

Gas Chromatography/
Mass Spectrometry

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Analysis of 24 Polar and Non-Polar Volatile Organic Compound (VOCs) Emissions from Stationary Sources by ATD-GCMS

known photochemical reaction precursors which facilitate the production of tropospheric, or ground-level, ozone. Ground-level ozone can have significant impacts on human health, and contributes to climate change throughout the world. VOC emissions from stationary sources, such as ducts, stacks and exhaust funnels in factories, refineries and mines, have been identified as significant contributors to air pollution and ground-level ozone formation.

US EPA Method 325, Method 18 and TO-17 have been promulgated for the measurement of VOC concentrations using thermal desorption (TD) gas chromatography (GC), or TD-gas chromatography/mass spectrometry (GC/MS). In 2014, the Chinese government issued "stationary source emission standards," (HJ 734-2014) which standardized analytical method parameters utilizing TD-GC/MS and provided guidance on the calculation of results.

Introduction

Volatile organic compounds (VOCs) have been recognized as a primary source of air pollution, and are

In this paper, a qualitative and quantitative method for the analysis of 24 polar and nonpolar VOCs was established using a PerkinElmer TurboMatrix™ ATD and a PerkinElmer Clarus® GC/MS with electron ionization (EI) source. The method is simple, sensitive and efficient to comply with regulatory requirements.

Experimental

Sample Preparation

A mixture of 24 VOCs was purchased from o2si smart solutions. Chromatographic grade methanol (HPLC grade, Fisher Scientific) was used for all standard dilutions.

Instrument precision was investigated by spiking six tubes with a 5 µg/mL calibration standard. The tuning standard, 4-bromofluorobenzene (BFB), was prepared at 25 µg/mL for the EPA instrument-tuning check. Figure 1 demonstrates the passing BFB tune evaluation sample. Figure 2 shows the mass spectrum used in the Tune Evaluation Test.

Mass	Reference Mass	Relative Abundance	Criterion	Pass/Fail
COMBINE(304:306)(295:297)				
50	95	16.4%	>= 15% and <= 40%	Pass
75	95	46.8%	>= 30% and <= 80%	Pass
95	BPI	100%	= 100%	Pass
96	95	6.6%	>= 5% and <= 9%	Pass
173	174	0.5%	< 2%	Pass
174	95	80.2%	> 50% and < 100%	Pass
175	174	6.5%	>= 5% and <= 9%	Pass
176	174	97.9%	> 95% and < 101%	Pass
177	176	6.2%	>= 5% and <= 9%	Pass

Figure 1. TurboMass 6.0 EPA BFB tune evaluation results.

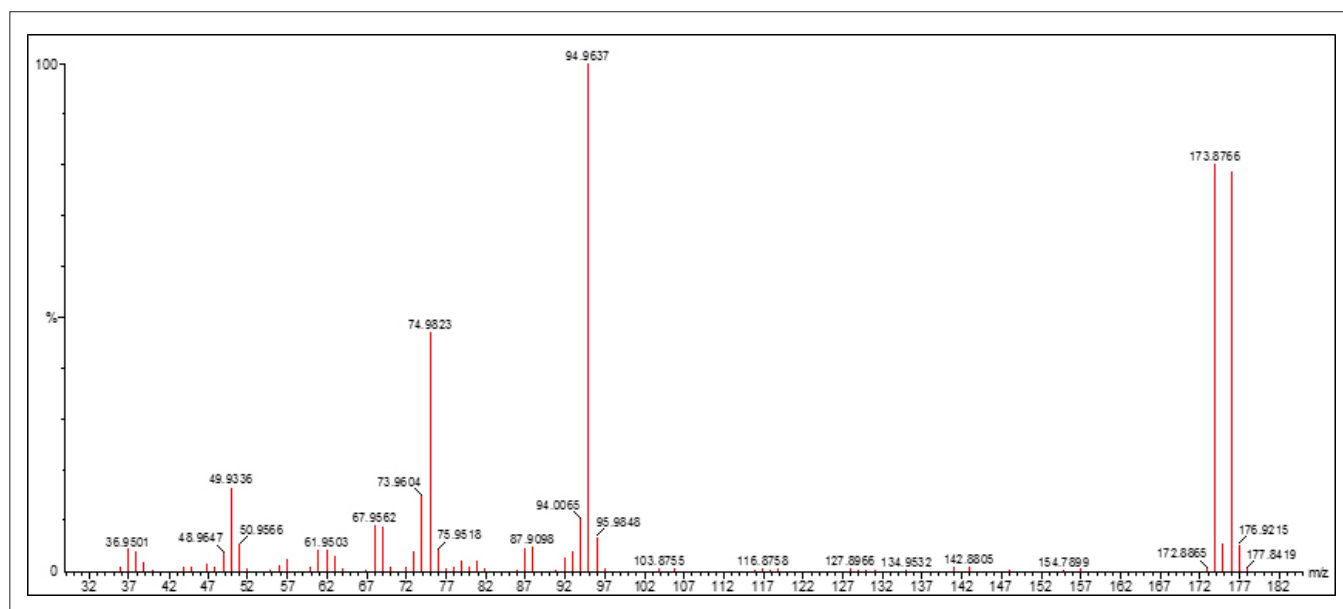


Figure 2. Mass spectrum of EPA BFB tune evaluation.

Instrumentation

A PerkinElmer Clarus GC/MS and TurboMatrix ATD were used to perform these experiments, with the conditions presented in Table 1. A PerkinElmer Elite-624 column (60 m x 0.32 mm x 1.8 µm) was used to separate the eluting compounds, and was directly connected to the thermal desorber transfer line.

Calibration

The mixture of 24 VOC compounds was diluted with chromatographic grade methanol to produce 5, 10, 20, 50, 100 µg/mL of calibration standards required for the experiments.

1 µL of calibration standards was introduced into the Carbotrap® 300 tubes to establish the calibration curve.

Table 1. Analytical parameters.

Thermal Desorber Parameters		GC Parameters	
Tube Desorb Temp	280 °C	Initial Oven Temp	40 °C
Tube Desorb Time	5 min	Oven Hold	2 min
Tube Desorb Flow	30 mL/min	Ramp	4 °C/min
Concentrator Trap Low	-10 °C	2 nd Oven Temp	160 °C
Concentrator Trap High	300 °C	Oven Hold	0 min
Concentrator Trap Hold	10 min	Ramp	15 °C/min
Concentrator Trap Heating Rate	40 °C/min	3 rd Oven Temp	200 °C
		Oven Hold	1 min
Valve Temp	250 °C	MS Parameters	
Transfer Line Temp	250 °C	Mass Range (amu)	33 to 300
Column Flow	2 mL/min	GC Inlet Line Temp	210 °C
Inlet Split	OFF	Ion Source Temp	180 °C
Outlet Split	2.0 mL/min	Function Type	SIFI
Dry Purge Flow Rate	50 mL/min	Ionization	EI
Dry Purge Time	1 min		

Results and Discussion

The total ion chromatogram of the calibration standard (Figure 3) shows baseline resolution of the selected compounds. Table 2 presents the analytical results for retention time (RT), quantitation ion, method dynamic range, precision, and signal to noise (S/N) at the reporting limit. The calibration curves were plotted as the peak area versus the amount of analyte. The determination coefficient

(r^2) was over 0.998, showing the reliability of the analysis in the range of 5 – 100 $\mu\text{g/mL}$. A calibration curve for toluene is shown in Figure 4. The precision data (RSD %) are in the range of 1.04 – 4.61%. The results for signal to noise at the reporting limit are calculated using extracted ion chromatograms by full scan function.

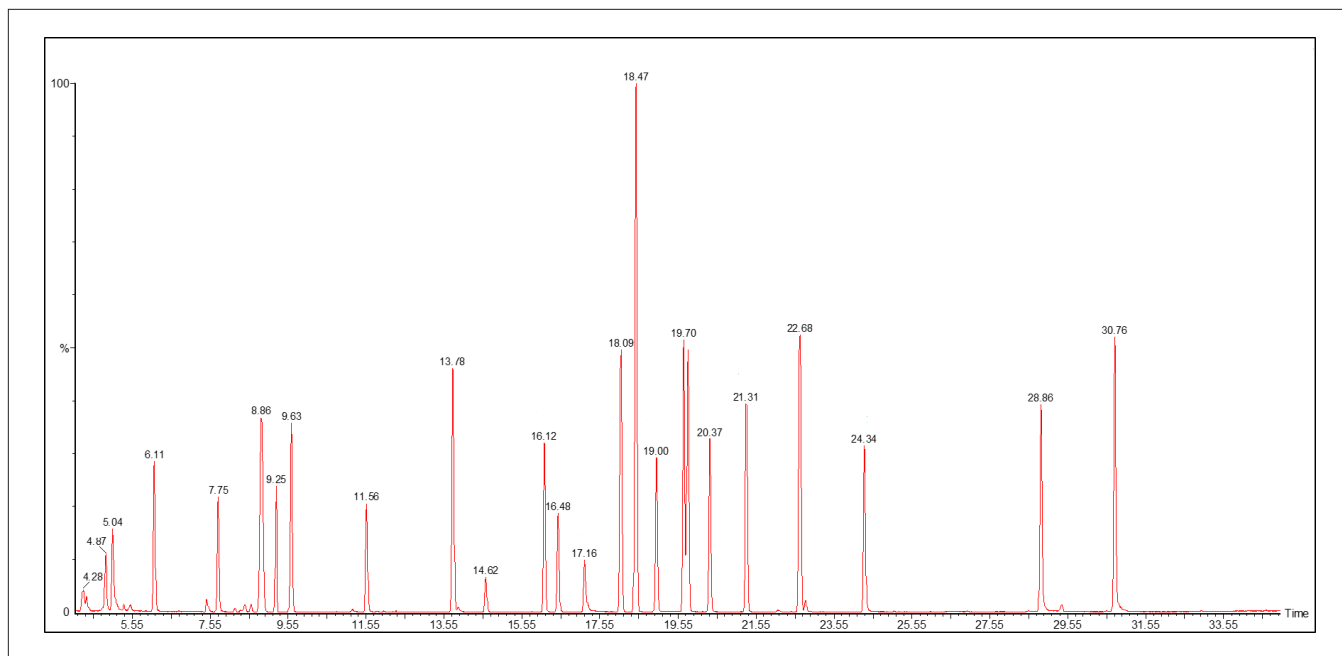


Figure 3. The total ion chromatogram of a 100 ng VOC standard desorbed from an ATD tube.

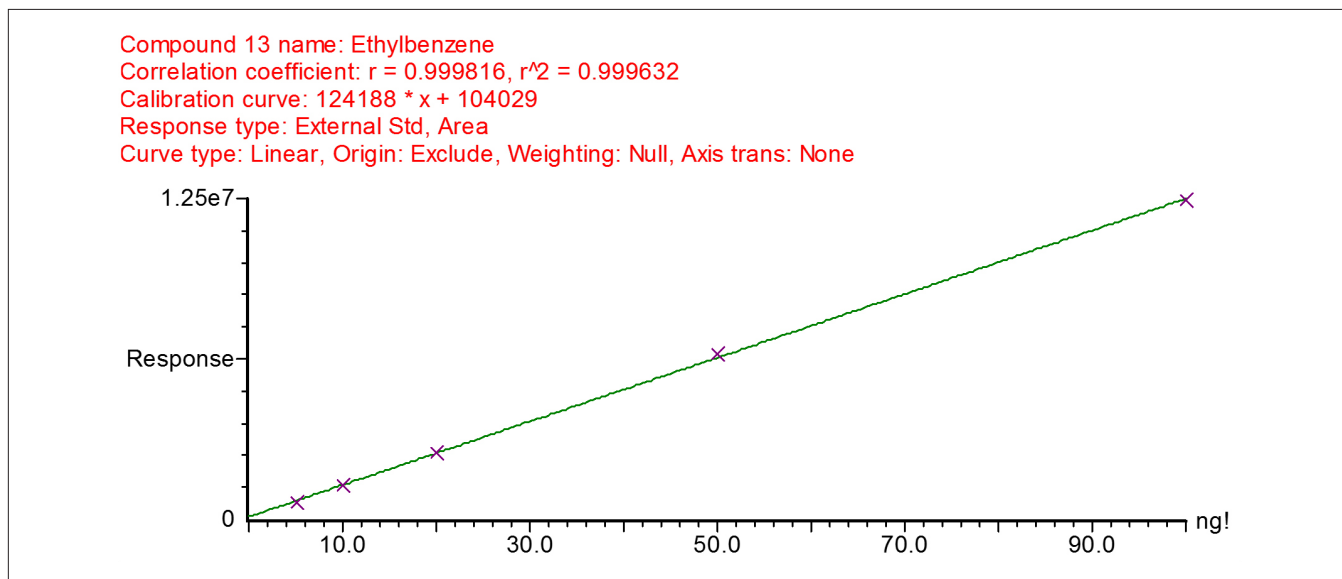


Figure 4. Calibration curve for ethylbenzene (5-100 ng).

Table 2. Results for retention time (RT), quantitation ion, method dynamic range, precision and signal to noise (S/N) at the reporting limit.

RT	Compound Name	Quantitation Ion	Linearity (5 – 100 ng)			Precision	Reporting Limit
			Slope	Intercept	r ²	RSD%	(S/N at 5 ng)
4.87	Acetone	58	16535	68421	0.9990	4.24	205
5.04	Isopropanol	45	71809	-16802	0.9997	3.40	387
6.11	Hexane	57	42577	127998	0.9994	1.86	64
7.75	Ethyl acetate	43	509	532	0.9994	2.09	76
8.86	Hexamethyldisiloxane	147	193406	90141.8	0.9996	1.27	1330
9.25	Benzene	78	122916	264450	0.9997	2.48	518
9.63	Heptane	43	49505	4750	0.9999	1.04	75
11.56	3-Pentanone	57	75813	195380	0.9993	2.05	96
13.78	Toluene	91	111996	129168	0.9996	1.40	1058
16.12	Butyl acetate	43	74244	-107117	0.9995	2.08	126
16.48	Cyclopentanone	55	47220	89362	0.9986	1.52	36
17.16	Ethyl lactate	45	217442	-2.044	0.9983	2.58	18
18.09	Ethyl benzene	63	124188	104029	0.9996	1.85	1549
18.47	p-Xylene	91	196777	155337	0.9997	1.86	1583
18.47	m-Xylene	91	196777	155337	0.9997	1.86	1583
19.00	PGEA	43	73720	-144654	0.9998	1.31	100
19.70	o-Xylene	91	102341	45085	0.9997	2.01	945
19.81	Styrene	104	81608	-7779	0.9998	1.45	1202
20.37	2-Heptanone	43	79890	-137705	0.9996	1.25	109
21.31	Anisole	108	57002	13556	0.9994	1.67	921
22.68	1-Decene	41	31208	-63958	0.9992	1.35	56
24.34	Benzaldehyde	106	37043	-38466	0.9989	4.61	846
28.86	2-Nonanone	58	70652	-24647	0.9990	2.00	692
30.76	1-Dodecene	69	30312	9985	0.9997	2.38	52

Summary

The analysis of 24 volatile organic compound emissions from stationary sources is easily achievable using a PerkinElmer TurboMatrix ATD and Clarus GC/MS system. Satisfactory analytical results exceed method criteria, even for regions with the most challenging regulatory reporting limits.