



# Determination of Volatile Organic Compounds in Air Using Thermal Desorber Chromatec TDA and Chromatec Crystal GC/MSD

## Abstract

A method for the analysis of volatile organic compounds in air is described. It is based on air sampling on sorbent tubes, followed by thermal desorption and gas chromatography mass spectrometry analysis (TD/GC/MS). Calibration curves for ranges of 1–500 and 1–1000 ng, depending on the substance, exhibit determination coefficients above 0.999. The chromatographic method was validated and the instrumental repeatability and trueness were established, a maximum RSD of 7% and a recovery of 92–109% were obtained.

## Introduction

Volatile organic compounds (VOCs) are monitored in the quality control of ambient and workplace air. The range covers various classes of organic compounds - hydrocarbons, halocarbons, alcohols, esters, etc.

Sampling is carried out by pumping air onto sorbent tubes, which are easily transported to the laboratory. By sampling the air volume is usually several liters, which allows to achieve a high degree of concentrating and determine analytes at the ppb level.

Depending on the components of interest various sorbents can be selected. In this study Tenax TA was used. It is the most universal sorbent that is used to analyze volatile and semi-volatile organic compounds.

The VOCs were analyzed using a Chromatec TDA thermal desorber, which allows automated analysis of up to 50 sample tubes. The TDA provides two-stage thermal desorption. At the first stage, the sample tube is heated and a flow of inert gas transfers the analytes into a cooled focusing trap. At the second stage, the trap rapidly heats up and the analytes are transferred to the GC column.

The TDA has the dry-purge option to remove water from the sorbent tube before desorption that improves performance for humid samples and eliminates the entry of moisture into a cold trap.

Other feature of the TDA is the separate purge gas channel. Thus, helium can be used as a carrier gas for

desorption from the focusing trap, and cheaper nitrogen for desorption from the sample tube.



## Methods

1. ISO 16017 Indoor, Ambient and Workplace Air - Sampling and Analysis of Volatile Organic Compounds by Sorbent Tube/Thermal Desorption/Capillary Gas Chromatography
2. US EPA Method TO-17 Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes
3. ASTM D6196 Standard Practice for Choosing Sorbents, Sampling Parameters and Thermal Desorption Analytical Conditions for Monitoring Volatile Organic Chemicals in Air

## Equipment

- Chromatec Crystal 9000 GC/MSD, SSL
- Capillary column BPX-Volatiles (60 m × 0.32 mm × 1.8 μm)
- Thermal Desorber Chromatec TDA
- Sorbent tubes Tenax TA
- Focusing trap Tenax TA
- Desorber (Chromatec, P/N 400-1903)
- Sampling Pump Chromatec PV-2 (P/N 400-1911)

## Analysis mode

<b>Run time</b>	32 min	
<b>Inlet</b>		
Temperature	220 °C	
Split	1:10	
<b>Column</b>		
Carrier gas	Helium	
Constant flow	1.2 mL/min	
<b>Oven</b>		
Rate, °C/min	Temp, °C	Time, min
	40	5
10	220	9
<b>MSD</b>		
Scan mode	t-SIM+Scan	
Ion source temperature	200 °C	
Transfer line temperature	220 °C	
<b>Thermal Desorber</b>		
Valve temperature	250 °C	
Transfer line temperature	250 °C	
Carrier gas	Helium	
Purge gas	Nitrogen	
Dry purge temperature	Ambient	
Dry purge flow	20 mL/min	
Dry purge time	2 min	
Desorption temperature	300 °C	
Desorption flow	30 mL/min	
Desorption time	5 min	
Trap low temperature	-10 °C	
Trap high temperature	300 °C	
Trap heating rate	2000 °C/min	
Trap heating time	2 min	

## Experimental

Stock standard solution (1000 µg/mL) was prepared from 45 specific compounds (purity > 98%). Methanol was used as the solvent. Liquid calibration solutions were prepared by diluting the stock standard. The following eight solutions were used to create the calibration – 1.0 µg/mL, 5.0 µg/mL, 10 µg/mL, 50 µg/mL, 100 µg/mL, 250 µg/mL, 500 µg/mL, 1000 µg/mL.

p-Fluorotoluene was used as the internal standard (ISTD). Stock ISTD solution (1000 µg/mL) was prepared from standard material (purity 99%). The solvent was methanol. Stock ISTD solution was diluted, the concentration in the ISTD solution was 10 µg/mL.

The sorbent tubes were conditioned using Desorber (P/N 400-1903) under nitrogen flow rate of 50 mL/min at 300 °C for 60 min.

Calibration and ISTD solutions were injected sequentially into the sorbent tube (Tenax TA). The volume of each solution was 1 µL. The solvent was purged in IUTD

(Injection Unit for Thermal Desorption Tubes), P/N 400-1931. The purge gas flow was 100 mL/min for 1 min.

## Results and discussion

For air analysis the sample volume is not constant. Therefore, it is convenient to calibrate according to the amount of the components injected onto the sorbent tube. In case of injection 1 µL of a standard mixture with a concentration of 1 µg/mL, analyte mass is 1 ng. Thereby, the calibration curve is actually created in ng.

Concentrations in liquid calibration solutions (µg/mL) are equal to the concentration of compounds (µg/m<sup>3</sup>) in the air by sampling 1 L. For example, a concentration of 1 µg/mL in liquid standard corresponds to 1 µg/m<sup>3</sup> for sampling 1 L of air.

### Analysis of standard mix

The enhanced sensitivity of the analytical system is achieved by acquisition in Selected Ion Monitoring (SIM) mode. On the other hand, for the positive confirmation of specific compounds a full scan mode is necessary. This enables the identification via library searching to be performed.

The Chromatec GC/MS instrument allows to perform the analysis in synchronized t-SIM+Scan mode. This provides high sensitivity and reliable identification.

Figure 1 shows the chromatogram of the calibration solution (10 µg/mL) that represents 10 µg/m<sup>3</sup> for 1 L of air. The chromatogram in the scan mode is shown on the upper part of the figure, and SIM in the lower part.

### Linearity

Eight-point calibration curve was plotted in the range from 1 to 1000 ng.

Table 1 highlights the linear calibration range, the determination coefficient and the relative standard deviation (RSD) of the relative response factors.

Most components showed good linearity in the range of 1 to 1000 ng. However, cyclic and aromatic hydrocarbons exhibited linearity of 1 to 500 ng. The determination coefficients (R<sup>2</sup>) were higher than 0.999 for all compounds. The relative standard deviations (RSD) of the relative response factors were less than 6%.

Figure 2 shows example calibration curves for vinylidene chloride, 1-pentanol and 1,3,5-trimethylbenzene.

### Repeatability

Repeatability was evaluated by analyzing 100 µg/mL laboratory control sample of the five replicated measurements.

The relative standard deviations (RSD) of the retention times and the relative responses were calculated (Table 1). The method showed good precision for most of the compounds, with %RSD values less than 7%.

## Recovery

The recovery of the method was obtained by sequential analysis of five tubes spiked with the same amount of a standard solution (100 µg/mL). The recovery for all target compounds are shown in Table 1, which ranged from 92% to 109%.

## Carryover

Figure 3 demonstrates the overlapped chromatograms for the high concentration standard (1000 µg/mL) and the subsequent blank sample. The second desorption of the same tube after analysis displays no carryover.

Moreover, the TDA has the cleaning function of the sorbent tube after desorption. Thus, the sorbent tube can immediately be used for the next sampling.

## Conclusion

A TDA instrument has been successfully used for the quantification of VOCs in air samples. The method showed good linearity, repeatability and no carryover.

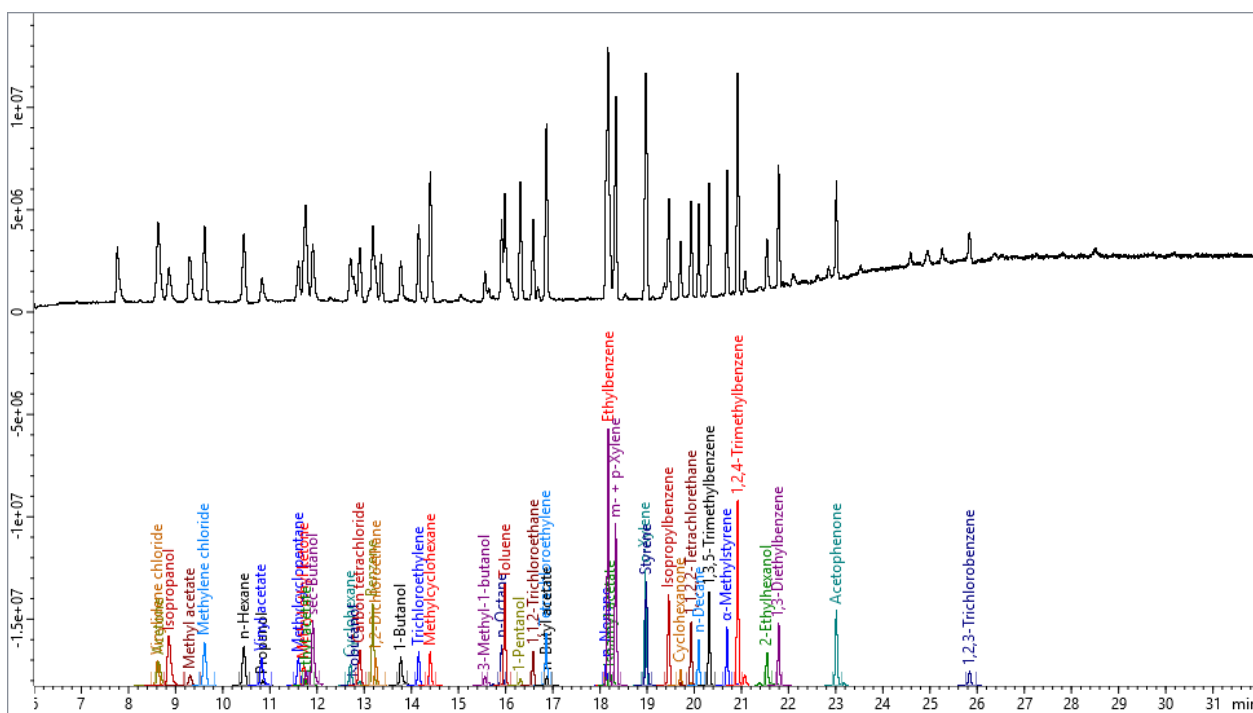


Figure 1 – t-SIM and Scan chromatograms of VOCs calibration solution, equal to 10 µg/m<sup>3</sup>

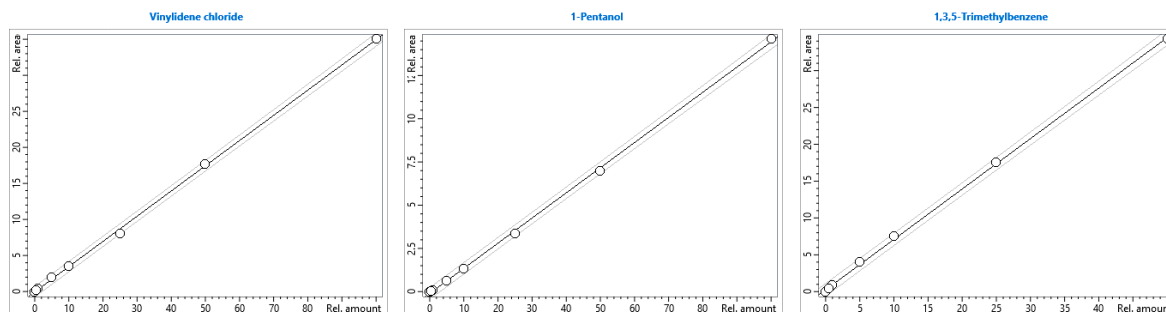


Figure 2 – Calibration curves for vinylidene chloride, 1-pentanol and 1,3,5-trimethylbenzene

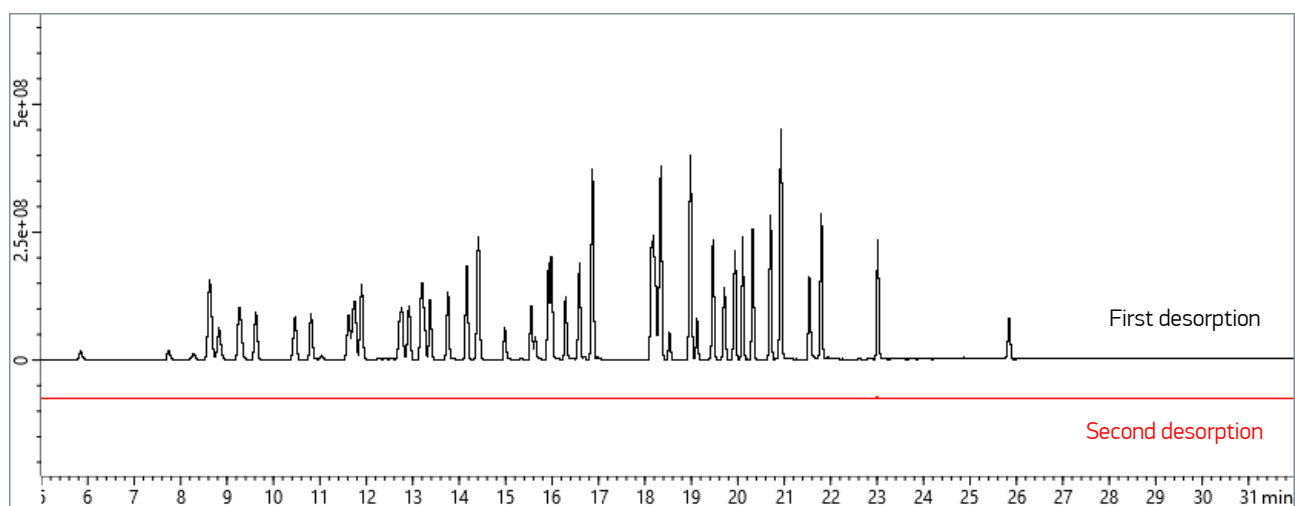


Figure 3 – Chromatograms of 1000 µg/mL standard and second desorption

Table 1. Retention Times, Quantifier Ions, Linearity, Repeatability of VOCs

No	Compound	RT, min	Quan ion	Calibration			Laboratory control sample (LCS), n = 5		
				Linear calibration range (LCR), ng	Linearity (R <sup>2</sup> )	RSD (RRF), %	RSD (RT), %	RSD (Response), %	Recovery, %
1	Vinylidene chloride	8.607	61	1 – 1000	0.9995	3.84	0.067	6.86	99
2	Acetone	8.623	58	1 – 1000	0.9990	4.68	0.061	5.73	109
3	Isopropanol	8.833	45	1 – 1000	0.9999	1.43	0.068	5.77	93
4	Methyl acetate	9.290	74	1 – 1000	0.9996	3.21	0.031	4.09	96
5	Methylene chloride	9.610	84	1 – 1000	0.9998	2.17	0.049	5.06	101
6	n-Hexane	10.451	57	1 – 1000	0.9997	2.30	0.042	5.21	103
7	Propanol	10.813	59	1 – 500	0.9998	1.86	0.055	4.25	99
8	Vinyl acetate	10.857	43	1 – 1000	0.9998	2.45	0.049	6.11	96
9	Methylcyclopentane	11.609	56	1 – 500	0.9998	2.53	0.052	1.74	94
10	Methyl ethyl ketone	11.714	72	1 – 1000	0.9994	3.62	0.040	4.94	99
11	Ethyl acetate	11.756	88	1 – 1000	0.9996	2.79	0.037	3.36	100
12	sec-Butanol	11.900	45	1 – 1000	0.9995	3.67	0.044	5.34	98
13	Cyclohexane	12.712	84	1 – 500	0.9995	4.37	0.035	6.64	105
14	Isobutanol	12.770	74	1 – 500	0.9996	3.40	0.050	4.48	100
15	Carbon tetrachloride	12.911	117	1 – 1000	0.9996	4.18	0.034	2.13	96
16	Benzene	13.179	78	1 – 1000	0.9993	4.33	0.028	5.29	97
17	1,2-Dichloroethane	13.237	62	1 – 1000	0.9993	4.36	0.033	5.06	101
18	n-Heptane	13.368	43	1 – 1000	0.9998	2.04	0.045	4.10	95
19	1-Butanol	13.775	56	1 – 1000	0.9996	3.18	0.044	3.44	96
20	Trichloroethylene	14.156	130	1 – 1000	0.9995	3.70	0.031	4.46	102
21	Methylcyclohexane	14.402	98	1 – 500	0.9997	3.49	0.016	1.13	96
22	3-Methyl-1-butanol	15.553	70	1 – 1000	0.9997	2.64	0.038	4.29	95
23	n-Octane	15.915	43	1 – 1000	0.9998	2.51	0.038	3.11	94
24	Toluene	15.983	91	1 – 1000	0.9995	3.70	0.028	2.70	105
25	1-Pentanol	16.298	70	1 – 1000	0.9994	3.92	0.037	3.48	96
26	1,1,2-Trichloroethane	16.582	97	1 – 1000	0.9996	3.60	0.036	2.40	99
27	Tetrachloroethylene	16.855	166	1 – 500	0.9996	2.93	0.035	2.76	105
28	n-Butyl acetate	16.876	73	1 – 1000	0.9995	3.70	0.035	3.28	97
29	n-Nonane	18.132	85	1 – 1000	0.9999	1.80	0.024	2.73	104
30	Ethylbenzene	18.174	91	1 – 500	0.9997	2.36	0.033	3.65	99
31	Isoamyl acetate	18.226	55	1 – 1000	0.9993	4.32	0.038	3.03	95
32	m- + p-Xylene	18.337	91	1 – 500	0.9990	5.61	0.043	2.24	92
33	o-Xylene	18.961	91	1 – 500	0.9990	5.26	0.032	3.06	95
34	Styrene	18.991	104	1 – 500	0.9996	2.91	0.030	2.83	96
35	Isopropylbenzene	19.455	105	1 – 500	0.9997	2.99	0.023	2.04	96
36	Cyclohexanone	19.714	98	1 – 500	0.9993	4.58	0.029	2.80	100

37	1,1,2,2-Tetrachlorethane	19.933	83	1 – 500	0.9998	2.50	0.024	2.36	92
38	n-Decane	20.101	57	1 – 1000	0.9996	3.30	0.030	2.01	95
39	1,3,5-Trimethylbenzene	20.321	105	1 – 500	0.9994	4.10	0.029	2.89	94
40	$\alpha$ -Methylstyrene	20.703	118	1 – 500	0.9998	2.31	0.029	1.31	102
41	1,2,4-Trimethylbenzene	20.922	105	1 – 500	0.9990	5.95	0.033	2.94	93
42	2-Ethylhexanol	21.544	57	1 – 1000	0.9996	3.56	0.032	1.99	92
43	1,3-Diethylbenzene	21.800	119	1 – 500	0.9996	3.46	0.021	4.53	98
44	Acetophenone	23.018	105	1 – 500	0.9993	4.02	0.019	1.91	95
45	1,2,3-Trichlorobenzene	25.842	180	1 – 1000	0.9998	2.07	0.018	2.85	96

