

Determining indoor air quality and identifying the origin of odour episodes in indoor environments

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Abstract

A methodology for identifying volatile organic compounds (VOCs) and determining air quality of indoor air has been developed. The air samples are collected using pump samplers by the inhabitants when they perceive odorous and/or discomfort episodes. Glass multi-sorbent tubes are connected to the pump samplers for the retention of VOC. The analysis is performed by automatic thermal desorption (ATD) coupled with gas chromatography-mass spectrometry (GC/MS). This methodology can be applied in cases of sick building syndrome (SBS) evaluation, in which building occupants experience a series of varied symptoms that appear to be linked to time spent in the building. Chemical pollutants concentrations (e.g., VOC) have been described to contribute to SBS. To exemplify the methodology, a qualitative determination and an evaluation of existing VOC were performed in a dwelling where the occupants experienced the SBS symptoms. Higher total VOC (TVOC) levels were detected during episodes in indoor air ($1.33 \pm 1.53 \text{ mg/m}^3$) compared to outdoor air ($0.71 \pm 0.46 \text{ mg/m}^3$). The concentrations of individual VOCs, such as ethanol, acetone, isopropanol, 1-butanol, acetic acid, acetonitrile and 1-methoxy-2-propanol, were also higher than the expected for a standard dwelling. The external source of VOC was found to be an undeclared activity of storage and manipulation of solvents located at the bottom of a contiguous building.

Key words: indoor air; thermal desorption; TVOC; VOC; sick building syndrome

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Introduction

Most indoor air pollution comes from sources inside the building, such as adhesives, carpeting, wood products or cleaning products, which may emit volatile organic compounds (VOCs) (Knöppel and Schauenburg, 1989; Salthammer, 1997; Hodgson *et al.*, 2000; Jensen *et al.*, 2001; Zhang and Xu, 2002). However, the outdoor air that enters the building can also be the main source of indoor air VOC pollution (EC, 1989, 1997; Mølhave, 1991, 1999; Weschler and Shields, 2000; Zuraimi *et al.*, 2003; Weisel *et al.*, 2005). Therefore, if an appropriate ventilation rate with good quality outdoor air is applied to the dwelling, VOC concentration could be maintained in an acceptable level (Holcomb and Seabrook, 1995; Weschler and Shields, 2000; Zuraimi *et al.*, 2003). If adequate ventilation is applied and VOC values continue high, probably strong local sources of these compounds are located inside or near the building (Weschler *et al.*, 1990).

The knowledge of the adverse effects on health associated to indoor air VOC is limited (Johansson, 1999; Edwards *et al.*, 2001; Venn *et al.*, 2003), compared to outdoor contamination (Jones, 1999). Several human exposure

studies have been carried out (Otto *et al.*, 1990; Mølhave, 1991; Wolkoff, 1995; Andersson *et al.*, 1997; Pappas *et al.*, 2000; Mølhave, 2001); however, the extrapolation between the results obtained and the real effects of indoor air VOC concentration is difficult (Holcomb and Seabrook, 1995; Wolkoff *et al.*, 1997). On the other hand, a various sampling strategies and total VOC (TVOC) concentration calculation methods used in the literature make data not comparable (Mølhave, 1992; EC, 1997; Mølhave *et al.*, 1997; Wolkoff *et al.*, 1997; Johansson, 1999). The European Commission (EC, 1997) and the international standard ISO 16000-6 defined the TVOC sampling and analysis procedures, focusing in the main indoor VOC families. TVOC has been recommended as a screening tool, due to that it does not have biological relevance, and is not recommended for making definitive conclusions about indoor air quality (Andersson *et al.*, 1997). However, it has some useful applications as an indicator of the presence of VOC indoors (Mølhave, 1992, 2000, 2003; Wolkoff and Nielsen, 2001).

The VOC indoor concentrations relate to the sick building syndrome (SBS). The cause of SBS is probably multifactorial and it is not usually accompanied by any organic lesion or physical sign, and generally is diagnosed by exclusion (EC, 1989). Some factors have been described

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to contribute to SBS, such as outdoor and indoor chemical contaminants (e.g., VOC) (WHO, 1982, 1986; EC, 1989).

The aim of this study was to establish a methodology to evaluate external VOC sources that contribute to indoor environments pollution. To exemplify the methodology, a characterisation of the indoor air quality of a dwelling where occupants experienced symptoms that resembled the SBS symptoms was determined. A mild neutropenia was observed in one of the inhabitants of the dwelling in the period 2005–2006, with absolute neutrophil counts (ANC) ranging from 1306 to 1319 cells/mm³. Before occupants started the complaints, in year 1998, ANC was 2540 cells/mm³ of this inhabitant. Neutropenia is a decrease in circulating neutrophils in the peripheral blood, and abnormal ANC values are below 1500 cells/mm³. The neutropenia can be caused by exposition to drugs and chemicals, such as industrial solvents (Williams *et al.*, 1977).

Nineteen samples were taken during a 3-month period to evaluate whether the VOC concentrations were higher than the expected for a standard dwelling, and to identify the possible sources and factors.

1 Materials and methods

1.1 Chemicals and materials

The VOC standards were purchased as commercial neat chemicals from Aldrich (Milwaukee, USA), Merck (Darmstadt, Germany) and Fluka (Buchs, Switzerland), with purity of not less than 98%. Perkin Elmer glass tubes (Pyrex, 6 mm external diameter, 90 mm in length), unsilanised wool and Carbotrap (20/40 mesh), Carbopack X (40/60 mesh) and Carboxen-569 (20/45 mesh) adsorbents were obtained from Supelco (Bellefonte, USA).

1.2 Sampling

Custom packed glass multi-sorbent cartridge tubes (Carbotrap 20/40, 70 mg; Carbopack X 40/60, 100 mg, and Carboxen-569 20/45, 90 mg) have been optimized for the retention of VOC in air samples (Ribes *et al.*, 2007). The tube cartridges are connected to remote-controlled specially-designed LCMA-UPC pump samplers (90–120 mL/min) equipped with inert sampling line and high precision total volume measurement (Roca, 2006).

The evaluation of VOC in three sampling phase were designed. The type of VOC present in indoor air was determined in first phase (24 h). The second control phase was based on integrated odour episodes sampling in several points of the dwelling. The odour episodes were sampled and characterised and the episodic concentrations of VOC were determined when medium or high odour intensity was percept by the inhabitants. In the third and last phase VOCs were from 8 a.m. to 14 p.m.

A minimization of sampling costs is achieved with this control program, as the samples are collected in the moment of the occurrence of odorous episodes, diminishes the number of samples necessary to obtain reliable data.

1.3 Analytical instrument

Analysis of VOC was performed by automatic thermal desorption (ATD) coupled with capillary gas chromatography-mass spectrometry detector (GC-MS), using a Perkin Elmer ATD 400 (Perkin Elmer, USA) and a thermo quest trace 2000 GC (ThermoQuest, USA) fitted with a thermo quest trace Finnigan MS according to Ribes *et al.* (2007). Mass spectral data are acquired over a mass range of 20–300 amu. A 6-min solvent delay time is applied for standards analysis to avoid saturation of mass spectrometer detector.

Qualitative identification of VOC is based on the match of the retention times and the ion ratios of the target quantification ions and the qualifier ions (Xcalibur 1.2).

Extreme precautions have been established for quality assurance, injecting periodically blank samples and a known concentration of toluene.

1.4 Total VOC calculation

TVOC is calculated following the recommended method by European Union (EC, 1997) and Mølhave *et al.* (1997). The main and more toxic compounds which were detected in our study and the minimum number of compounds were quantified individually. The rest of compounds were quantified by the response factor of toluene. The summation of all that values was the TVOC value.

1.5 Case study

VOC were dynamically sampled during a 3-month period (May to July, 2006) in several locations of a dwelling. The 24-h, episodes and 6-h samples were taken. When the episodes occurred, the occupants started to feel sick, basically due to the irritation of their mucous membranes and eyes, and headache and difficulty to concentrate were accentuated. The episodes were quite variable, from 5 min to 2–3 h during 10 a.m. to 14 p.m. and 16 p.m. to 21 p.m. The dwelling is located in the first floor of a 6-floor building in a moderate population density district with medium traffic flow in Barcelona. The flat size is 120 m², where one bedroom, one bathroom and the dinning room have street external windows (Fig. 1). Inside exhausts ventilate the kitchen and the other bathroom, and 3 bedrooms are ventilated through an inside patio. The flat is not provided with air conditioning and ventilates through open doors and windows. However, ventilation rates were considered being adequate and indoor air was assumed being well mixed. The dwelling has not been decorated within the previous 7 years and did not contain newly purchased furniture during the air sampling. Two people (non smokers) and a cat live in the flat.

Six sampling points were distributed among the dwelling near the VOC potential emission sources (Fig. 1). Only air sampled in F came from street. Air sampled in A and D came from interior patios, although it is considered as outdoor air, probably present higher VOC concentrations than in the street.

Eight 24-h samples, eight episode samples, and three 6-h samples were taken during the experimental period,

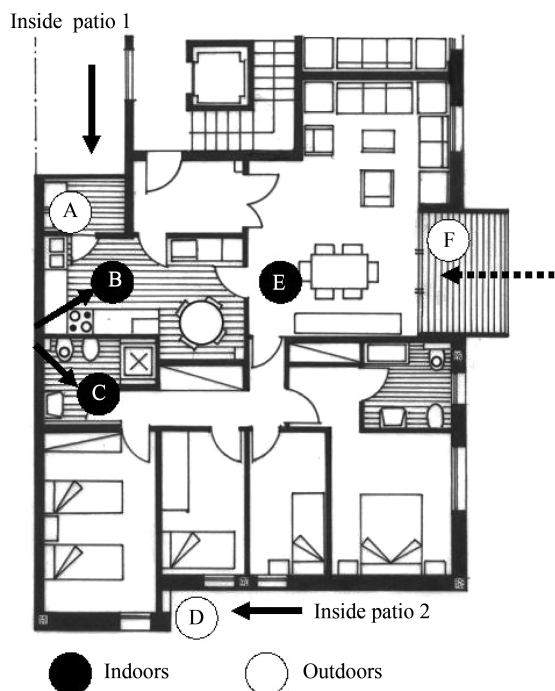


Fig. 1 Potential emission sources (black arrows) and sampling points in the dwelling. A: inside patio 1 (outdoor), where three exhausts (the building water, gas and electricity cupboards ventilation exhausts) coming from downstairs were located at 20 cm from the pavement; B: kitchen exhaust; C: bathroom exhaust; D: inside patio 2 (outdoor); E: dining room; F: terrace (outdoor).

with sampling volume range 112–146, 17–96, and 36–58 L, respectively. The outdoor meteorological conditions were similar during the sampling in the three different phases. The temperature, humidity, and pressure was in the range of 21–28°C, 47%–65% and 1015–1022 hPa, respectively. Therefore, indoor VOC concentrations should not be influenced by external factors.

2 Results and discussion

2.1 Individual compound

One hundred and thirteen VOC have been identified qualitatively. A 40% of these compounds had already

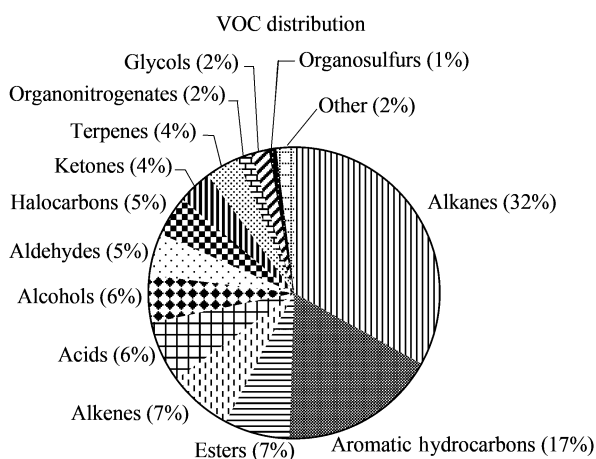


Fig. 2 VOC families distribution for all compounds identified qualitatively. Percentage of compounds of each family in respect to all compounds identified.

been identified as major indoor air VOC (Holcomb and Seabrook, 1995). Alkanes, aromatic hydrocarbons, esters, alkenes, carboxylic acids and alcohols are the main compounds in the majority of samples (Fig. 2), where alkanes and aromatic hydrocarbons contribute a half. The 24-h, 6-h, and episode samples show similar compound distributions; however, concentrations of dichloromethane, toluene, DL-limonene, *m* + *p*-xylenes and NN-dimethylformamide are higher in 24-h control samples.

Ethanol, acetone, isopropanol, 1-methoxy-2-propanol, 1-butanol, acetic acid, *p*-dichlorobenzene, toluene, *m* + *p*-xylenes and acetonitrile are the main compounds in all samples. For 24-h samples, the concentrations were in the range of 30–98, 32–63, 11–46, 28–147, and 62–139 $\mu\text{g}/\text{m}^3$ for ethanol, acetone, isopropanol, toluene and acetic acid, respectively (Table 1). As it was expected, in episode samples the values are higher, ranging between 49–2787, 41–142, 19–125, 14–95, and 19–211 $\mu\text{g}/\text{m}^3$ for ethanol, acetone, acetic acid, 1-butanol and 1-methoxy-2-propanol, respectively (Table 1).

In non-industrial established buildings the concentrations of individual VOC are usually below 5 $\mu\text{g}/\text{m}^3$, with only a few compounds exceeding 50 $\mu\text{g}/\text{m}^3$, such as *m* + *p*-xylenes, toluene, DL-limonene, acetone, and ethanol (Brown *et al.*, 1994; Johansson, 1999). In contrast, in this study the concentration of isopropanol, 1-butanol, acetonitrile and 1-methoxy-2-propanol was higher than 50 $\mu\text{g}/\text{m}^3$ and has a maximum value 2786.97 $\mu\text{g}/\text{m}^3$ in the case of ethanol (Table 1). Those compounds are not expected to be detected in such high concentration in a dwelling, as their release is not originated by the common sources of VOC in indoor air homes (Jones, 1999), like cleaning products, floor waxes, paints or vehicle exhausts (Weschler *et al.*, 1990).

The rest of compounds including mainly aromatic hydrocarbons, halocarbons, alkanes and terpenes were detected in the same concentration range for all sampling points, and in the same order of magnitude of other indoor air carried out in USA, the Netherlands, U.K., Canada, Germany, Finland, Korea, and Hong Kong (Hartwell *et al.*, 1984; Gupta *et al.*, 1984; Lebreton *et al.*, 1986; Pellizzari *et al.*, 1986; Krause *et al.*, 1987; Wallace *et al.*, 1987; Montgomery and Kalman, 1989; Chan *et al.*, 1990; Proctor *et al.*, 1991; Holcomb and Seabrook, 1995; Koistainen, 1995; Baek *et al.*, 1995; Lee *et al.*, 2002; Guo *et al.*, 2004). Therefore, the general distribution of VOC in indoor air is the standard for an established dwelling.

Indoor air samples show a similar VOC composition to outdoor air samples, as outdoor air is an important source of indoor air pollution, and usually reflects indoors (Johansson, 1999). For outdoor air, ethanol, 1-methoxy-2-propanol and 1-butanol concentrations were in the order of $A > D > F$, where the concentrations in A were 6 to 18 times more than in the street outdoor air (F). The concentrations were higher in the interior patios, probably due to a less mixing and diffusive activities. In indoors, because of the lack of ventilation point C (bathroom), has the highest concentrations of the above-mentioned

Table 1 Individual VOC concentration ($\mu\text{g}/\text{m}^3$) in the quantified samples

Sample	24-h sample		Ep								6-h sample		
	A1–A4	C1–C4	A5	C5	D1	BE1	D2	BE2	BE3	D3	D4	BE4	F1
Alkanes													
<i>n</i> -Hexane	2.47–13.06	0.99–7.59	2.65	4.20	1.15	1.06	1.07	1.12	0.84	1.18	3.00	0.77	0.58
<i>n</i> -Heptane	5.53–11.76	1.80–26.24	3.44	3.60	2.70	3.71	2.20	5.95	1.85	3.38	8.59	2.20	1.73
<i>n</i> -Octane	2.91–3.69	1.06–2.96	1.48	1.51	0.83	1.29	0.90	1.09	0.67	0.78	0.76	0.63	0.41
<i>n</i> -Nonane	0.28–15.14	0.27–4.18	11.63	8.01	3.51	7.45	3.38	2.78	3.78	3.10	2.60	3.67	1.54
<i>n</i> -Decane	7.23–20.30	1.74–9.05	6.60	2.98	n.d.	4.59	1.95	1.50	2.54	2.02	4.27	2.23	0.79
<i>n</i> -Undecane	1.18–1.70	0.53–1.93	1.82	1.07	0.36	1.08	1.23	0.75	2.01	1.40	0.54	1.17	0.14
<i>n</i> -Dodecane	2.40–7.75	0.82–6.24	n.d.	n.d.	0.16	0.50	0.81	0.57	1.88	1.29	0.29	0.98	n.d.
2-Methylpentane	< loq	< loq	< loq	< loq	< loq	< loq	< loq	< loq	< loq	< loq	< loq	< loq	< loq
3-Methylpentane	3.50–4.32	1.01–8.45	1.96	2.27	1.06	0.62	1.00	1.25	0.81	1.24	3.96	0.95	0.81
<i>n</i> -Tridecane	0.30–2.72	0.92–2.65	2.18	2.09	0.62	1.88	0.96	0.60	1.08	0.62	0.32	0.84	n.d.
<i>n</i> -Tetradecane	0.29–1.27	0.88–1.48	2.46	1.83	0.23	0.87	0.75	0.39	0.39	0.43	0.35	0.65	n.d.
<i>n</i> -Pentadecane	0.48–15.82	0.37–4.77	12.37	4.08	2.42	4.22	3.63	2.13	4.00	2.11	1.66	1.93	0.57
<i>n</i> -Hexadecane	2.48–5.23	1.18–2.32	5.74	2.34	0.75	1.73	1.65	0.82	1.91	1.09	0.64	0.78	n.d.
Cyclohexane	0.81–3.59	0.34–1.90	0.65	0.70	0.40	0.28	0.40	0.58	0.30	0.45	1.28	0.54	0.37
Methylcyclohexane	1.58–3.30	0.79–2.52	0.94	1.18	0.66	0.72	0.63	0.75	0.70	0.70	1.19	0.63	0.41
Alcohols													
Ethanol	38.28–79.53	29.54–98.30	622.39	2786.97	49.24	75.95	149.59	101.91	94.68	89.83	286.95	443.72	106.88
Isopropanol	30.66–46.06	11.29–31.02	15.94	17.89	33.26	8.15	6.98	35.07	54.71	5.43	259.96	75.72	28.77
1-Butanol	14.67–24.17	27.95–55.60	42.79	95.23	15.29	35.80	50.13	22.60	20.52	14.20	12.40	31.47	7.19
3-Ethyl-1-hexanol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Glycols													
2-Methoxyethanol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1-Methoxy-2-propanol	18.22–59.91	8.53–19.22	210.48	134.80	22.47	30.37	36.01	18.75	41.59	28.93	36.70	378.47	11.79
2-Ethoxyethanol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2-Butoxyethanol	1.38–60.83	0.66–21.34	n.d.	0.79	0.85	2.20	1.58	0.72	1.07	0.70	n.d.	n.d.	n.d.
2-Butoxyethoxyethanol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Aldehydes													
Butanal	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Pentanal	5.36–11.16	5.05–12.32	3.60	5.78	2.03	3.43	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Hexanal	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Heptanal	1.82–2.91	2.02–2.50	2.32	2.50	0.88	3.06	1.50	0.78	1.57	0.87	0.47	1.59	0.30
<i>n</i> -Nonanal	2.82–5.13	7.01–13.34	19.18	19.66	1.54	12.45	12.27	4.95	11.13	8.47	2.95	8.50	0.66
Benzaldehyde	0.81–14.35	3.05–13.13	8.35	5.16	3.92	2.14	1.52	5.78	2.11	4.28	3.71	1.43	2.62
Formaldehyde	–	–	–	–	–	–	–	–	–	–	94.90	108.20	8.10
Ketons													
Acetone	31.76–62.51	36.04–58.92	86.93	69.23	70.95	94.65	85.24	141.75	66.00	41.13	114.10	132.48	116.97
Methyl ethyl ketone	2.98–12.40	1.09–5.38	2.59	3.42	0.82	0.80	n.d.	n.d.	2.93	4.29	9.58	3.23	1.57
Cyclohexanone	0.53–1.37	0.37–0.46	0.47	0.43	0.17	0.28	0.26	0.14	0.26	0.15	n.d.	n.d.	n.d.
Methyl isobutyl ketone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Acetophenone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Halocarbons													
Dichloromethane	4.95–19.79	12.52–21.40	3.53	8.63	0.98	2.45	2.22	0.91	2.12	1.48	3.25	16.15	0.52
Chloroform	16.81–15.28	0.72–1.40	3.94	3.18	0.24	0.41	0.30	0.27	0.30	0.32	0.66	0.18	0.19
Trichloroethylene	1.67–9.46	1.43–8.96	1.12	2.23	0.51	0.76	0.45	0.38	1.18	1.98	2.00	0.37	0.56
Tetrachloroethylene	2.33–13.12	3.78–9.75	1.33	2.90	1.49	1.99	2.08	1.84	1.73	2.13	2.16	1.38	0.97
<i>p</i> -Dichlorobenzene	1.37–2.52	16.08–48.22	2.30	20.15	13.65	23.72	15.76	4.62	16.46	11.38	1.07	8.27	0.24
Trichloronitromethane	0.29–2.76	0.61–1.78	1.47	1.49	2.92	3.65	1.99	0.28	0.62	1.03	4.23	1.56	1.67
1,1,1-Trichloroethane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Esters													
Methyl acetate	2.99–5.25	1.54–4.14	1.15	1.58	15.63	0.72	0.89	0.73	0.81	1.23	13.40	23.75	8.47
Ethyl acetate	14.10–36.05	3.94–11.72	9.97	14.97	2.56	3.28	6.39	3.77	2.94	3.70	6.61	2.71	1.52
Butyl acetate	13.30–24.47	6.75–24.78	15.03	11.75	1.75	3.21	5.23	3.51	5.29	5.84	1.86	2.57	0.80
iso-Propylacetate	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2-Ethoxyethyl acetate	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Texanol iso-butyrate	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Aromatic hydrocarbons													
Benzene	8.71–27.7	3.77–10.36	2.61	3.85	2.52	1.65	1.50	2.09	1.02	1.74	2.83	0.54	0.49
Toluene	41.90–147.29	27.85–130.55	29.54	32.61	22.49	21.47	25.52	50.95	20.01	33.36	33.20	24.44	14.40
Ethylbenzene	8.00–23.78	3.68–5.01	6.17	8.85	3.39	2.79	3.41	4.90	4.65	6.44	3.52	2.09	1.84
<i>m</i> + <i>p</i> -Xylene	30.08–40.63	10.04–30.45	9.36	12.76	13.88	4.58	7.20	15.45	10.03	15.96	8.07	4.12	3.47
Styrene	1.55–3.27	0.32–1.40	0.70	0.76	0.39	0.28	0.22	0.28	1.00	1.23	0.74	0.79	0.50
1,2,4-Trimethylbenzene	13.06–15.49	1.40–17.10	4.22	2.93	2.99	2.62	2.43	3.68	3.05	3.22	2.17	2.13	1.39
<i>m</i> -Ethyltoluene	3.98–11.26	0.86–4.00	2.19	1.66	1.27	1.12	1.21	1.75	1.51	1.81	1.09	1.05	0.72
1,3,5-Trimethylbenzene	2.28–5.17	0.70–2.82	1.88	1.51	1.07	1.06	1.14	1.94	n.d.	0.93	0.66	0.47	0.36
<i>n</i> -Propylbenzene	0.02–0.03	0.01–0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02
Naphtalene	0.03–0.08	0.03–0.05	0.05	0.04	0.04	0.03	0.03	0.04	0.04	0.04	0.03	0.04	0.01

Table 1 continued

Tetrahydrofuran	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2-Pentylfuran	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
<i>o</i> -Ethyltoluene	1.38–2.99	0.30–1.41	1.00	0.63	0.39	0.49	0.44	0.55	0.57	0.59	0.33	0.41	0.24
<i>p</i> -Ethyltoluene	0.42–2.42	0.67–1.07	0.49	0.68	0.40	0.64	0.46	0.40	0.77	0.72	0.28	0.40	0.13
Acids													
Acetic acid	62.11–114.20	64.47–138.99	91.45	124.67	59.91	43.30	22.86	19.25	42.89	83.47	69.81	207.84	38.09
Pentanoic acid	5.28–7.01	3.24–9.58	n.d.	n.d.	n.d.	11.28	n.d.	n.d.	n.d.	n.d.	1.04	4.85	0.87
Hexanoic acid	9.71–12.83	7.77–24.96	n.d.	n.d.	1.83	23.40	15.75	4.39	25.16	4.20	1.94	14.61	2.05
Octanoic acid	n.d.–49.75	n.d.–29.47	n.d.	n.d.	0.60	n.d.	n.d.	n.d.	38.81	n.d.	n.d.	2.58	n.d.
Terpenes													
α -Pinene	6.15–15.20	5.36–8.74	4.39	7.34	1.48	2.80	2.16	1.41	2.62	1.75	0.37	1.63	0.12
DL-Limonene	30.28–32.52	3.46–9.90	8.31	20.87	1.12	3.30	2.58	1.67	3.11	1.43	0.50	6.04	0.23
β -Pinene	0.57–1.72	1.81–2.02	1.69	4.96	1.04	2.07	1.52	0.91	2.05	1.32	0.67	6.22	0.21
3-Carene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Amides													
<i>N,N</i> -Dimethylformamide	14.15–37.40	n.d.–0.22	2.6	n.d.	n.d.	11.74	7.24	n.d.	13.32	n.d.	n.d.	n.d.	n.d.
Organosulfurs													
Carbon disulfide	0.49–2.10	0.77–2.14	0.82	1.46	2.22	0.44	1.5	2.01	28.79	10.54	76.91	23.35	15.22
Organonitrogenates													
Acetonitrile	0.20–0.33	0.07–0.47	0.45	1.23	0.27	0.05	0.05	0.07	0.36	0.26	4.34	397.38	21.51
Σ other	55.62–97.38	40.54–101.66	122.62	160.16	43.86	65.08	60.89	71.87	53.61	48.62	155.42	52.21	44.06
TVOCs	534.5–1269.2	329.8–1078.4	1399.4	3631.6	427.2	539.7	559.1	552.7	604.2	464.8	1250.3	2012.9	453.1

Ep: episodes; n.d.: not detected; < loq: below limit of quantification; –: not determined; Σ other: remaining compounds identified and quantified by the response factor of toluene; TVOCs: total volatile organic compounds.

compounds, followed by points B and E (Table 1), where the concentrations were in the range of a standard dwelling (Holcomb and Seabrook, 1995).

The ethanol indoor/outdoor ratio was in the range 5–19 in respect to the interior patios for point C, and 26 in respect to point F. Similar ratios were observed for 1-methoxy-2-propanol and 1-butanol. These high indoor/outdoor ratios indicated that there were also indoor building sources that influence the dwelling air quality, as the street outdoor air concentrations cannot contribute significantly even with many openings and inadequate ventilation rates. However, the interior patios could contribute, as their air concentrations are much higher than the street outdoor air. The known activities around the dwelling neither explained the presence of these concrete VOC nor their quite high concentrations. The possible sources probably came from industrial processes developed in the nearness of the studied flat, and entering the dwelling through the interior patios and the kitchen and bathroom exhausts.

An exhaustive revision of the activities realized in the adjacent buildings of the studied dwelling, conducted by the environmental municipality services and the police, allowed the finding of a no declared manipulation and storage facility of industrial solvents. However, a monitoring in this facility was not possible as an investigation was being conducted. One year later (December, 2007), a monitoring was done in the studied dwelling, showing lower levels of the most important VOC detected in the first sampling period and the total absence of acetonitrile.

The main health effects linked to human exposure to ethanol, 1-methoxy-2-propanol, 1-butanol and acetonitrile through inhalation are sore throat, cough, respiratory system irritation, eye redness, headache, poor concentration capacity and nausea (International Chemical Safety Cards (WHO/IPCS/ILO)). These symptoms coincide with the suffered by the dwelling inhabitants. On the other hand,

several of the determined compounds are harmful, irritant, and toxic and may cause sensitization or even cancer, as their associated R-phrases show (Tables 2 and 4).

In addition, 1-butanol, 2-butoxyethanol, *n*-hexadecane, and pentanoic acid concentrations have been always detected above the odour threshold concentration. Other compounds such as benzaldehyde, ethylbenzene and hexanoic acid only overpass the concentration odour threshold in 24-h samples.

2.2 Total volatile organic compounds

Higher TVOC values were detected in episodes (540–3632 $\mu\text{g}/\text{m}^3$) and 6-h samples (2013 $\mu\text{g}/\text{m}^3$) in indoor air than in terrace and interior patios outdoor air (427–1399 $\mu\text{g}/\text{m}^3$) (Table 1). TVOC values found in European standard dwellings in several studies ranged from 40 to 1050 $\mu\text{g}/\text{m}^3$ (Bornehag and Stridh, 2000). In addition to this, Seifert (1990) estimated a target indoor air quality guideline value based on two empirical field studies in German and Dutch homes (WHO, 1989; Lebrete *et al.*, 1986; Krause *et al.*, 1987; Seifert and Abraham, 1982), suggesting that TVOC concentrations in indoor air should

Table 2 Distribution of compounds with R-phrases associated

R-phrases	Percentage (%)
R-67: Vapours may cause drowsiness and dizziness	23
R-38: Irritating to skin	14
R-65: Harmful: may cause lung damage if swallowed	13
R-36: Irritating to eyes	9
R-66: Repeated exposure may cause skin dryness or cracking	6
R-20: Harmful by inhalation	5
R-40: Possible risk of cancer	5
R-22: Harmful if swallowed	4
R-62: Possible risk of impaired fertility	3
R-63: Possible risk of harm to the unborn child	3
Other R-phrases	12

Table 3 Distribution of compounds with combined R-phrases associated

Combined R-phrases	Percentage (%)
R36/38: Irritating to eyes and skin	25
R20/21: Harmful by inhalation and in contact with skin	15
R48/20: Harmful: danger of serious damage to health by prolonged exposure through inhalation	15
R36/37: Irritating to eyes and respiratory system	10
R20/21/22: Harmful by inhalation, in contact with skin and if swallowed	10
R36/37/38: Irritating to eyes, respiratory system and skin	5
R37/38: Irritating to respiratory system and skin	5
R48/23/24/25: Toxic: danger of serious damage to health by prolonged exposure through inhalation, in contact with skin and if swallowed	5
R48/23: Toxic: danger of serious damage to health by prolonged exposure through inhalation	5
R48/20/22: Harmful: danger of serious damage to health by prolonged exposure through inhalation and if swallowed	5

not exceed 300 µg/m³. Generally, TVOC calculated values do not include very volatile organic compounds (0°C < boiling point < 50°C), and only include the range of compounds obtained in the analytical window between hexane and hexadecane on a non-polar column (ISO 16000-6). In these cases, compounds such as ethanol and acetone are not included in the TVOC value. However, as in the present study these compounds do have been included, and all indoor samples analysed overtake the previously mentioned guideline value, indicating that these compounds are responsible the high concentrations found indoors. Excluding ethanol and acetone, the TVOC value would be in the range of an European standard dwelling. In addition, Møhlhave (1991) suggested four exposure ranges of TVOC: comfort range (< 0.2 mg/m³), multifactorial exposure range (0.2–3 mg/m³), discomfort range (3–25 mg/m³) and toxic range (> 25 mg/m³). In this study, the occupants of the dwelling are in a multifactorial exposure range, where they can suffer mucous and skin irritation and general discomfort.

3 Conclusions

It can be concluded that there was an indoor pollution, coming from several major compounds including mainly ethanol, acetone, acetic acid and 1-methoxy-2-propanol, that alters the VOC family distributions expected for a standard dwelling (Seifert, 1990). These compounds are used as solvents in a wide range of industrial activities. The chemical analysis method used, the results obtained in this study and the comparison of values previously determined in worldwide dwellings not affected by external industrial activities, have shown that the origin of VOC indoor concentrations was external.

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