

Simultaneous Evaluation of Odor Episodes and Air Quality in Urban Areas by Multi-Sorbent Sampling and TD-GC/MS Analysis

Contributed Article

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Odor Episodes and Air Quality

Odor episodes and environmental air quality are topics of worldwide concern, mainly due to industrial facilities in the vicinity of inhabited areas. Several atmospheric pollutants, mainly volatile organic compounds (VOC), are responsible for odor episodes of varying degrees of annoyance. Interest in determining VOC both in indoor and outdoor air has increased over the last several decades, as they are known precursors of photochemical smog formation as well as can cause short- and long-term adverse health effects (irritation of mucous membranes, psychological stress and long-term toxic reactions) and discomfort (bad odors). Generally, specific atmospheric pollutants are established and measured chemically in real-time outdoors and indoors. Indoor air quality (residential, commercial, office and public buildings) would depend mainly on the emissions from sources like building materials and appliances, consumer products, tobacco smoke and intake of outdoor air.

Multi-Sorbent Bed Adsorbent Tubes

A validated analytical method, based on thermal desorption (TD) coupled to gas chromatography (GC) and mass spectrometry (MS), is used for air-quality measurements of volatile organic compounds in indoor and outdoor air, including alkanes, aromatic hydrocarbons, aldehydes, alcohols, chlorides, esters, ketones, terpenes, amides, carbon disulfide and isocyanates (Table 1, Figure 1). Sorbent materials with a wide range of properties (surface and pores structure) are commercially available both for industrial/occupational and environmental applications (1, 2, 3). For air quality determination and pollution control a good combination of different sorbents (2) allows us the qualitative and quantitative determinations of a wide range of C2-C14 VOCs, around 200-300 compounds present in a standard urban sample. A multi-sorbent tube filled with carbon blacks Carbotrap™ (20/40 mesh, weak sorption strength, 70 mg) and Carboxen™ X (40/60 mesh, medium sorption strength, 100 mg) as well as Carboxen™ 569 (spherical carbon molecular sieve, 20/45 mesh, high sorption strength, 90 mg) (Supelco, Bellefonte, PA, USA) has been selected (4). Adsorbents are placed in glass tubes arranged from weak to strong sorption strength (sampling direction, desorption in reverse). Air quality criteria can be applied to the chemical compounds concentrations obtained with the presented methodology.

Sampling

VOC are dynamically sampled connecting custom packed glass multi-sorbent cartridge tubes (Carbotrap, Carboxen X and Carboxen 569) to an air collector pump sampler specially designed

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Figure 1. GC chromatogram for stock standard solution. Correspondent VOC reference numbers are listed in Table 1

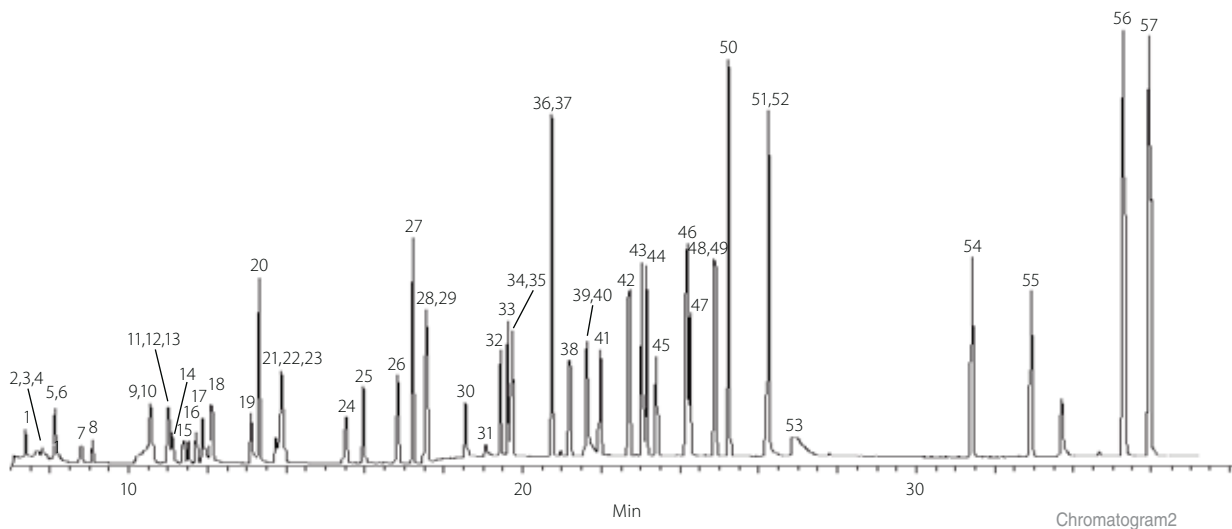


Table 1. Method target VOC analytes, retention time (RT, min) and quantification ions m/z 1 (low concentration range) and m/z 2 (high concentration range)

Target VOCs	VOC Ref. No.	RT (min)	Quantification Ions	
			m/z 1	m/z 2
Ethanol	1	7.4	45	46
Propanal	2	7.5	58	58
Acetone	3	7.56	43	44
Carbon disulfide	4	7.84	76 [▲]	76
Methyl acetate	5	8.14	74 [▲]	74
Isopropanol	6	8.16	45	59
Tert-butylmethylether	7	8.81	73	57
n-Hexane	8	9.11	57	86
Butanal	9	10.16	44	72
Ethyl acetate	10	10.48	61	88
Chloroform	11	11.02	83	87
Methylethylketone	12	11.12	72	57
Tetrahydrofuran	13	11.12	42	72
1,1,1-Trichloroethane	14	11.42	97	117
Cyclohexane	15	11.54	56	84
Carbon tetrachloride	16	11.74	117	121
Isobutanol	17	11.9	43	74
Benzene	18	12.12	78	51
1-Butanol	19	13.11	56	31
Trichloroethylene	20	13.13	130	134
Methylcyclohexane	21	13.77	55	98
Pentanal	22	13.78	44	86
Methyl methacrylate	23	13.83	100 [▲]	100
Methylisobutylketone	24	15.53	43	100
Toluene	25	15.97	92	65
1,1,2-Trichloroethane	26	16.83	166	168
Tetrachloroethylene	27	17.22	166	168
Butyl acetate	28	17.55	73 [▲]	73

▲ Compound with only one characteristic quantification ion

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in the LCMA-UPC laboratory (Figure 2). The operating flow ranges between 40 and 200 mL/min. Samples can be taken dynamically during 24-hour controls or during odor episodes. By means of remote control (both radio frequency and mobile phone), the air sampler can be activated during odor episodes when medium and high odor intensity and nuisance is percept (5).

Analytical Instrumentation

The analysis of VOC is performed by Thermal Desorption GC/MS. Mass spectral data are acquired over a mass range of 20-300 amu (Table 2). Qualitative identification of target compounds is based on the match of the retention times and the ion ratios of the target quantification ions and the qualifier ions (Table 1).

Quantification of field samples is conducted by the external standard method. Limits of detection (LOD), determined applying a signal-to-noise ratio of 3, range from 0.001 to 10 ng. The studied compounds show repeatabilities (% relative standard deviation values) $\leq 25\%$, accomplishing the EPA performance criteria (6). Extreme precautions are established for quality assurance, injecting periodically blank samples and a known concentration of toluene (4).

Target VOCs	VOC Ref. No.	RT (min)	Quantification Ions	
			m/z 1	m/z 2
Hexanal	29	17.59	44	72
N,N-Dimethylformamide	30	18.56	73	58
N-Methylformamide	31	19.06	59	30
Ethylbenzene	32	19.45	106	65
n-Nonane	33	19.63	57	128
m-Xylene	34	19.73	106	77
p-Xylene	35	19.73	106	77
o-Xylene	36	20.75	91 [▲]	91
Styrene	37	20.75	104 [▲]	104
Heptanal	38	21.2	44	86
2-Butoxyethanol	39	21.64	57	87
α -Pinene	40	21.65	93	136
Cyclohexanone	41	21.97	98	83
Propylbenzene	42	22.71	91	120
n-Decane	43	23.04	71	142
1,3,5-Trimethylbenzene	44	23.15	105	120
β -Pinene	45	23.4	93	136
1,2,4-Trimethylbenzene	46	24.16	105	120
Benzaldehyde	47	24.25	77	106
Isocyanatocyclohexane	48	24.88	82	125
Limonene	49	24.88	93	136
p-Dichlorobenzene	50	25.24	140	75
n-Undecane	51	26.22	57	156
Phenol	52	26.32	94	66
1-Octanol	53	26.88	41	84
Naphthalene	54	31.4	128	102
Isothiocyantocyclohexane	55	32.9	55	141
2-Methylnaphthalene	56	35.34	142	115
1-Methylnaphthalene	57	35.9	142	115

Table 2. Instrument Settings and TD-GC/MS Operating Conditions

TD	TD
Desorption Temp.: 300 °C	Capillary Column: DB-624 (60 m x 0.25 mm x 1.4 μ m)
Desorption Time: 10 min	Temperature Program: 40 °C (1 min), 6 °C min ⁻¹ until 230 °C (5 min)
Transfer Line: 200 °C	Carrier Gas: He (19.1 psi)
Cold Trap Sorbent: Tenax + Carbotrap	
Cold Trap Low: -30 °C	MS
Cold Trap High: 300 °C	Interface: 250 °C
Desorption Flow Rate: He (50 mL min ⁻¹)	Ionization Source: 200 °C
Inlet Split: 4 mL min ⁻¹	Ionization mode: Electron impact
Outlet Split: 7 mL min ⁻¹	Electron Energy: 70 eV
Split Ratio: 12%	Mass Range: 20-300 amu



Figure 2. Collector pump sampler



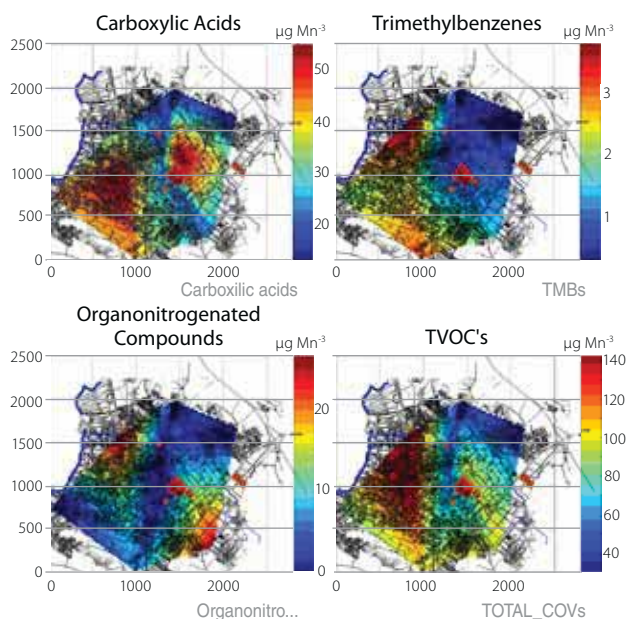
Collector Pump

Outdoor Air Applications

Outdoors, a sampling system can be used in situations involving permanent and discontinuous odor episodes in air, either in urban, industrial, waste treatment facilities or rural areas. A thorough analysis of the meteorological conditions in the area during the sampling period in combination with the chemical information obtained through the individual VOC determination and an inspection of the activities on the site allow an irrefutable tracking of the permanent odor sources and to generate a list of potential odor episodic sources.

To exemplify the results obtained from chemical control (VOC concentrations, both 24-hour average and maximum episodic values), interpolated concentration maps are represented in a study area (Figure 3). Those maps are important tools for determining the origin of VOC emissions in a concrete study area, showing focuses with higher concentrations.

Figure 3. Concentration maps of three families of compounds and TVOC in Banyoles city (Catalonia, Spain).



Indoor Air Applications

Most indoor air pollution originates from sources inside the building, such as adhesives, carpeting, wood products or cleaning products. However, the outdoor air that enters the building through e.g. air intake vents and windows can also be a source of indoor air VOC pollution. Examples are pollutants from motor vehicle exhausts, plumbing vents, building exhausts (kitchen and bathroom exhausts) and combustion products from a nearby garage. It has to be noted that VOC have been generally less studied than other indoor air contaminants, even though their concentrations have been described to contribute to the Sick Building Syndrome (SBS).

To exemplify the methodology, a characterisation of the indoor air quality of a dwelling where occupants experienced symptoms that resembled the SBS symptoms was done in May-July 2006 in Barcelona city. It was observed that there was indoor air pollution by several major compounds including ethanol, acetone, acetic acid and 1-methoxy-2-propanol, which altered the VOC family distributions expected for a standard dwelling. The external source of VOC was found to be a not declared activity of storage and manipulation of solvents located at the bottom of a contiguous building (7).

Conclusions

The presented methodology can identify in outdoor air the compounds that cause odor episodes as well as their sources. A real inventory of all potential emitting activities can be obtained, including not only nearby emitters but also sources that are several kilometres away. Air quality criteria can be applied to the chemical compound concentrations obtained with the presented methodology.

In indoor air, the methodology has been demonstrated to be useful in an urban dwelling. It has been observed that people repetitively exposed long-term to relatively high levels of VOC can modulate their physiological response to a given compound. Legislated guideline recommendations should be established. In the interim period, VOC indoor concentrations should be maintained as low as reasonably achievable (ALARA) (8).

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