

# Development of the AIR material emissions proficiency testing scheme for the analysis of volatile organic compounds

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## Introduction

The testing of products, such as building materials, automotive interiors, packaging products and electronic components, for emissions of volatile organic compounds (VOCs) is becoming increasingly important. Test items, or representative portions thereof, are placed in climate controlled chambers and the VOCs released are sampled onto sorbent tubes and analysed using a thermal desorption gas chromatographic (TD-GC) method. This work describes the development of a new proficiency test (PT) sample designed to assist laboratories undertaking this analytical step.

## Sample Preparation

Prototype test samples consisted of thermal desorption (TD) tubes packed with Tenax<sup>TA</sup> sorbent were spiked with 15 VOCs (Table 1) ranging in volatility from hexane (C<sub>6</sub>) to hexadecane (C<sub>16</sub>). These compounds were chosen as being representative of those emitted from a range of products.

**Hexane; Benzene; Hexanal; Methyl isobutyl ketone (MiBK); Toluene;  
 Butyl acetate; Cyclohexanone; o-Xylene; α-Pinene; Limonene;  
 123-Trimethylbenzene; Phenol; 4-Phenylcyclohexene;  
 Butylated hydroxytoluene (BHT); Hexadecane**

Figure 1: Compounds Loaded onto Sorbent Tubes

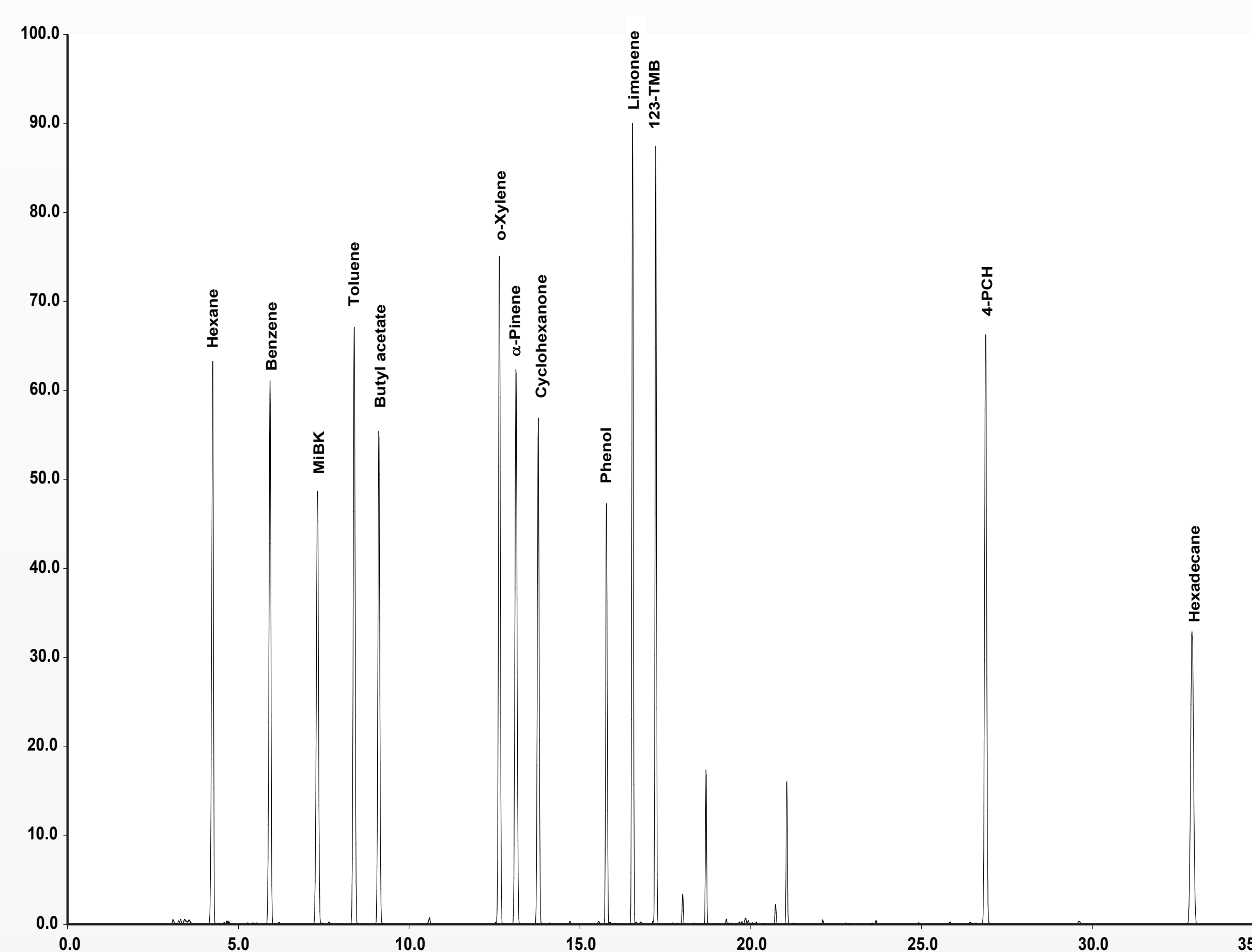


Figure 2: Materials Emissions Test Sample Chromatogram

## Spiking rig for VOC sample production

Samples were prepared using a dynamic gas phase loading system (Figure 1) that replicates how sorbent tubes collect real air samples. This operation, based on procedures set out in ISO 6145-4, injects a solvent mix at a constant rate into a heated chamber, where it is then volatilised and diluted to form a stable VOC atmosphere. Precise quantities of this VOC enriched air are then metered individually onto each of 30 sorbent tubes using mass flow controllers. Proprietary software controls rig operations and adaptive feedback control, through the use of an on-line Flame Ionisation Detector (FID), used to monitor the batch-to-batch spiking of tubes.

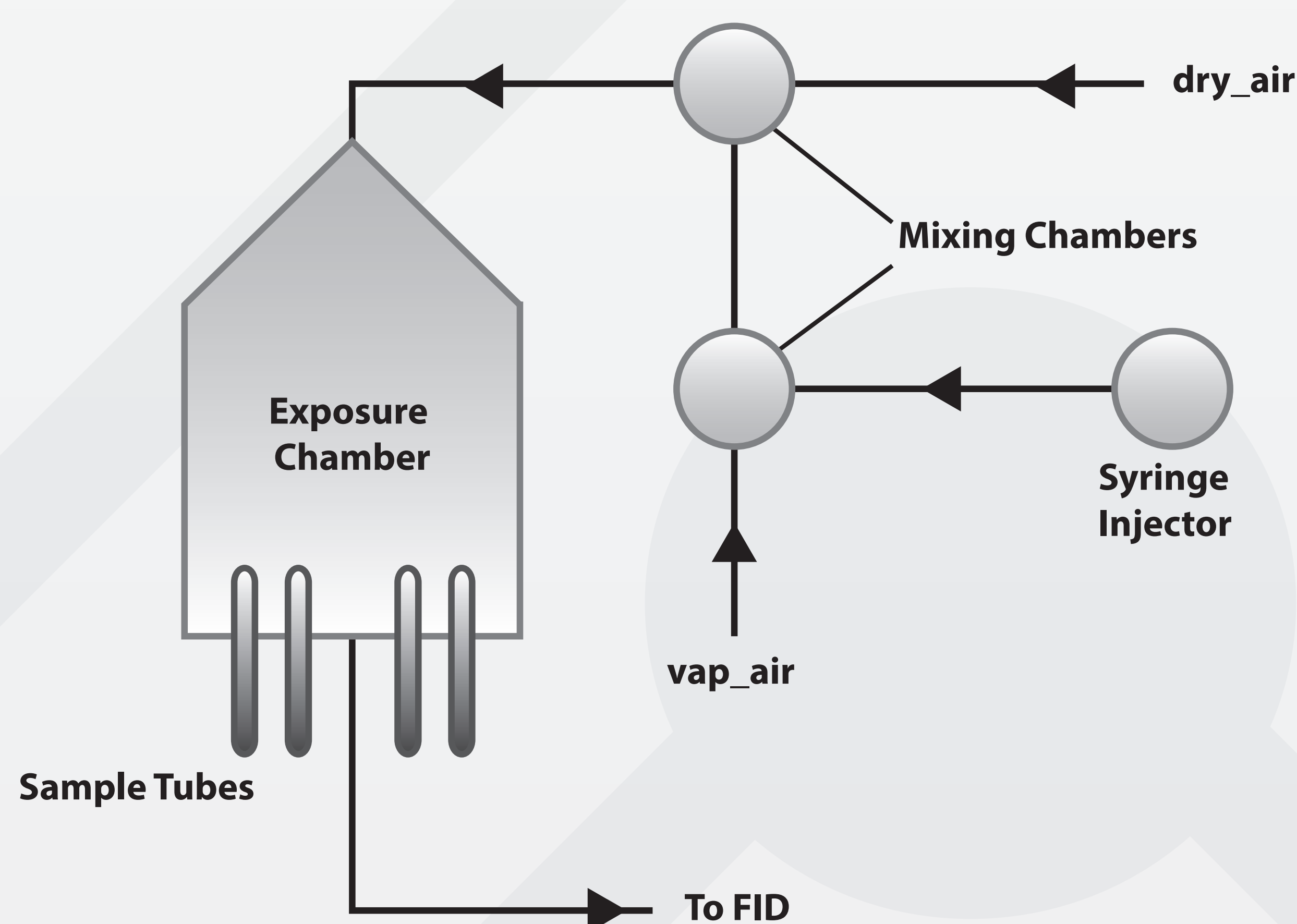


Table 1: Schematic of Dynamic Gas Phase Tube Loading System

## Homogeneity Testing

Representative samples (3–5 tubes with the 15 compounds spiked in the range 50–300 ng) were taken from a number of test runs and analysed by TD-GC-FID. A typical chromatogram is shown in Figure 2.

## Stability Testing

A batch of 60 identical sample tubes (the 15 compounds spiked at a nominal 150 ng spike) was prepared, stored sealed with brass end caps and left at room temperature to replicate conditions that would be encountered in a typical PT round.

Spiked sorbent tubes were tested ( $n = 6$ ) on days 1, 7, 14, 28 and 56 to assess their suitability as potential PT test materials, and on days 120, 200 and 360 to assess their suitability as potential instrumental check, training or repeat PT samples. Data is presented in Figure 3.

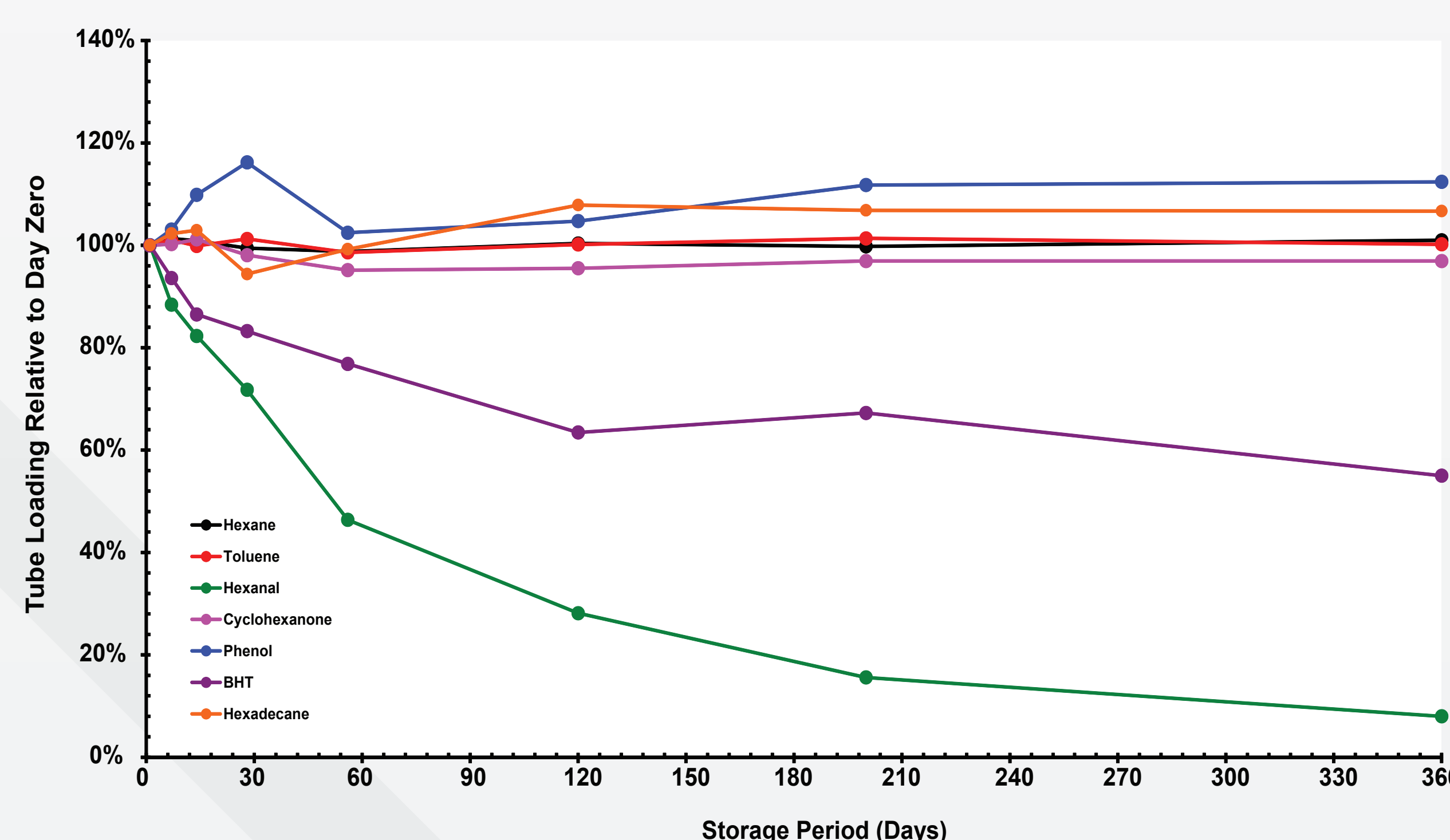


Figure 3: Results of 12-month Stability Trial

## Results

The coefficient of variation (CV) on measured sorbent tube replicates was < 2.5% and the measured variability of the associated mass flow controllers was < 0.25%. This demonstrated that the tube spiking rig is capable of producing PT samples to the required quality and that tube analysis rather than tube spiking is the dominant source of imprecision.

Agreement between theoretical spike and measured spike values was within ± 5% bar hexadecane where measured spike values, although precise, were significantly lower (~ 50%) than theoretical spike values. Here the study demonstrates that spiking a sorbent tube from the gas-phase becomes increasingly challenging for VOCs that have higher boiling points.

The storage trial showed satisfactory stability for 12 of the 15 test compounds, at both 3 and 12 month time intervals. Initial variation in phenol results was attributed to chromatographic issues which have been resolved and phenol is stable over the short-term. The gradual formation of ozone-mediated phenol artefacts on sorbent tubes however may be an issue if samples are stored for longer periods. Hexanal and BHT showed significant losses and were deemed unsuitable for inclusion in future PT samples.

## Conclusions

A material emissions PT sample for the analysis of VOCs on sorbent tubes has successfully been developed to assist laboratories undertaking TD-GC measurement to procedures codified in ISO 16000-6 and CEN TS 16516.