

GERSTEL AppNote 261

# Ambient Air Analysis with Dynamic Focusing

Leonhard Nünemann, Andreas Hoffmann, Maikel Haferkamp, and Kurt Thaxton

GERSTEL GmbH & Co.KG, Eberhard-Gerstel-Platz 1, 45473 Mülheim an der Ruhr, Germany

## Key Words

Thermal desorption, TD 3.5<sup>+</sup>, active air sampling, EPA TO-17, ISO 16000-6, dynamic focusing

## Abstract

The collection of volatile organic compounds (VOCs) from ambient air is either achieved actively by sampling onto a sorbent tube using a sampling pump, or passively using the tube as a diffusive sampler without pumping air through it. Active sampling is preferable because of easier quantification, shorter sampling time, and wider compound range that can be determined using a single tube.

There are various national and international standards dealing with the analysis of VOCs via thermal desorption coupled with gas chromatography and a mass spectrometry (TD-GCMS).

Following thermal desorption from the tube, analytes are focused in a cold trap using cryogenic cooling, (commonly liquid nitrogen). For labs that cannot use liquid nitrogen, a novel cryogen free trapping technique for VOCs was developed by scientists at GERSTEL: Dynamic Focusing.

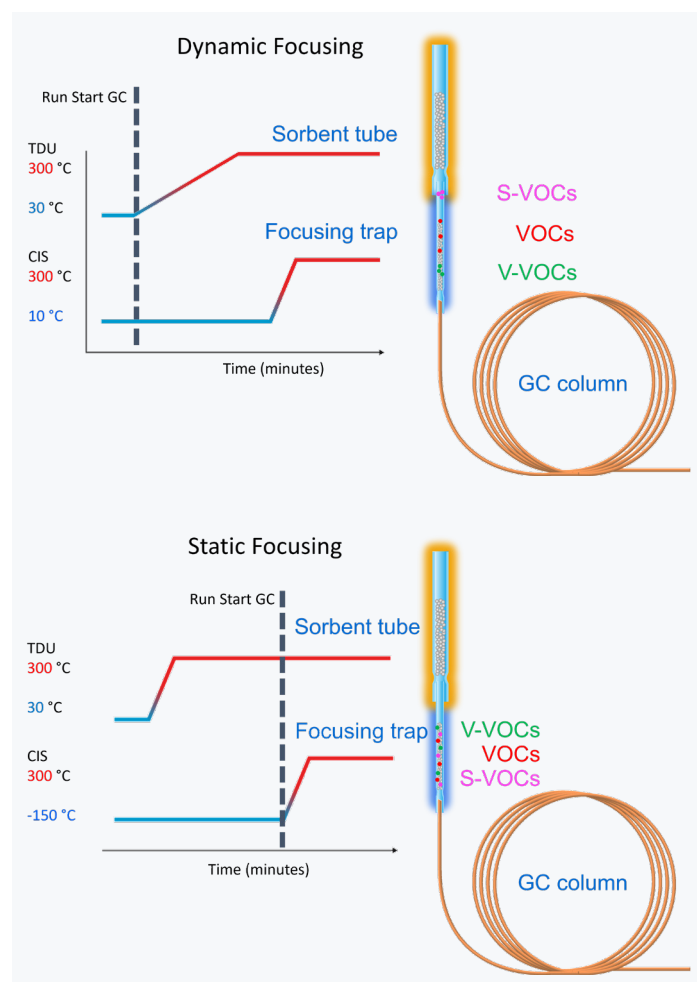
The dynamic focusing technique has been thoroughly tested for use with methods such as U.S. EPA TO-17 and ISO 16000-6. While ISO 16000-6 focuses on the determination of VOCs ranging in volatility from n-C6 to n-C16, or in boiling point from 50 °C to 260 °C, EPA TO-17 includes very volatile organic compounds (VOCs) such as propene. The use of Dynamic Focusing produces method compliant results over the full range of volatility covered by these methods, without the need for either cryogenes or problematic in-line valves.

## Introduction

Thermal desorption is performed in two defined main stages: Tube desorption combined with cold trapping, and trap desorption. During tube desorption, analytes that were collected on the sorbent bed in the larger sample tube are released and focused in the much smaller trap. Trapping usually occurs at temperatures as low as -150 °C or by using a sorbent. In the trap desorption stage, analytes are then released from the trap by rapid heating and are transferred to the GC column in which they are separated by boiling point and/or polarity and are finally detected by a mass selective detector.

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Dynamic focusing uses a liner packed with relatively weak sorbent. The trap temperature is set to +10 °C. Instead of trapping and desorbing in two separate stages, the stages are overlapped. The medium to high boilers are trapped by the sorbent and desorbed when the trap is heated. The very volatile compounds, on the other hand, are not trapped but rather slowed down sufficiently by the sorbent to be focused into a sharp band resulting in sharp peaks. The GC run is triggered at the beginning of tube desorption ensuring that no volatiles pass the system undetected. The sequences of individual steps that make up dynamic and static focusing are shown in the following graphics.



**Figure 1:** Schematic of dynamic focusing (top) and static focusing (bottom).

## Experimental

## Materials

Tubes: Tenax™ TA, Carbotrap® - GERSTEL, Air Toxics tubes – Camsco®

Chemicals: CLP 04.1 VOA Internal Standard Spike Mix - Restek, VOC analytical standards - Supelco & Merck, Methanol Supra-Solv® - Merck, gas standard: TO-15 Subset 25 component Mix, 1ppm (34434) and TO-14A Internal Standard/Tuning Mix, 1ppm (34408)– Restek

## Instrumentation

GERSTEL TD Core system on Agilent 8890 GC and 5977B MSD, complemented with an GERSTEL ISDP or ISDP+ accessory for fully automated addition of gas or liquid internal standards before analysis.

## Analysis Conditions TD Core System

CIS 4

split (10:1)

purge flow to split vent: 10 mL/min at 0.01 min  
10 °C (3.3 min); 12 °C/s; 280 °C (7 min)

TD 3.5+

solvent vent/dry purge, vent time 3.3 min  
30 °C (0 min); 400 °C/min; 280 °C (7 min)

## Analysis Conditions Agilent 8890 GC

Column 60 m Rxi 624 SilMS (Restek)

$d_i = 0.25 \text{ mm}$   $d_f = 1.4 \text{ }\mu\text{m}$

Pneumatics He;  $P_i = 16.24 \text{ psi}$

constant flow = 1 mL/min

Oven 35 °C (3.5 min); 10 °C/min; 240 °C; 30 °C/min  
300 °C (5 min)

## Analysis Conditions Agilent 5977B MSD

Full scan 33-300 amu

The performance of dynamic focusing was tested with methods that meet the criteria of EPA TO-17 and ISO 16000-6.

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### TO-17

For TO-17, two calibrations were made. One 10-point calibration in the lower concentration range for LOD/LOQ determination ranging from 0.5 to 5 ppb and another 5-point calibration over a working range from 2 to 10 ppb.

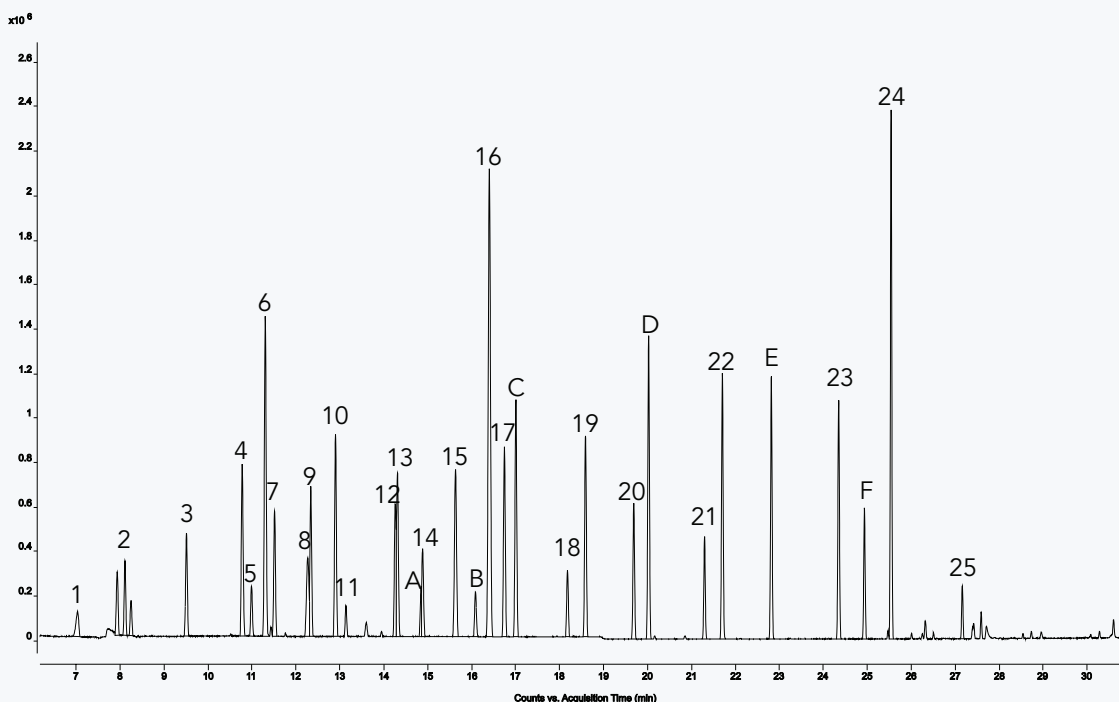
The methods were validated for the analytes shown in Table 1

using the listed internal standards. The performance criteria which must be met are:

- LOD  $\leq$  0.5 ppb
- Analytical Precision of 20%
- Precision for distributed volume pairs 25%

**Table 1:** TO-17 gas phase VOCs (1-25) and internal standards (A-F).

| Analytes           |                                |    |                       |    |                               |
|--------------------|--------------------------------|----|-----------------------|----|-------------------------------|
| 1                  | Propylene                      | 10 | n-Hexane              | 19 | Bromodichloromethane          |
| 2                  | 1,3-Butadiene                  | 11 | Vinyl acetate         | 20 | Methyl isobutyl ketone (MIBK) |
| 3                  | Vinyl Bromide                  | 12 | Butanone (MEK)        | 21 | 2-Hexanone (MBK)              |
| 4                  | Acetone                        | 13 | Ethyl acetate         | 22 | Dibromochloromethane          |
| 5                  | 2-Propanol                     | 14 | Tetrahydrofuran (THF) | 23 | Bromoform                     |
| 6                  | Carbon disulfide               | 15 | Cyclohexane           | 24 | 4-Ethyltoluene                |
| 7                  | Allyl chloride                 | 16 | iso-Octane            | 25 | Benzyl chloride               |
| 8                  | Methyl tert-butyl ether (MTBE) | 17 | n-Heptane             |    |                               |
| 9                  | Dichloroethylene               | 18 | 1,4-Dioxane           |    |                               |
| Internal Standards |                                |    |                       |    |                               |
| A                  | Bromochloromethane             | C  | Difluorobenzene       | E  | Chlorobenzene-d5              |
| B                  | Dichloroethane-d4              | D  | Toluene-d8            | F  | 1-Bromo-4-fluorobenzene       |



**Figure 2:** MS spectra (Scan data) of TO-17 gas standard and internal standards.

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### Limit of Detection - LOD

The limit of detection was determined by spiking 7 AirToxic tubes with a concentration within the expected LOD range (within a factor of 5, here 1.5 ppb was used). The LOD was then calculated according to 40 CFR136 Appendix B, by multiplying the standard deviation of the 7 determinations with the relevant student t-value (in this case: one sided = 99 %,  $v = n-1 = 6$ ,  $t = 3.14$ ).

### Precision

The analytical precision was determined both as repeatability for two identically spiked tubes, and over the whole calibration range. For the latter, the relative spread for two different sampling volumes (distributed sampling) was compared.

### ISO 16000-6

Tests were performed to ensure that the technique can be applied for analytes covering the whole volatility range specified in ISO 16000-6. The following criteria were applied for the analytes shown in Table 2:

- Blank values: The peak areas resulting from blank run must be <10% of the analyte peak area
- Calibration – linearity test (F-test Mandel)
- Precision must be better than 15%
- LOQs must meet the method requirements
- Audit accuracy within  $s(x) \pm 10\%$

**Table 2:** VOCs (liquid phase) used for method validation (dissolved in Methanol).

|          |                 |                        |
|----------|-----------------|------------------------|
| Benzene  | n-Butyl acetate | Cumene                 |
| Toluene  | Ethylbenzene    | $\alpha$ -Pinene       |
| n-Octane | m-Xylene        | 1,2,4-Trimethylbenzene |

The analytes listed in table 2 were also used in the proficiency test. Recovery and carryover were determined for a broader VOC range using an alkane-mixture (n-Hexane to n-Hexadecane).

### Blanks

The blank values of 10 different Tenax™ TA tubes were determined. It was also tested whether the analysis of the highest calibration point standard caused analyte carryover in the following analysis.

### Calibration

A calibration for TVOC determination was performed using 6 calibration levels (5 - 250  $\mu\text{g}/\text{m}^3$ , 3 replicates each). The method was validated using 3 quality control standards prepared independently from the calibration standards. The calibration was checked for linearity using the F-Test (Mandel).

### Precision

The precision of the method was tested for two analyte concentrations using 5 Tenax™ TA tubes for each level. Repeatability was checked by determining the relative standard deviation. The variances of the two levels were also compared to see if the relative scattering of the determined values was equally distributed for both concentration levels.

### Limit of Quantification - LOQ

The LOQ was determined according to DIN 32645 using the blank value method. 10 Tenax™ TA tubes were spiked with a concentration within the range of the expected LOQ (here the lowest calibration concentration of 5  $\mu\text{g}/\text{m}^3$  was used).

### Accuracy

The accuracy of the method was proven by participation in a proficiency test according to DIN EN ISO 16017 1, DIN ISO 16000-6.

The analytes used in the proficiency test are listed in table 2. The expected concentration range for each substance was given as 10-200  $\mu\text{g}/\text{m}^3$ .

## Results and Discussion

### TO-17 Data

Performance was tested against the method criteria for the compounds listed in Table 1. The validation was successful for all analytes.

A linear calibration with  $R^2$ -values above 0.99 could be achieved for most compounds, with some of the more polar compounds being slightly lower due to the use of a mid-polar column (Rxi-624 MS). In Figure 3, curves of the equidistant 5-point calibrations (2 to 10 ppb) of four selected low boiling compounds are shown.

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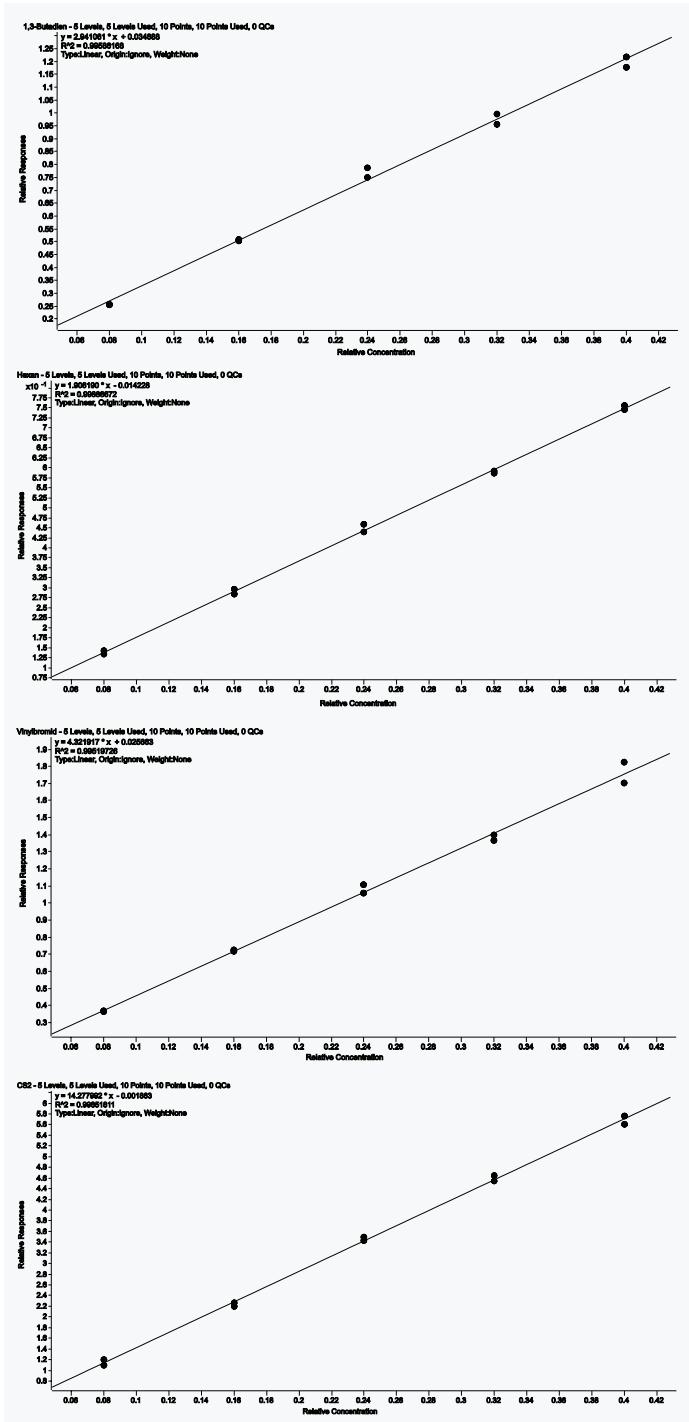


Figure 3: Calibration curves for 1,3-Butadiene, n-Hexane, Vinyl bromide and Carbon disulfide.

Precision was within the defined ranges for both methods. The required 0.5 ppb limit of detection could be reached for all analytes. Figure 4 shows the main m/z-signals (EIC) of the selected four compounds at 0.5 ppb.

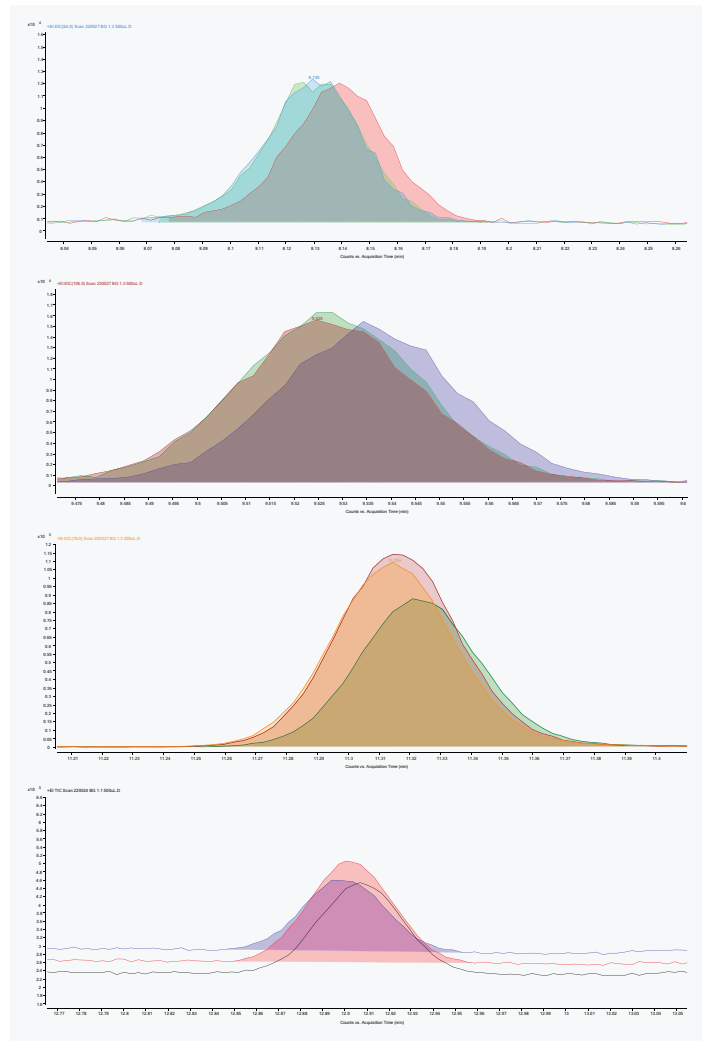


Figure 4: MS spectra (EIC data) of 1,3-Butadiene, Vinyl bromide, Carbon disulfide and n-Hexane at 0.5 ppb with values for relative standard deviation and relative response factor (3 repetitions).

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For the low boiling compounds, additional performance criteria like Signal-to-noise-ratio (S/N) and relative retention factors (RRF) were inspected as well.

The results for S/N at a concentration of 0.5 ppb, the relative standard deviation (RSD) for three different concentration levels as well as the relative retention factors (RRFs) are shown in Table 3.

**Table 3:** S/N-ratio, RSDs and RRFs for the VVOCs.

| Analyte           | S/N     |         | RSD [%, n=3] |       | RRF      |         |
|-------------------|---------|---------|--------------|-------|----------|---------|
|                   | 0.5 ppb | 0.5 ppb | 3 ppb        | 6 ppb | absolute | RSD [%] |
| Propylene         | 12.4    | 14.1    | 6.2          | 7.5   | 0.09     | 12.5    |
| 1,3-Butadiene     | 30.6    | 3.0     | 3.3          | 1.8   | 0.37     | 16.9    |
| Vinyl bromide     | 70.1    | 3.4     | 2.2          | 5.6   | 0.52     | 16.4    |
| Acetone           | 194.3   | 10.6    | 16.3         | 13.0  | 0.60     | 8.2     |
| Isopropyl alcohol | 121.3   | 31.2    | 18.3         | 4.8   | 0.02     | 18.9    |
| Carbon disulfide  | 515.2   | 13.9    | 1.8          | 4.6   | 2.11     | 18.3    |
| Allyl chloride    | 5.4     | 10.5    | 1.1          | 4.5   | 0.09     | 23.3    |
| MtBE              | 14.9    | 6.7     | 5.6          | 2.3   | 0.60     | 10.8    |
| Dichloroethylene  | 29.2    | 5.9     | 1.2          | 0.3   | 0.11     | 24.5    |
| n-Hexane          | 69.5    | 15.4    | 6.3          | 0.3   | 0.27     | 20.6    |

#### ISO 16000-6 Data

The Dynamic Focusing technique for the VOC range meets the requirements of method ISO 16000-6.

Apart from cyclo-siloxanes, characteristic for column bleed (D3, D4, D5), no significant blank values were found when testing the 10 tubes. All calibration curves were best described using a linear

function. Precision was within the given range and the LOQ was below the lowest calibration level of 5 µg/m<sup>3</sup> for all validated analytes. A round robin test was passed successfully, all determined analyte concentrations were within the specified tolerance ranges. The results of the round robin are shown in Table 4.

**Table 4:** Results of the proficiency test VOC (DIN ISO 16000-6, DIN EN ISO 16017-1).

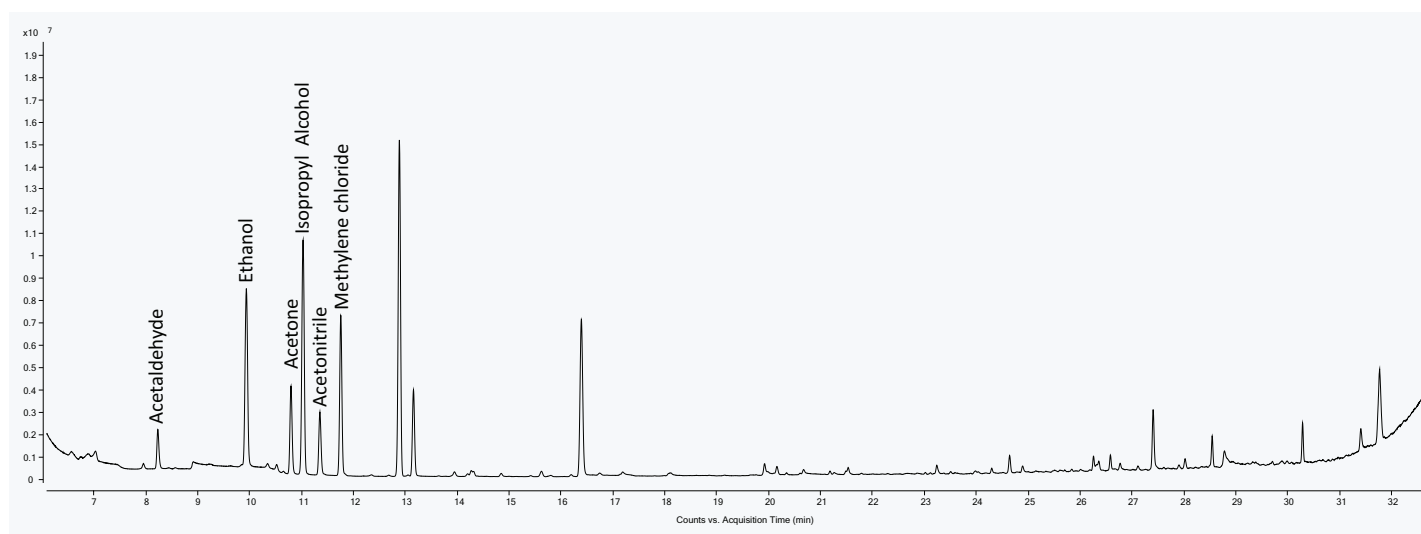
| Analyte                | Sample #1                   |                              |                                |         | Sample #2                   |                              |                                |         |
|------------------------|-----------------------------|------------------------------|--------------------------------|---------|-----------------------------|------------------------------|--------------------------------|---------|
|                        | Result [µg/m <sup>3</sup> ] | Average [µg/m <sup>3</sup> ] | Reference [µg/m <sup>3</sup> ] | Z-Score | Result [µg/m <sup>3</sup> ] | Average [µg/m <sup>3</sup> ] | Reference [µg/m <sup>3</sup> ] | Z-Score |
| 1,2,4-Trimethylbenzene | 43.1                        | 50.4                         | 54.9                           | -1.45   | 30.9                        | 26.3                         | 31.1                           | 1.76    |
| α-Pinene               | 69                          | 86.8                         | 87.2                           | -2.05   | 67.3                        | 69                           | 67.5                           | -0.25   |
| Benzene                | 21.4                        | 24.8                         | 28.3                           | -1.36   | 62.7                        | 59                           | 61.3                           | 0.63    |
| Cumene                 | 36.1                        | 33.7                         | 36.8                           | 0.71    | 43.7                        | 33.8                         | 36.1                           | 2.94    |
| Ethylbenzene           | 61.9                        | 70.4                         | 72.9                           | -1.21   | 44.2                        | 43.3                         | 45.4                           | 0.21    |
| m-Xylene               | 105                         | 136                          | 132.4                          | -2.25   | 89.3                        | 90.3                         | 87.7                           | -0.11   |
| n-Butyl acetate        | 32.7                        | 37.6                         | 42.2                           | -1.3    | 126                         | 138                          | 140.1                          | -0.94   |
| n-Octane               | 55.9                        | 66                           | 67.1                           | -1.54   | 121                         | 132                          | 131.8                          | -0.79   |
| Toluene                | 82                          | 101                          | 102.7                          | -1.92   | 53.8                        | 50.8                         | 51.7                           | 0.58    |

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### Real Air Sample

The method was tested by taking a 1L sample of laboratory air on a Carbotrap® 300 tube. Two tubes were sampled and analyzed using the developed method.

Various solvents could be detected in the lab air, the measured concentration of the identified analytes was in the low ppb range. The resulting full scan chromatogram of the sample is shown in Figure 4.



**Figure 4:** Full scan chromatogram resulting from a 1L air sample taken in a laboratory used for sample preparation.

### Conclusions

Dynamic Focusing is a suitable cryogen free trapping alternative for use in thermal desorption analysis of air for the determination of VOCs as well as for very volatile organic compounds (VOCs) as low boiling as propylene. The performance has been proven in a round robin test. Dynamic focusing works successfully without the need to reverse the flow of the focusing trap, thus removing the need for complicated valving systems which are often the source of false positives (carryover) or false negatives (losses to the valve material). Valves often leak and require elaborate leak testing procedures much more complicated than those used with dynamic focusing.

For VOC sampling from humid environments onto tubes with stronger, hydrophilic, charcoal-based sorbents, effective water management is essential. For high humidities (around 60%) the tubes must be purged before analysis, for even higher humidity it is often advisable to reduce the sampling volume as well. Dry purging can be performed in a fully automated way using either the GERSTEL ISDP or ISDP+ accessories (although dry purging was not needed to be successful here for 50% RH air).

Reducing the water content of course comes at a cost of increased LOQs, but having high water levels on the tube can result in under reporting.

For the ISO 16000-6 range of VOCs on Tenax™ TA, no additional conditioning steps are necessary. For the more volatile analytes finding the right sorbent for the application is essential. If a broad range of analytes are to be determined, tubes with multiple sorbent beds are needed. Ideally the sorbent should not form artifacts that influence results for the targeted analytes.

Since water is partially collected on the sorbent as well, the safe sampling volume (SSV) of the sorbent is reduced. When large amounts of water are sampled, the polar analytes might break through more easily.

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### Acknowledgements

The authors would like to thank Elvetheria Juritsch and Dr. Morgane Even from BAM, Berlin, Germany, for fruitful discussions.

### References

- [1] Compendium Method TO-17, *Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes*, Center for Environmental Research Information Office of Research and Development U.S. Environmental Protection Agency Cincinnati, January **1999**
- [2] ISO 16000-6:**2021** *Determination of organic compounds (VVOC, VOC, SVOC) in indoor and test chamber air by active sampling on sorbent tubes, thermal desorption and gas chromatography using MS or MS FID*