoropentane, recoveries are 10% and 16% respectively. This suggests that not only have these substances been desorbed from the trap by the high concentration solvent vapor, but the resulting high quantity of dichloromethane on the surface of the adsorbent has reduced the capacity of the trap for these compounds. The  $R_{IS}$  reflects these observations, being much reduced and hence indicating that the sampling conditions have changed significantly from those expected.

The dichloromethane peak, at 2.5 minutes, dominates the resulting chromatogram (Figure 5). However, what would the data have looked like if the method had not been tuned to  $m/z = 84$ ? In other words, if the dichloromethane event had occurred without the knowledge of the analyst. Reconstruction of the chromatogram with the response to  $m/z = 84$  excluded yields a different picture. In this new chromatogram of the same analysis the analytes are all visible and only a reduced dichloromethane peak remains (Figure 5). During routine analysis, operating the mass spectrometer in selective ion monitoring mode, the effect on the sampling efficiency of such a transient vapor event could be overlooked with significant under-reporting of the concentrations of the analytes. However, the  $R_{IS}$  value derived for this experiment shows the adsorbent performance has significantly changed during sampling, and that the data should not be used.

Table VII Ratio of Peak Areas Relative to Those Observed Under Normal Sampling Conditions Under Different Failure Modes<sup>11</sup>

	Short Sampling Time	Long Sampling Time	High Sample Flow	Transient Vapor Event
1-Fluoropentane	0.32	6.57	2.10	0.10
n-Octane	0.48	9.20	2.26	0.58
Benzene	0.27	6.08	2.39	0.16
Pentan-2-one	0.39	9.69	2.54	0.67
Toluene	0.33	10.0	3.04	0.36
1-Fluorononane	0.43	9.89	3.57	0.38
1-Xylene	0.44	11.1	2.23	0.34
Propylbenzene	0.48	12.0	2.34	0.43



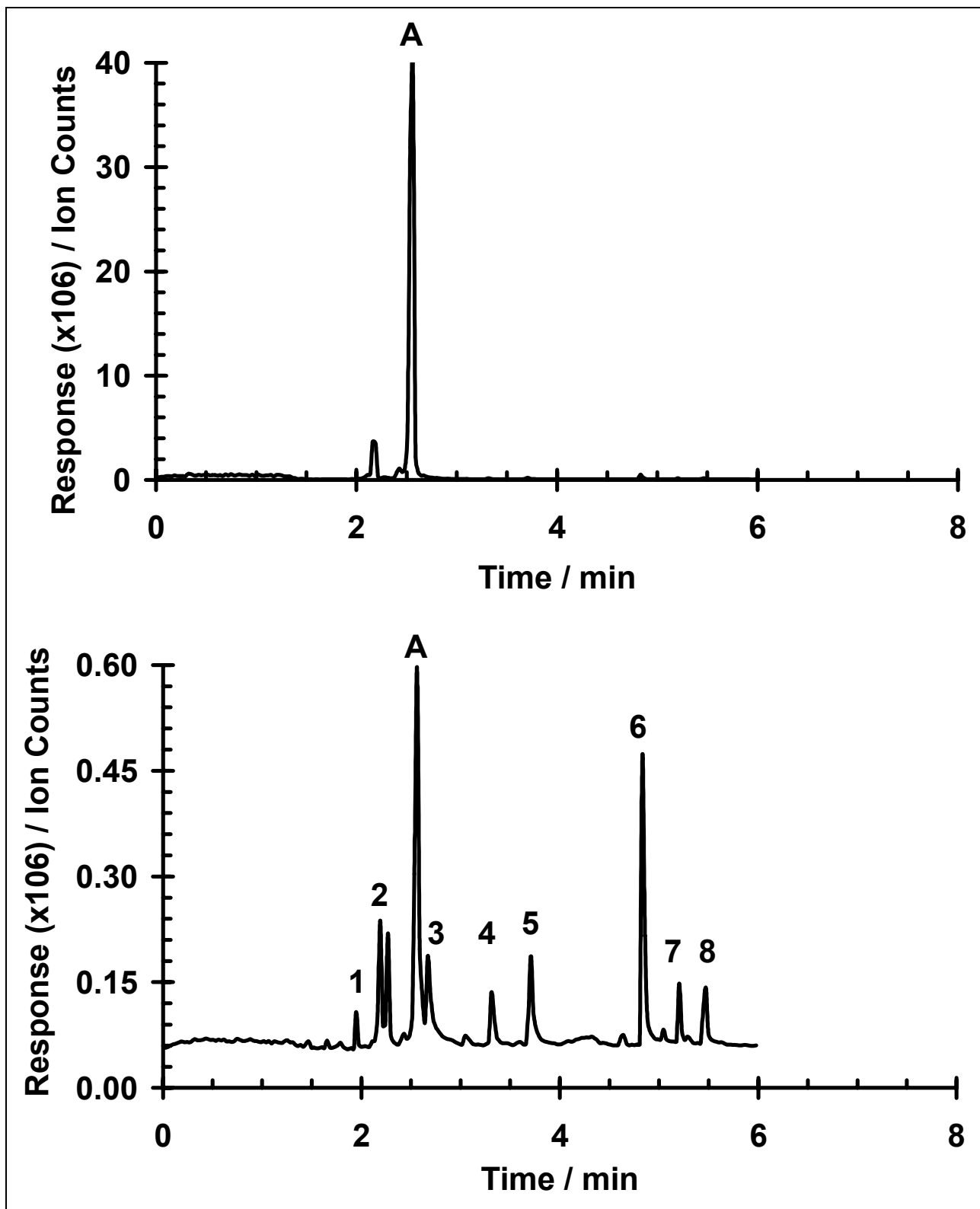


Figure 5. The top chromatogram shows the analysis of an adsorbent trap briefly exposed to a high concentration of dichloromethane vapor during sampling. As expected, the dichloromethane peak (A) dominates the chromatogram. The lower chromatogram shows the same analysis. However, the chromatogram has been constructed without the ion  $m/z = 84$ . The dichloromethane peak now appears greatly reduced in magnitude, so the trace volatile organic compounds in the sampled air are now visible. This demonstrates how a severely compromised sample can, without adequate validation methods, appear to be of acceptable quality, particularly if a selected ion monitoring mode is in use<sup>11</sup>.

## DISCUSSION

A multiple trap sampler procedure has indicated how both the accuracy and precision of VOC analysis may be improved. Further, the introduction of a controlled quantity of at least two internal standards during sampling onto an adsorbent trap significantly improves the precision of the air analysis. The reliability of the analysis is also greatly improved because comparison of the two standards enables changes in sampling conditions and mechanical faults that have occurred during the sampling and subsequent handling and analysis to be identified.

Failures relating to the activity and condition of the adsorbent were not investigated in this study because of the problems in degrading an adsorbent reproducibly. Breakthrough experiments on poorly conditioned adsorbents indicate a reduction in the capacity of the adsorbent towards all trapped species. Thus poorly or non-conditioned adsorbents will manifest themselves in a manner similar to the experiments with too long sample times or too high sample flow rates. Similarly, it can be seen that the performance of the analytical column and detection system (not included in this study) can be monitored through analysis of the chromatography of the internal standards. Further, there is no reason why molecular probes may not be introduced as internal standards to provide more detailed information as to the state of the separation and detection systems.

Internal standards used in conjunction with mass spectrometric detection also allow some tentative quantitation of unknowns isolated in the analysis without prior calibration. Once an unknown has been identified, its response factor relative to an internal standard may be estimated, enabling its concentration in the original air sample to be deduced.

The proposed approach is more complicated than many procedures used currently in VOC analysis, but analysis of the fault sequences has not yet revealed a combination of failures that would go undetected and result in a flawed experiment being passed as reliable. Thus it is possible to provide VOC measurements with a chemical "Water Mark." The next stage is to reduce the complexity of the process and extend it to other areas of VOC analysis, most notably passive sampling and solid phase micro-extraction procedures.

Finally, this work indicates that high concentration transients affect active samplers and their analytical methodologies strongly. Given that active sampling is dependent upon environmental factors outside the control of the analyst, it is imperative that such methodologies incorporate validation procedures along the lines described in this work.

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