

STUDY OF INDOOR EXPOSURE FROM A LABORATORY DEDICATED TO THE ANALYSIS OF DIOXINS

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Introduction

Adverse health effects associated with exposure to volatile organic compounds (VOCs) have been well documented in the scientific literature and public organizations¹. PCDDs/Fs analysis requires the use of volatile solvents, implying high airborne VOCs concentrations. It is necessary to ensure that people working at these labs are not exposed to high levels of these compounds.

The objectives of this paper are measurement, analysis and quantification of VOCs at a lab dedicated to the analysis of PCDDs/Fs at the University of Alicante, and the comparison of the measured concentrations with TLV-TWA values as a way of knowing whether lab workers are exposed to health risks. Passive samplers were chosen to carry out the sampling.

Materials and methods

This study was carried out at the Chemical Engineering Department of the University of Alicante. Measurements were conducted in two different campaigns (September 2010 and January 2011) of 30 days each. Indoor air samples were simultaneously collected at three different sites: a PCDDs/Fs analysis laboratory, a research room and an office. The research room is located a few meters from the laboratory, and connected with it, while the office is far from lab. Workers attending laboratory may be exposed to higher VOCs levels compared to those who work at a research room or an office, which is associated with paper and computer work.

Passive samplers were placed in representative locations, far away from windows, doors, sources of potential pollutants and approximately 1.5 m above the floor^{2,3}. All sites were naturally ventilated. Two passive samplers were placed at each location to take measures in duplicate. Blank passive samplers were analyzed to check any device contamination, as well as solvent extractor blank. Solvents commonly used at the laboratory were listed to make the search of them during the analysis easier.

Radiello® air diffusive passive samplers developed by Fondazione Salvatore Maugeri⁴ (Padova, Italy) were chosen for the assessment of VOCs concentrations during the campaigns. These devices are suitable for indoor and outdoor air monitoring and workplace air control. The Radiello® consists of two essential parts: the adsorbing cartridge (code 130) containing 530±30 mg of activated charcoal with particle size 35-50 mesh; and a diffusive body, a cylindrical outer surface acting as a diffusive membrane (code 120). Volatile organic compounds are trapped by adsorption and recovered by carbon disulfide displacement. Analysis was performed by gas chromatography-mass spectrometry (GC-MS).

Prior to chromatography analysis, each sample extraction was placed directly in the Radiello® glass tube (supplied by the device) with 2 ml of CS₂ (Ref. 342270 Sigma-Aldrich). Two internal standards were used: 5 µl of toluene-d₈ (Ref. 48593 Sigma-Aldrich) and 5 µl of 4-bromofluorobenzene (Ref. 48083 Sigma Aldrich) in methanol, both with concentration of 2000 µl·ml⁻¹. It was decided to use these two different standards to cover the whole range of appearance of compounds during the chromatography. Several tests were carried out using hexadecane as a solvent extractor, in order to obtain the most volatile organic compounds and to compare the concentration deduced from the CS₂ solvent. No light compounds were detected in the first part of the chromatogram (peaks occluded by the solvent when using CS₂).

GC-MS analysis was conducted after desorption. The equipment used for eluents analysis was a gas chromatograph (Agilent Technologies 7890A) with split/splitless injector coupled with an inert mass spectrometer (Agilent 5975C). The column used was SPBTM-1 SULFUR (30 m x 0.32 mm x 4 µm). Chromatograph parameters were as follows: the carrier gas was helium at 1 ml·min⁻¹ constant flow; volume

injection 1 µl; splitless; inlet temperature 250 °C; Oven program: 35 °C for 5 min, 5 °C·min⁻¹ up to 90 °C and isotherm for 3 min; 10 °C·min⁻¹ up to 220 °C and isotherm for 5 min. Mass parameters were as follows: ionization source at 250 °C; mass quadrupole analyzer at 150°C and SCAN acquisition (m/z 35-200). The mass detector was switched off from 2.90 min to 5 min since this is the interval during which CS₂ eluted.

Results and discussion:

It is well known that VOCs measured indoors are a result of both indoor and outdoor sources⁵. The main outdoor sources are automobile exhaust or store fuels and environmental compounds, while indoor sources are related to building materials, cleaning products, air fresheners, furnishing, paints or tobacco smoke^{3,6}.

Up to 98 different VOCs have been identified and quantified during the campaigns carried out at the three sites selected for the research at the university: alcohols, terpenes, esters and hydrocarbons. However, only target VOCs (solvents used at the laboratory) results presented here. Table 1 shows the concentration of VOCs measured at three sites, considering both campaigns. Fick's first law was used to calculate concentrations, and temperature dependence was taken into account with the diffusion coefficient. This table also shows TLV-TWA values and the classification of the compounds detected according to HAPs⁸ and IARC¹. Elution tendencies were studied according to boiling point (subscript *a*, *b* or *c* have been used). Compounds have also been classified by a *Comparison Factor (CF)* to provide a glimpse of the precision of compound identification. The higher the *CF*, the more accurate the identification is.

Table 1. Solvents detected at different sites assessed

COVs concentration (µg/Nm ³)												
	Compound		Laboratory		Office		Research Room		TLV-TWA	IARC	HAPs	
September 2010	Ethanol	b	0.01	d	---	0.01	d	2053571	Gr.1			September, 2010
	Acetone	c	2.60	f	2.60	e	2.50	e	1941964			
	Dichloromethane	a	0.27	d	0.02	f	0.07	d	187500	Gr.2B	x	
	Hexane	a	5.80	e	0.16	e	1.40	d	383929		x	
	Cyclohexane	a	0.26	d	0.02	d	0.12	g	1125000			
	Toluene	a	2.90	d	0.10	d	0.88	d	205357	Gr.3	x	
	Nonane	a	0.06	d	0.003	e	0.01	d	1142857			
January, 2011	Ethanol	b	0.01	e	0.005	e	0.002	e	2053571	Gr.1		January, 2011
	Acetone	c	0.29	d	---	0.09	d	1941964				
	Dichloromethane	a	0.19	d	0.003	f	0.01	e	187500	Gr.2B	x	
	Hexane	a	1.70	d	0.03	e	0.41	d	383929		x	
	Cyclohexane	a	0.03	d	0.004	e	0.01	d	1125000			
	Toluene	a	3.90	d	0.07	d	0.94	d	205357	Gr.3	x	
	Nonane	a	0.06	e	0.11	e	0.05	d	1142857			
Boiling point tendency:							Comparison factor (CF):					
a: General tendency b: Alcohol tendency c: No Tendency							d: CF > 900 e: 800 < CF < 900					
--- Concentration under the limit of detection							f: 700 < CF < 800 g: CF < 700					

As expected, results show that target solvent concentrations are higher at the laboratory than at the research room and office. The fact that the research room is close to the lab makes that higher concentrations are measured than at the office.

Although acetone is used at the laboratory, the fact that concentrations are almost constant at the three different places (2.602, 2.550 and 2.544 $\mu\text{g}\cdot\text{Nm}^3$ at laboratory, office and research room respectively), suggests that environmental factors may be blame. Ethanol has a behavior similar to acetone, with concentrations nearly constant at the three locations. This could be due to the presence of ethanol in several cleaning products⁶. Hexane (5.84 and 1.73 $\mu\text{g}\cdot\text{Nm}^3$) and toluene (2.85 and 3.90 $\mu\text{g}\cdot\text{Nm}^3$) are the main solvents present at the lab air during September and January campaigns, respectively. Apart from ethanol and acetone, all compounds measured at the research room follow the same tendency as the laboratory. Hexane and toluene are the highest concentrations as well. This may be due to interzonal air flow indoor⁵ amongst the lab and the research room.

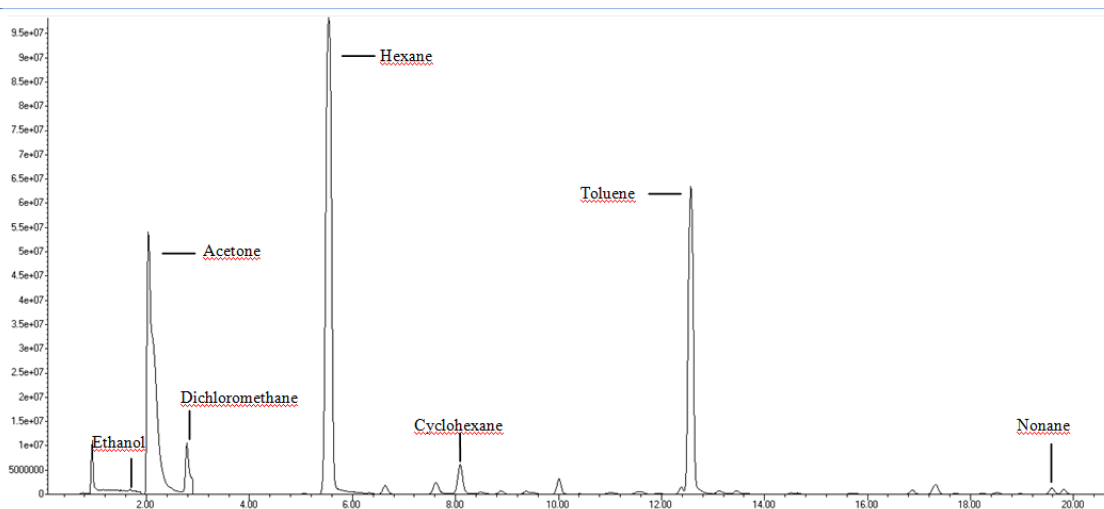


Figure1. Chromatogram obtained for laboratory during September 2010

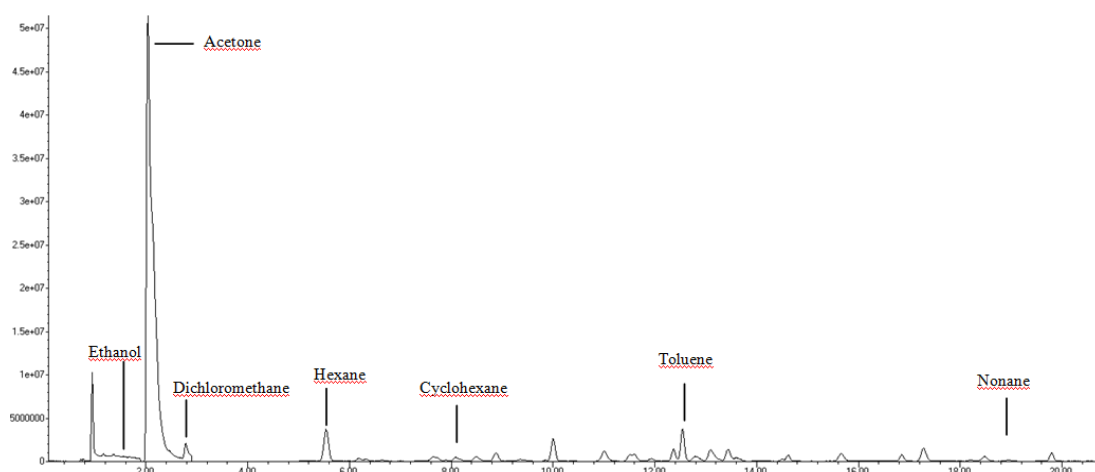


Figure2. Chromatogram obtained for office during September 2010

The office site, which is far from the lab, has the lowest concentrations measured at the three different sites. This site can be considered as a blank indoor ambient sample, demonstration in Figure 1 and 2. It can be observed that although almost the same compounds are detected at both sites, VOCs concentrations are higher at the laboratory.

If results are compared with other studies, VOCs concentrations are lower than measurements carried out at others laboratories⁹. On one hand, the laboratory assessed has natural ventilation, and on the other hand it has fume hoods where lab workers develop their activity (passive samplers have been placed far from these fume hoods). Lower concentrations can be mainly attributed not only to suitable use of the facilities by workers, but also to equipments working properly. All compounds, at three assessment sites, are at concentrations far from TLV-TWA values, what means that it is not a health hazard working at any of these places.

For the rest of compounds (98 different compounds were identified and quantified), concentrations were similar for the three sites. It can be suggested that for these compound outdoor sources are the main contribution. Some difference can be appreciated. For instance, limonene is detected at all sites; however, concentration levels are higher at the office ($10.9 \mu\text{g}\cdot\text{Nm}^3$) than at the lab ($0.05 \mu\text{g}\cdot\text{Nm}^3$) or at the research room ($0.15 \mu\text{g}\cdot\text{Nm}^3$). The main source of limonene at the office is believed to be resultant from floor wax or lemon fresh spray⁶.

The relationship between boiling point and retention time has also been studied, although results are not shown in this paper. To those compounds which lead *General Tendency*, the higher their boiling point is, the higher the retention time is. Ethanol and acetone do not follow this tendency.

This study was conducted in order to ensure that personal working at the Chemical Engineering Department exposed to VOCs are not at risk. It was confirmed that for certain COVs associated with laboratory products, the personnel exposure is higher for those who work at the lab than for who at the office. Nevertheless, concentration levels are below legal limits.

Acknowledgements:

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