## Application Note 119

# Highly efficient monitoring of VOCs in stack emissions using sorbent tubes analysed by TD–GC–MS in accordance with European standard method CEN/TS 13649

## Summary

This Application Note demonstrates that Markes International's automated thermal desorption systems offer excellent results for monitoring volatile organic compounds (VOCs) in stationary source emissions in accordance with the updated version of the European standard method CEN/TS 13649 released in 2014. The value of repeat analysis for method development and result verification is also demonstrated.

## Introduction

Volatile organic compounds (VOCs) play key roles in photochemical reactions in the atmosphere – in particular, they contribute to formation of harmful particulates, and are involved in the generation of low-level ozone. Moreover, due to their toxicity many VOCs have a significant impact on human and environmental health in their own right.

Emissions from industry contribute significantly to global levels of man-made VOCs, and as a result in 2001 the European technical committee for air quality (CEN/TC 264) released a standard method[1] that defined a procedure for monitoring VOCs from stationary sources, such as in stack gases.

This procedure involved the collection of airborne vapours onto glass tubes packed with activated carbon, followed by extraction of analytes with carbon disulfide ($CS_2$) and analysis by gas chromatography–mass spectrometry (GC–MS). However, in the years since this method was released, thermal desorption has become far more popular than solvent extraction for analysis of airborne VOCs.

As a result of this, in 2014 CEN/TC 264 released a revised edition of CEN/TS 13649,[2] which (as an alternative to solvent extraction) specifies the collection of airborne vapours onto sorbent-packed steel tubes, followed by analysis of the tubes using thermal desorption (TD)–GC–MS.

TD is now widely considered to be superior to solvent extraction for reasons of practicality and analytical performance (for the reasons listed in Table 1), and its inclusion in CEN/TS 13649 brings this method into line with other national and international standard methods for VOC analysis.[3]

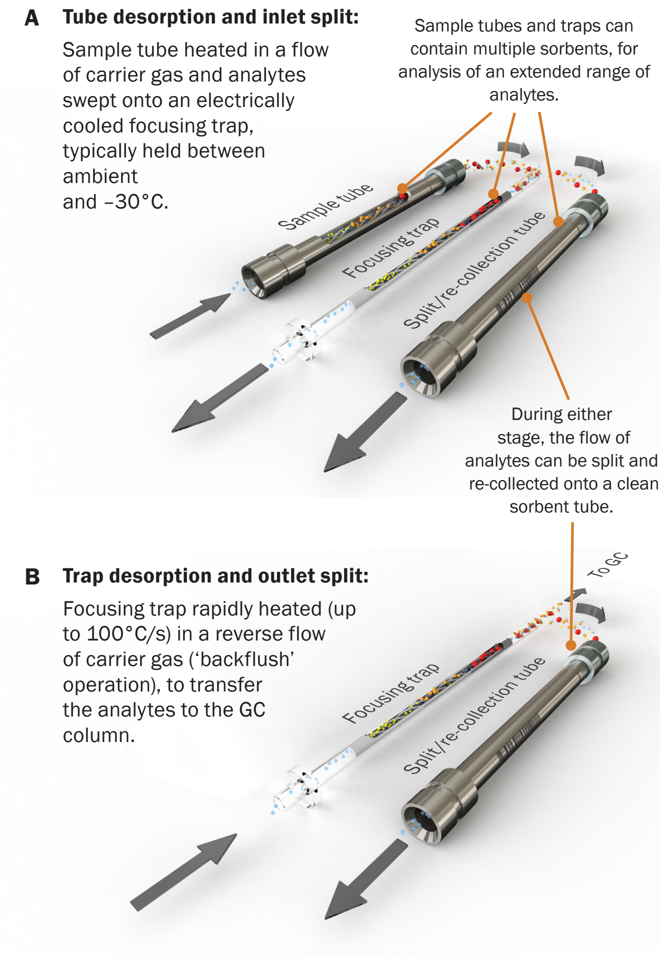
In this Application Note, we highlight the outstanding performance of a TD–GC–MS system for analysis of a standard mix of compounds in accordance with CEN/TS 13649, and follow this with a real-life sample of exhaust from a busy restaurant.

| Solvent extraction | Thermal desorption |
|---|---|
| Repeat analysis of a single sample is possible, but reproducibility is affected by the high volatility of $CS_2$. | Repeat analysis of a single sample is straightforward using re-collection of split flows, improving sample security. Excellent reproducibilities allow this feature to be used for method validation. |
| Ultra-pure $CS_2$ is expensive and costly to dispose of. | There is no need for solvent, which substantially reduces running costs. |
| The solvent extraction process is labour-intensive and prone to error (and difficult to automate), resulting in poor reproducibility. | Thermal desorption is easily automated and gives high reproduciblities. |
| The solvent dilution effect lowers sensitivity. | Two-stage thermal desorption greatly improves sensitivity. |
| Solvents are highly toxic, leading to operator risk. | The sampling and analytical process is safe for operators. |
| The sorbent tubes are single-use, increasing running costs and generating waste. | The sorbent tubes can be re-used up to 100 times, reducing waste. |
| The charcoal sorbent is hydrophilic, increasing water interference with GC columns and detectors. | The sorbents used are generally hydrophobic, reducing water interference. |
| The glass sorbent tubes used are fragile. | Although glass tubes can be used for TD if desired, stainless steel tubes are more popular because they are resistant to mechanical damage. |

**Table 1:** Comparison of solvent extraction and thermal desorption for VOC analysis.

### Background to thermal desorption

Thermal desorption (TD) is a versatile GC pre-concentration technology that is used to analyse volatile and semi-volatile organic compounds (VOCs and SVOCs) in a wide range of sample types. By concentrating organic vapours from a sample into a very small volume of carrier gas (Figure 1), TD maximises sensitivity for trace-level target compounds, helps to minimise interferences, and routinely allows analyte detection at the ppb level or below. It also greatly improves sample throughput, by allowing full automation of sample preparation, desorption/extraction, pre-concentration and GC injection.



**A Tube desorption and inlet split:**
Sample tube heated in a flow of carrier gas and analytes swept onto an electrically cooled focusing trap, typically held between ambient and –30°C.

Sample tubes and traps can contain multiple sorbents, for analysis of an extended range of analytes.

During either stage, the flow of analytes can be split and re-collected onto a clean sorbent tube.

**B Trap desorption and outlet split:**
Focusing trap rapidly heated (up to 100°C/s) in a reverse flow of carrier gas ('backflush' operation), to transfer the analytes to the GC column.

**Figure 1:** How two-stage thermal desorption works.

The new 'xr' range of TD instruments from Markes International enhance these capabilities, offering a wide analyte range ($C_2$–$C_{44}$ including reactive species), automated re-collection and re-analysis of split portions for method validation and compliance with standard methods, optional internal standard addition for improved confidence in results, and electronic/manual options for control of carrier gas. In this study we use the TD100-xr™ for fully automated analysis of up to 100 sorbent tube samples.

## Experimental

The sampling and analytical protocol used in this study is fully compliant with the method stipulated in CEN/TS 13649.

**Standards:**
A methanol solution of 21 compounds typical of those monitored under CEN/TS 13649, each at 2000 mg/L, was diluted to 5, 10, 20, 50 and 100 µg/mL. The internal standard was a solution of (trifluoromethyl)benzene and 1-bromo-4-fluorobenzene in methanol, each at 2500 mg/L, and this was diluted to 50 µg/mL.

Sample solutions (1 µL analyte mix and 1 µL internal standard) were introduced onto conditioned sorbent tubes with a Calibration Solution Loading Rig (CSLR™, Markes International), using 100 mL/min nitrogen carrier gas for 3 min (equivalent to a sampling volume of 300 mL gas-phase sample). Under these conditions, the 5, 10, 20, 50 and 100 µg/mL concentrations would be equivalent to 4.2, 8.3, 16.7, 41.7 and 83.3 ppb for a real air sample.

**Real-world sample:**
300 mL of air taken from the exhaust of a restaurant during a busy lunchtime period, using an ACTI-VOC™ low-flow pump (Markes International).

**TD:**

| | |
|---|---|
| TD instrument: | TD100-xr (Markes International) |
| Tube: | Universal tube (Markes International part number C3-AXXX-5266)[3] |
| Trap: | Air Toxics Analyser/Soil Gas trap (Markes International part number U-T15ATA-2S)[4] |
| Tube dry purge time: | 1.0 min |
| Tube dry purge flow: | 60 mL/min |
| Internal standard flow: | 10 mL/min |
| Desorption temp: | 300°C |
| Desorption time: | 5 min |
| Trap low: | 25°C |
| Trap high: | 250°C for 3 min |
| Outlet split flow: | 10 mL/min |
| Split ratio: | 7.7:1 |
| Heating rate: | Max (100°C/s) |
| TD flow path temp: | 120°C |

**GC:**

| | |
|---|---|
| Carrier gas: | Helium |
| GC column: | DB-1, 30 m × 0.25 mm × 1.0 µm |
| Mode: | Constant-flow, 1.5 mL/min |
| Oven ramp: | 35°C (3 min), then 15 °C/min to 85°C (0 min), then 25°C/min to 220°C (1 min) |

**Quadrupole MS:**

| | |
|---|---|
| Ion source: | 250°C |
| MS transfer line: | 230°C |
| Full scan range: | m/z 36–180 (0–2.2 min), m/z 33–270 (2.2+ min) |

## Results and discussion

### 1. Analysis of standard mix

Figure 2 shows the analysis of the CEN/TS 13649 standard containing 100 ng of each compound on-tube (equivalent to sampling 300 mL of ambient air containing 83 ppb of each analyte). The retention time and quant ions for each compound are shown in Table 2.

In this analysis, trap desorption efficiency and a steep GC temperature ramp lead to good peak shape and therefore optimum sensitivity – as illustrated for the case of the challenging polar compound isopropanol (Figure 2B). This is achieved while keeping the run time short and avoiding any compromise in compound separation (Figure 2C).

### 2. Analysis of a high-concentration standard

For high-concentration samples (*e.g.* with analyte concentrations of 100–1000 µg/mL), a high split ratio should be used to reduce the risk of detector contamination and consequent interference with future runs.

To assess the performance of the system for such samples, 1 µL of the standard solution containing 1000 µg/mL per analyte (equivalent to sampling 300 mL of ambient air containing 833 ppb of each analyte) was injected onto the sorbent tube, and a split ratio of 33:1 applied during trap desorption.

The resulting analysis (Figure 3, blue) demonstrates that clear peak separation is maintained and that quantitative analysis is not compromised. A re-analysis of the same tube (Figure 3, blue) shows minimal carryover (<0.5%), indicating that compound concentrations will not be underestimated due to analyte retention.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1 | Acetone | 7 | Hexamethyldisiloxane | 12 | 1-Methoxy-2-propyl acetate | 19 | Anisole |
| 2 | Isopropanol | IS1 | (Trifluoromethyl)benzene | 13 | Ethylbenzene | IS2 | 1-Bromo-4-fluorobenzene |
| 3 | Hexane | 8 | Heptane | 14,15 | *m*-/*p*-Xylene | 20 | 1-Decene |
| 4 | Ethyl acetate | 9 | Toluene | 16 | 2-Heptanone | 21 | 2-Nonanone |
| 5 | Benzene | 10 | Cyclopentanone | 17 | Styrene | 22 | 1-Dodecene |
| 6 | 3-Pentanone | 11 | Butyl acetate | 18 | *o*-Xylene | | |

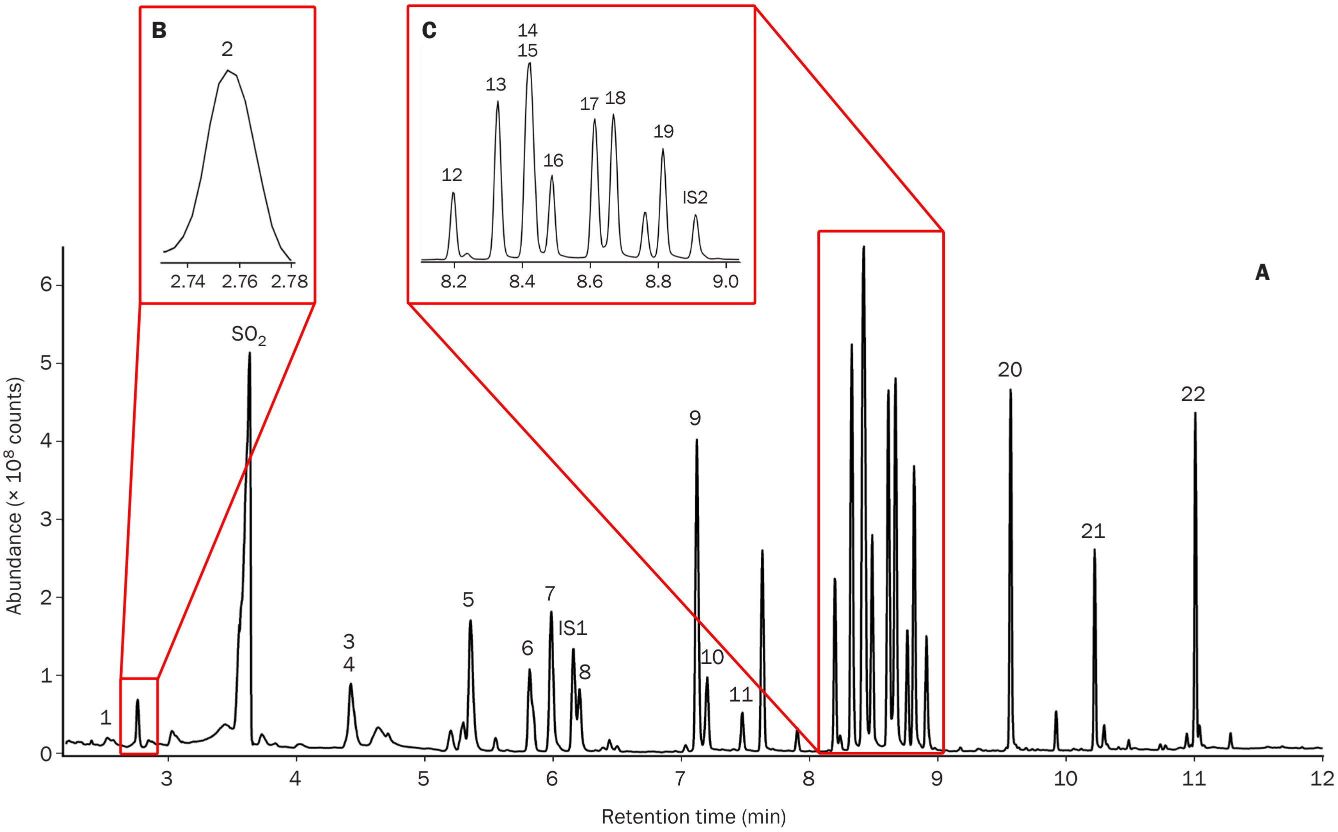
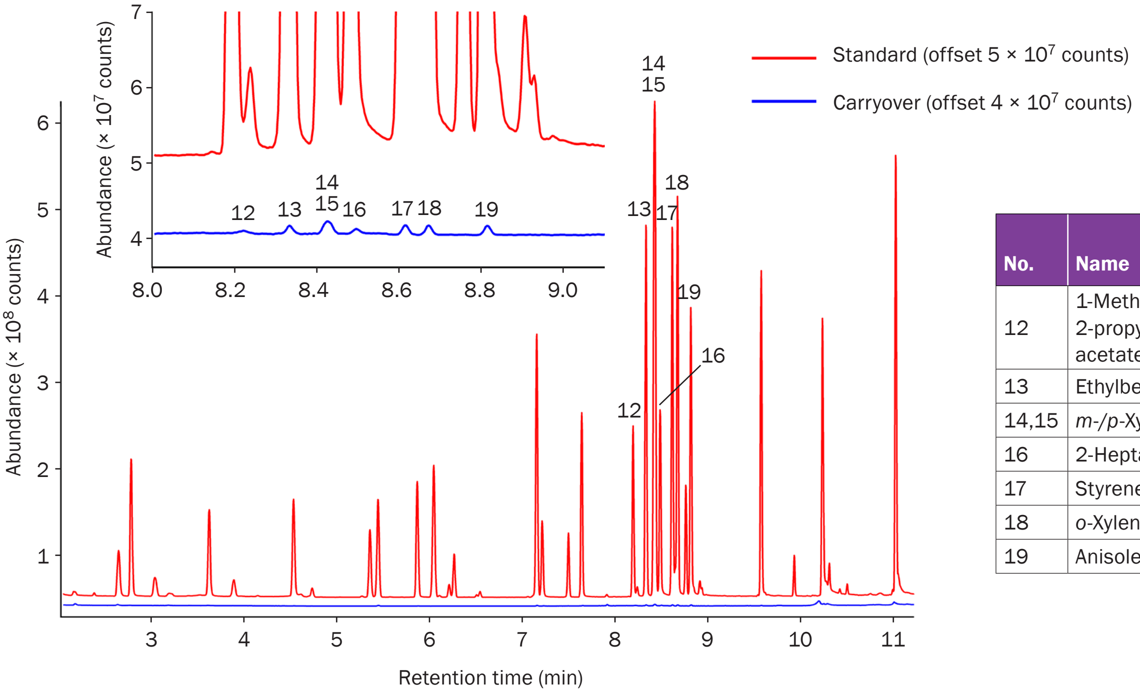


**Figure 2:** (**A**) Analysis of tubes containing the CEN/TS 13649 standard at 100 ng per analyte. (**B**) Expansion showing good peak shape for isopropanol. (**C**) Expansion showing good peak separation.

| No. | Name | Retention time (min) | Quant ion | Linearity ($R^2$) | RSD (%) (n = 5) | | MDL (mg/m$^3$) |
|---|---|---|---|---|---|---|---|
| | | | | | RT | Peak area | |
| 1 | Acetone | 2.46 | 58 | 0.996 | 0.180 | 5.9 | 0.013 |
| 2 | Isopropanol | 2.72 | 45 | 0.999 | 0.118 | 5.8 | 0.005 |
| 3 | Hexane | 4.39 | 41 | 0.994 | 0.058 | 3.5 | 0.016 |
| 4 | Ethyl acetate | 4.43 | 43 | 0.998 | 0.086 | 5.0 | 0.004 |
| 5 | Benzene | 5.31 | 78 | 0.998 | 0.059 | 4.4 | 0.004 |
| 6 | 3-Pentanone | 5.82 | 57 | 0.997 | 0.041 | 2.2 | 0.002 |
| 7 | Hexamethyldisiloxane | 5.96 | 147 | 0.996 | 0.050 | 5.6 | 0.003 |
| IS1 | (Trifluoromethyl)benzene | 6.13 | 146 | – | 0.049 | 3.4 | – |
| 8 | Heptane | 6.18 | 43 | 0.999 | 0.047 | 6.3 | 0.004 |
| 9 | Toluene | 7.10 | 91 | 0.999 | 0.048 | 4.2 | 0.003 |
| 10 | Cyclopentanone | 7.19 | 55 | 0.998 | 0.041 | 3.8 | 0.002 |
| 11 | Butyl acetate | 7.63 | 43 | 0.999 | 0.039 | 2.4 | 0.002 |
| 12 | 1-Methoxy-2-propyl acetate | 8.18 | 43 | 0.999 | 0.046 | 2.8 | 0.002 |
| 13 | Ethylbenzene | 8.31 | 91 | 0.998 | 0.053 | 2.9 | 0.002 |
| 14,15 | *m*-/*p*-Xylene | 8.40 | 91 | 0.998 | 0.044 | 2.7 | 0.002 |
| 16 | 2-Heptanone | 8.47 | 43 | 0.998 | 0.040 | 4.1 | 0.003 |
| 17 | Styrene | 8.60 | 104 | 0.999 | 0.034 | 4.0 | 0.003 |
| 18 | *o*-Xylene | 8.65 | 91 | 0.996 | 0.042 | 2.9 | 0.002 |
| 19 | Anisole | 8.80 | 108 | 0.997 | 0.042 | 3.1 | 0.002 |
| IS2 | 1-Bromo-4-fluorobenzene | 8.89 | 95 | – | 0.030 | 5.0 | – |
| 20 | 1-Decene | 9.55 | 41 | 0.997 | 0.029 | 4.5 | 0.004 |
| 21 | 2-Nonanone | 10.21 | 58 | 0.988 | 0.024 | 8.0 | 0.005 |
| 22 | 1-Dodecene | 11.00 | 69 | 0.996 | 0.027 | 3.5 | 0.003 |

**Table 2:** Results obtained for the list of compounds cited in CEN/TS 13649.



| No. | Name | Carryover (%) |
|---|---|---|
| 12 | 1-Methoxy-2-propyl acetate | 0.50 |
| 13 | Ethylbenzene | 0.28 |
| 14,15 | *m*-/*p*-Xylene | 0.31 |
| 16 | 2-Heptanone | 0.59 |
| 17 | Styrene | 0.29 |
| 18 | *o*-Xylene | 0.26 |
| 19 | Anisole | 0.37 |

**Figure 3:** Analysis of tubes containing the CEN/TS 13649 standard at 1 µg per analyte (red), and the carryover after a second desorption of the same tube (blue). Inset: Expansion showing detail for compounds 12–19, with corresponding carryover values indicated in the table.

### 3. Linearity

System linearity was assessed by determining the ratio between the peak areas of the internal standards and the analytes at five concentrations in the range 5–100 µg/mL, which is consistent with concentrations likely to be encountered in stack emissions. Figure 4 shows the excellent linearity for seven compounds from the CEN/TS 13649 mix that span the full range of volatilities and polarities.

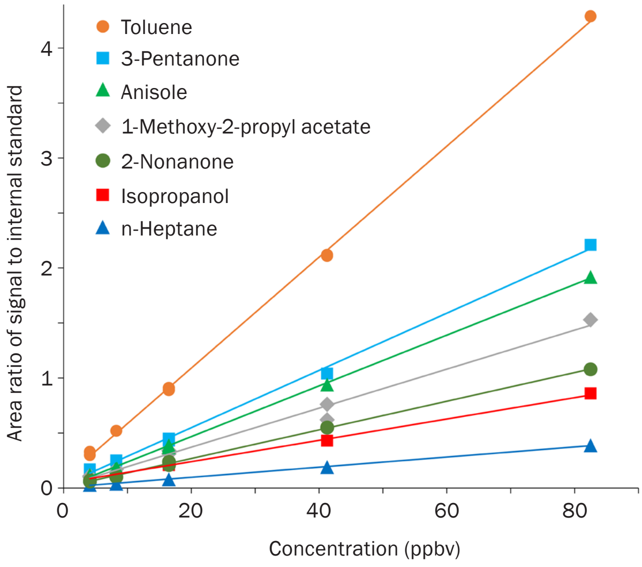


**Figure 4:** Linearity plots for seven compounds from the CEN/TS 13649 mix, over a concentration range corresponding to 4–82 ppbv in a 300 mL sample volume.

### 4. Reproducibility and MDLs

Reproducibilities and method detection limits (MDLs) were assessed by analysing eight replicate tubes containing 1 µL of the 5 µg/mL standard solution (equivalent to sampling 300 mL of ambient air containing 4.2 ppb of each analyte).

Retention-time RSDs are all less than 0.1%, peak-area RSDs are below 8%, and MDLs range from 0.002–0.013 mg/m$^3$ (Table 2), demonstrating the system's excellent repeatability and stability.

### 5. Quantitative re-collection of split flows

Markes' TD instruments have the ability to re-collect samples by directing the split flow (which would otherwise carry excess sample to vent) onto a sorbent tube. This process of re-collection can either be onto the tube from which the sample was originally desorbed, or onto a clean tube. This process can be fully automated, and offers a significant advantage over solvent extraction, because it allows a single sample to be analysed multiple times. Sample splitting and re-collection makes method validation easier, and more importantly avoids the need to collect another sample should the analysis unexpectedly fail to proceed correctly.

Figure 5 shows a repeat analysis of the CEN/TS 13649 mix at 100 ng per analyte, run with an 8:1 split (equivalent to sampling 300 mL of ambient air containing 83 ppbv of each analyte), illustrating quantitative re-collection over a wide range of volatilities. Note the consistency of peak position and shape.

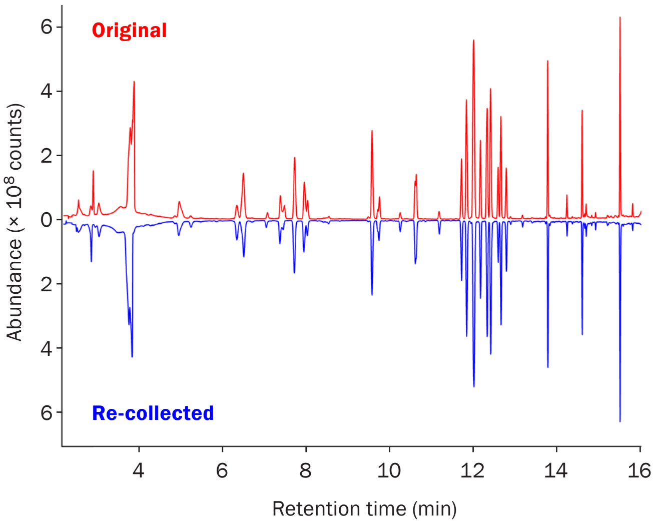


**Figure 5:** Analysis of tubes containing the CEN/TS 13649 standard at 100 ng per analyte (red), and analysis of the same sample following re-collection with an 8:1 outlet split (blue).

When a re-collected sample is analysed, a slight reduction in peak area is to be expected, and this is just discernible in Figure 5, where the re-collected sample is expected to show 87% of the original analyte response.

The reliability of quantitative re-collection can be verified by comparing the responses obtained from successive repeat analyses with the values expected theoretically. Figure 6 shows that the experimental values obtained (using an 8:1 split) are in very good agreement with the expected decay curve.

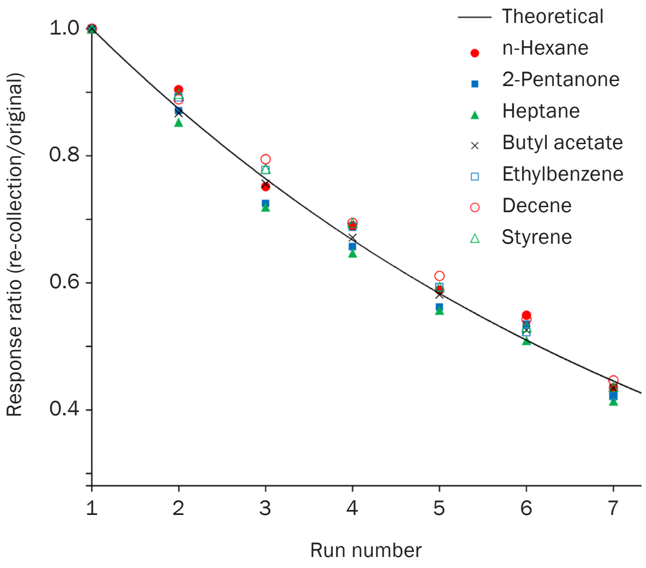


**Figure 6:** Analyte responses from seven successive re-collections and repeat analyses of key compounds in the CEN/TS 13649 mix, using an 8:1 split. The black line indicates the theoretical decay.

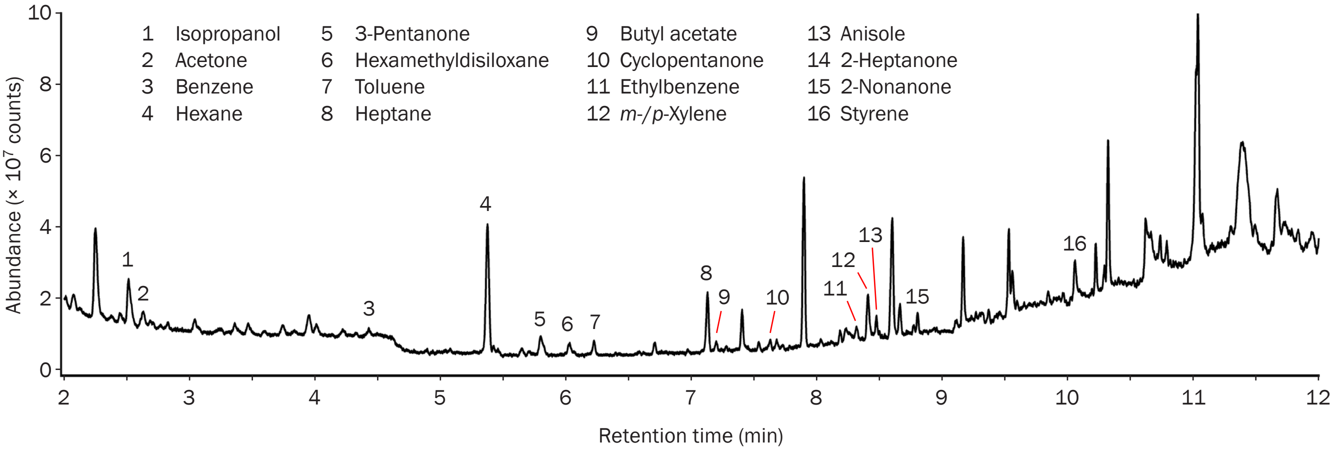


**Figure 7:** Analysis of 300 mL of air taken from a restaurant vent during a busy lunchtime period, with 16 compounds listed in CEN/TS 13649 indicated.

### 6. Analysis of real-world emission

To establish the performance of the TD–GC–MS system in a real-world scenario, 300 mL of air was taken the exhaust of a restaurant during a busy lunchtime period, using an ACTI-VOC low-flow pump. Analysis was then conducted as described earlier, using an outlet split of 8:1. As shown in Figure 7, a number of compounds relevant to CEN/TS 13649 are identified, including several at trace levels.

## Conclusions

This Application Note demonstrates that Markes International's automated, cryogen-free thermal desorption systems offer excellent results for monitoring VOCs from stationary source emissions in accordance with the European standard CEN/TS 13649.

A particular feature of this method is its improved performance and simplicity compared to solvent extraction. In addition, method development and validation of results is straightforward because of the ability to carry out sample splitting and re-collection for repeat analysis in an automated fashion.

## References and notes

1. EN 13649:2001 – Stationary source emissions – Determination of the mass concentration of individual gaseous organic compounds – Activated carbon and solvent desorption method, European Committee for Standardization, 2001.
2. CEN/TS 13649:2014 – Stationary source emissions – Determination of the mass concentration of individual gaseous organic compounds – Sorptive sampling method followed by solvent extraction or thermal desorption, European Committee for Standardization, 2014.
3. These include: US EPA Method TO-17; US EPA Method 325; ISO 16000-6; ISO 16017-1; ISO 16017-2; ASTM D6196; EN 14662-1; EN 14662-4; Chinese EPA Method HJ 644; Chinese EPA Method HJ 734; NIOSH Method 2549; LFTGN 04.
4. CEN/TS 13649 recommends TD tubes packed with a range of sorbents, with these being chosen on the basis of the analytes of interest. It is common for sorbent tubes to be packed with two to three sorbent materials to increase the range of analytes that can be retained. This study used a three-bed 'Universal' tube (Markes International), which can quantitatively retain all target compounds designated in CEN/TS 13649, including polar and non-polar compounds ranging from $C_{2/3}$ to $C_{30/32}$, and reactive species. It also offers low water retention, reducing any problems from water interference that might be caused by sampling humid environments.
5. Using an ambient-temperature trap-low reduces the risk of water interference that can occur in traps cooled to <5°C, as well as eliminating operational problems that may be caused by ice formation. The optimised sorbent combination in the 'Air Toxic Analyser' cold trap used can retain VOCs as low as $C_3$ even at ambient temperature, ensuring that analytes of interest are not lost as a result of this relatively high trap temperature. In addition, the narrow-bore design of Markes cold traps and the unsurpassed trap heating rate of the TD100-xr result in excellent peak shape and high sensitivity.

## Trademarks

ACTI-VOC™, CSLR™ and TD100-xr™ are trademarks of Markes International.