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Indoor Air Quality - Volatile Organic Compounds: Sources, Sampling and Analysis

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1. Introduction

Since the 70s, research has found in Europe and in the United States that individuals spend between 70 and 90% of their time indoors. Health studies have found that exposures to a variety of air pollutants indoors can be substantially higher than outdoors, even in urban environment. Volatile Organic Compounds (VOCs) are often considered among the more important indoor pollutants, because of by their continue emission from many sources and their diffusion properties. With the aim to evaluate the occupants' discomfort and health effects and in order to develop guidelines and standards, Indoor Air Quality (IAQ) assessment and control is an essential step. IAQ assessment will complain:

- Sources: Identification and characterization of sources, as emissions from materials, products or activities, is best done under laboratory conditions; so it is possible measuring rates of emissions (especially chemicals such as VOCs). Exposure characterization is the second level of source identification; after the measurement of contaminants' concentrations in controlled environment, characterised by known sources, adsorbing and absorbing surfaces, these data can be used in validation of current exposure models.
- Sampling methods: In order to determine concentrations of VOCs and exposures of building occupants via inhalation, field studies can be carried out by sampling methods (and analysis) in accordance with existing official methods (EC, NIOSH, OSHA, ACGIH, etc.). This way may be expensive and cumbersome; in addition, it can be not exhaustive in predicting the discomfort and health impact. A greater number of perspectives are offered by using some "descriptors" that can be more adequate in characterizing anthropogenic pollution. Specific sampling methods may be reserved for contaminants with specific toxic effects (e.g., formaldehyde, benzene, monomers, etc.). Measurements of specific contaminants' can be necessary for sources that cause high room concentrations for relatively short periods (e.g., in case of freshly applied coatings on walls, etc.). Currently, diffusion (passive) samplers are mainly used in order to evaluate long term exposures (days to weeks and more)
- Analysis and data meaning: existing analytical methods are validated and generally show adequate limits of detection (LODs) and limits of quantification (LOQs) even in measuring subtoxic contaminants' concentrations. Analytical methods for the more

frequent indoor contaminants are presented and commented. More difficulties lie in the interpretation of results, due to the limited indications suggested by European and International Standards (such as EN, EN ISO, etc.) that will be discussed. The difficulty in data evaluation is growing depending on the simultaneous occurrence of contaminants at subtoxic concentration.

In this chapter, there will be presented the way to handle the problem in IAQ assessment, and some practical applications, in order to provide the logical pathway to face the majority of actual cases.

2. Indoor air quality and VOCs

Research on pollutant sources is needed to identify pollutants and emission levels from building materials and other products. Work in this area will serve two purposes: (1) providing measurement protocols and data to employ in exposure reduction actions, and (2) providing correlations between research on health effects and pollutant sources of contaminant critical levels. Finally, research is required to determine definition, causes of, and solutions to multiple chemical sensitivity (MCS). Identifying the physiologic nature of MCS is the first step in understanding whether and how IAQ eventually contributes to the syndrome. Maroni et al. (1995) recommended the following definitions that should be used in the description of indoor related complaints and illnesses:

- Building-Related Environmental Complaints (BREC): Complaints of poor IAQ or poor indoor air environment. BREC are usually registered in the complaint (annoyance) part of questionnaire studies.
- Building-Related Symptoms (BRS) or Building Related Health Complaints (BRC): The health complaints (subjective symptoms) reported by the single individual as occurring inside a building and usually subsiding shortly after leaving it.
- Sick Building Syndrome (SBS): denotes a situation where a significant number of the occupants of a building complain of a typical group of general, unspecific, and irritating symptoms, including particularly headache, lethargy, dry eyes, blocked nose, and sore throat. The symptoms usually fade after the person has left the indoor environment but the specific cause is unidentified.
- Building-Related Illness (BRI): clinical condition with defined symptoms and signs in which the cause (aetiology) is building-related and identifiable.

The difference between BRI and SBS is that the building problems are identified in the former and undiagnosed in the latter. The term "sick building" probably should not be used on its own, but it might be replaced with the expression "building with indoor climate problems" or "problem building."

VOCs are often more important in assessing IAQ because of their ubiquity; VOCs may be used like "descriptors" that can be more adequate in characterizing anthropogenic pollution. Specific sampling methods may be reserved for contaminants with specific toxic effects (e.g., formaldehyde, benzene, monomers, etc.). In many cases, investigations of the indoor air are carried out because of complaints about poor IAQ, which are made by persons living or working indoors. Such complaints may be perception of unknown or unpleasant odours, headache, irritation of the eyes, nose and throat, dryness of the skin or symptoms like tiredness, lack of concentration and unspecific hypersensitivity reactions. Investigations resulting from observed or suspected health problems of occupants are quite similar and require the same sampling strategy.

3. Sources

Identification of indoor pollutant sources may be very important; emission from point (or surface) sources generates a pronounced concentration gradient near the source. The existence of such concentration gradients can be used to trace the source in an indoor environment by a careful selection of sampling sites. This strategy can lead to recommendations on how to improve indoor air quality, e.g. removing identified materials and strong emitters.

Maroni et al (1995) proposed these recommendations concerning source control:

Material Selection

- Manufacturers should be required to provide sufficient information for the evaluation of their products' safety. Protection of legitimate confidentiality must not impede evaluation.
- Standardization and harmonization of emission testing procedures must continue at international level. Meanwhile, research and application of different techniques and methodological intercomparison should be encouraged.
- Labelling of products and their ranking for safety and emission properties should be encouraged to facilitate appropriate selection and use by consumers. The choice of process may vary according to the nature of the risk involved and the local priorities.

Biological Contaminants

- The growth of moulds and other microorganisms in the indoor environment should be avoided. This can be achieved effectively by elimination of moisture.
- Good housekeeping and sanitation rather than the use of biocides are appropriate control measures also for mites.

Volatile Organic Compounds (VOCs)

- Overall exposure to VOCs should be kept at the lowest possible level primarily by proper control of the emission sources.
- Pending improved methods, the total volatile organic compounds concept is a useful tool for practical assessment of the overall quality of materials and of indoor air. However, at least the type of major VOC species must be known.
- More research is recommended for the sensory effects of VOC mixtures and for some individual compounds typically present in indoor air mixtures for which little toxicological knowledge is available; this recommendation is strongly current, due to the growing interest in persistent organic pollutants (POPs) as endocrine disruptors, also in classic subtoxic concentrations.

4. Sampling methods

The primary objective of taking indoor air is to determine the quality of indoor air with the aim of assessing any risk to the health of the population and of individuals due to indoor air pollution. Monitoring is useful also in testing effectiveness of remedial actions, such as modifications to a building, its systems or equipment, aimed at reducing indoor air pollution. The measurements for testing their effectiveness are comparison measurements before and after the remedial actions. It is also important to record intermediate and long-

term trends of indoor air pollution concentration. Respective analysis of trends will help to maintain, improve and establish abatement or risk management procedures. Finally, beside screening measurements, it can be very helpful to evaluate indoor air concentrations at abnormal or "worst-case" conditions of the indoor climate (temperature, humidity, ventilation etc.) and during particular activities. Sampling and analytical methods may be also used in validation of indoor pollution models.

To determine reference values of indoor air pollutants, the following elements of sampling strategy shall be used in addition to the basic information characterising every sampling method (EN 14412, 2004):

- Time of sampling: to rule out any seasonal effects the individual sampling events shall be evenly distributed over the year. The time of individual sampling shall be fixed in a way that representative concentration values can be assessed. However, for sampling for \geq one week, the choice of sampling time tends to be less important.
- Sampling duration and sampling frequency: the duration of sampling has to be set in a way that the limits of determination for all compounds of interest are exceeded and that representative readings are obtained. It is necessary to maintain a sampling duration of one week or a multiple to achieve a maximum of representativity per sampling site. This is to assess all different pollution loads that occur on the different days of the week at least once. One sampling per site is adequate.
- Sampling site and determinations with resolution in space. The sampling site shall be representative, e.g. the centre of the room most inhabited by all occupants shall be used.

General methods (like NIOSH, OSHA or similar) developed for industrial workplaces may be adapted for VOC determination in air; as an example, we report the synthesis of NIOSH Method 2549 (Table 1.1).

APPLICABILITY: This method has been used for the characterization of environments containing mixtures of volatile organic compounds (see Table 1.2). The sampling has been conducted using multi-bed thermal desorption tubes. The analysis procedure has been able to identify a wide range of organic compounds, based on operator expertise and library searching.

INTERFERENCES: Compounds which coelute on the chromatographic column may present an interference in the identification of each compound. By appropriate use of background subtraction, the mass spectrometrists may be able to obtain more representative spectra of each compound and provide a tentative identity (see Table 1.2).

OTHER METHODS: Other methods have been published for the determination of specific compounds in air by thermal desorption/gas chromatography [1-3]. One of the primary differences in these methods is the sorbents used in the thermal desorption tubes.

REAGENTS:

1. Air, dry
2. Helium, high purity
3. Organic compounds of interest for mass spectra verification (See Table 1.2).*
4. Solvents for preparing spiking solutions: carbon disulfide (low benzene chromatographic grade), methanol, etc. (99+% purity)

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: Thermal sampling tube, $\frac{1}{4}$ " s.s. tube, multi-bed sorbents capable of trapping organic compounds in the C₃-C₁₆ range. Exact sampler configuration depends on thermal desorber system used. See Figure 1 as an example.

SAMPLING AND MEASUREMENT

SAMPLER:	THERMAL DESORPTION TUBE (multi-bed sorbent tubes containing graphitized carbons and carbon molecular sieve sorbents [See Appendix])
FLOW RATE:	0.01 to 0.05 L/min
VOL	-MIN: 1L -MAX: 6L (<i>even more for non industrial environments</i>)
SHIPMENT:	Ambient in storage containers
SAMPLE STABILITY:	Compound dependent (store @ -10 °C)
BLANKS:	1 to 3 per set
TECHNIQUE:	THERMAL DESORPTION, GAS CHROMATOGRAPHY, MASS SPECTROMETRY
ANALYTE:	See Table 1.1
DESORPTION:	Thermal desorption
INJECTION VOLUME:	Defined by desorption split flows (See Appendix)
TEMPERATURE	-DESORPTION: 300 °C for 10 min -DETECTOR (MS): 280 °C -COLUMN: 35 °C for 4 min; 8 °C/min to 150 °C, 15 °C/min to 300 °C
CARRIER GAS:	Helium
COLUMN:	30 meter DB-1, 0.25-mm ID, 1.0- μ m film (<i>or equivalent</i>)
CALIBRATION:	Identification based on mass spectra interpretation and computerized library searches.
RANGE:	not applicable
ESTIMATED LOD:	100 ng per tube or less
PRECISION (S_r):	not applicable

Table 1.1. NIOSH method 2549: volatile organic compounds (modified).

2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible tubing.
3. Shipping containers for thermal desorber sampling tubes.
4. Instrumentation: thermal desorption system, focusing capability, desorption temperature appropriate to sorbents in tube (~300°C), and interfaced directly to a GC-MS system.
5. Gas chromatograph with injector fitted with 1/4" column adapter, 1/4" Swagelok nuts and Teflon ferrules (or equivalent).
6. Syringes: 1- μ L, 10- μ L (liquid); 100- μ L, 500- μ L (gas tight).
7. Volumetric Flasks, 10-mL.
8. Gas bulb, 2 L.

SPECIAL PRECAUTIONS: Some solvents are flammable and should be handled with caution in a fume hood. Precautions should be taken to avoid inhalation of the vapours from solvents as well. Skin contact should be avoided.

SAMPLING:

NOTE: Prior to field use, clean all thermal desorption tubes thoroughly by heating at or above the intended tube desorption temperature for 1-2 hours with carrier gas flowing at a rate of at least 50 mL/min. Always store tubes with long-term storage caps attached, or in containers that prevent contamination. Identify each tube uniquely with a permanent number on either the tube or tube container. Under no circumstances should tape or labels be applied directly to the thermal desorption tubes.

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Remove the caps of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.

NOTE: With a multi-bed sorbent tube, it is extremely important to sample in the correct direction, from least to maximum strength sorbent.

3. For general screening, sample at 0.01 to 0.05 L/min for a maximum sample volume of 6 L. Replace caps immediately after sampling. Keep field blanks capped at all times. Tubes can act as diffusive samplers if left uncapped in a contaminated environment.
4. Collect a "humidity test" sample to determine if the thermal adsorption tubes have a high water background.

NOTE: At higher sample volumes, additional analyte and water (from humidity) may be collected on the sampling tube. At sufficiently high levels of analyte or water in the sample, the mass spectrometer may malfunction during analysis resulting in loss of data for a given sample.

5. Collect a "control" sample. For indoor air samples this could be either an outside sample at the same location or an indoor sample taken in a non-complaint area.
6. Ship in sample storage containers at ambient temperature. Store at -10°C.

SAMPLE PREPARATION:

1. Allow samples to equilibrate to room temperature prior to analysis. Remove each sampler from its storage container.
2. Analyze "humidity test" sampler first to determine if humidity was high during sampling (step 10).
3. If high humidity, dry purge the tubes with purified helium at 50 to 100 mL/min for a maximum of 3 L at ambient temperature prior to analysis. .
4. Place the sampler into the thermal desorber. Desorb in reverse direction to sampling flow.

CALIBRATION AND QUALITY CONTROL:

1. Tune the mass spectrometer according to manufacturer's directions to calibrate.
2. Make at least one blank run prior to analyzing any field samples to ensure that the TD-GC-MS system produces a clean chromatographic background. Also make a blank run after analysis of heavily concentrated samples to prevent any carryover in the system. If carryover is observed, make additional blank runs until the contamination is flushed from the thermal desorber system.
3. Maintain a log of thermal desorber tube use to record the number of times used and compounds found. If unexpected analytes are found in samples, the log can be checked to verify if the tube may have been exposed to these analytes during a previous sampling use.
4. Run spiked samples along with the screening samples to confirm the compounds of interest. To prepare spiked samples, use the procedure outlined in the Appendix .

MEASUREMENT:

1. See Appendix for conditions. MS scan range should cover the ions of interest, typically from 20 to 300 atomic mass units (amu). Mass spectra can either be identified by library searching or by manual interpretation (see Table 1.2). In all cases, library matches should also be checked for accurate identification and verified with standard spikes if necessary.

EVALUATION OF METHOD:

The method has been used for a number of field screening evaluations to detect volatile organic compounds. Estimate of the limit of detection for the method is based on the analysis of spiked samples for a number of different types of organic compounds. For the compounds studied, reliable mass spectra were collected at a level of 100 ng per compound or less. In situations where high levels of humidity may be present on the sample, some of the polar volatile compounds may not be efficiently collected on the internal trap of the thermal desorber. In these situations, purging of the samples with 3 L of helium at 100 mL/min removed the excess water and did not appreciably affect the recovery of the analytes on the sample.

Compound/ Synonyms	CAS# RTECS	Empirical Formula	MW ^a	BP ^b (°C)	VP ^c @ 25°C mm Hg kPa		Characteristic Ions, m/z
Aromatic Hydrocarbons							
Benzene /benzol	71-43-2 CY1400000	C ₆ H ₆	78.11	80.1	95.2	12.7	78*
Xylene /dimethyl benzene	1330-20-7 ZE2100000	C ₈ H ₁₀	106.7				91, 106*, 105
o-xylene				144.4	6.7	0.9	
m-xylene				139.1	8.4	1.1	
p-xylene				138.4	8.8	1.2	
Toluene /toluol	108-88-3 XS5250000	C ₇ H ₈	92.14	110.6	28.4	3.8	91, 92*

Compound/ Synonyms	CAS# RTECS	Empirical Formula	MW ^a	BP ^b (°C)	VP ^c @ 25°C mm Hg kPa		Characteristic Ions, m/z
Aliphatic Hydrocarbons							
n-Pentane	109-66-0 RZ9450000	C ₅ H ₁₂	72.15	36.1	512.5	68.3	43, 72*, 57
n-Hexane /hexyl-hydride	110-54-3 MN9275000	C ₆ H ₁₄	86.18	68.7	151.3	20.2	57, 43, 86*, 41
n-Heptane	142-82-5 MI7700000	C ₇ H ₁₆	100.21	98.4	45.8	6.1	43, 71, 57, 100*, 41
n-Octane	111-65-9 RG8400000	C ₈ H ₁₈	114.23	125.7	14.0	1.9	43, 85, 114*, 57
n-Decane /decyl hydride	124-18-5 HD6500000	C ₁₀ H ₂₂	142.29	174	1.4	0.2	43, 57, 71, 41, 142*
Ketones							
Acetone /2-propanone	67-64-1 AL3150000	C ₃ H ₆ O	58.08	56	266	35.5	43, 58*
2-Butanone /methyl ethyl ketone	78-93-3 EL6475000	C ₄ H ₈ O	72.11	79.6	100	13	43, 72*
Methyl isobutyl ketone /MIBK, hexone	108-10-1 SA9275000	C ₆ H ₁₂ O	100.16	117	15	2	43, 100*, 58
Cyclohexanone /cyclohexyl ketone	108-94-1 GW1050000	C ₆ H ₁₀ O	98.15	155	2	0.3	55, 42, 98*, 69
Alcohols							
Methanol /methyl alcohol	67-56-1 PC1400000	CH ₃ OH	32.04	64.5	115	15.3	31, 29, 32*
Ethanol /ethyl alcohol	64-17-5 KQ6300000	C ₂ H ₅ OH	46.07	78.5	42	5.6	31, 45, 46*
Isopropanol /1-methyl ethanol	67-63-0 NT8050000	C ₃ H ₇ OH	60.09	82.5	33	4.4	45, 59, 43
Butanol /butyl alcohol	71-36-3 E01400000	C ₄ H ₉ OH	74.12	117	4.2	0.56	56, 31, 41, 43
Glycol Ethers							
Butyl cellosolve butoxyethanol	/2- 111-76-2 KJ8575000	C ₆ H ₁₄ O ₂	118.17	171	0.8	0.11	57, 41, 45, 75, 87
Diethylene glycol ethyl ether /Carbitol	111-90-0 KK8750000	C ₆ H ₁₄ O ₃	134.17	202	0.08	0.01	45, 59, 72, 73, 75, 104
Phenolics							
Phenol /hydroxybenzene	108-95-2 SJ3325000	C ₆ H ₅ OH	94.11	182	47	0.35	94*, 65, 66, 39
Cresol	1319-77-3 G05950000	C ₇ H ₇ OH	108.14				108*, 107, 77, 79
2-methylphenol	95-48-7			190.9	1.9	0.25	
3-methylphenol	108-39-4			202.2	1.0	0.15	
4-methylphenol	106-44-5			201.9	0.8	0.11	

Compound/ Synonyms	CAS# RTECS	Empirical Formula	MW ^a	BP ^b (°C)	VP ^c @ 25°C mm Hg kPa		Characteristic Ions, m/z
Chlorinated Hydrocarbons							
Methylene chloride /dichloromethane	75-09-2 PA8050000	CH ₂ Cl ₂	84.94	40	349	47	86*, 84, 49, 51
1,1,1-Trichloroethane /methyl chloroform	71-55-6 KJ2975000	CCl ₃ CH ₃	133.42	75	100	13.5	97, 99, 117, 119
Perchloroethylene /hexachloroethane	127-18-4 KX3850000	CCl ₃ CCl ₃	236.74	187 (subl)	0.2	<0.1	164*, 166, 168, 129, 131, 133, 94, 96
o,p-Dichlorobenzenes		C ₆ H ₄ Cl ₂	147.0				146*, 148, 111, 113, 75
/1,2-dichlorobenzene	95-50-1 CZ4500000			172-9	1.2	0.2	
/1,4-dichlorobenzene	106-46-7 CZ4550000			173.7	1.7	0.2	
1,1,2-Trichloro-1,2,2-trifluoroethane /Freon 113	76-13-1 KJ4000000	CCl ₂ FCClF ₂	187.38	47.6	384	38	101, 103, 151, 153, 85, 87
Terpenes							
d-Limonene	5989-27-5 OS8100000	C ₁₀ H ₁₆	136.23	176	1.2		68, 67, 93, 121, 136*
Turpentine (Pinenes)	8006-64-2	C ₁₀ H ₁₆	136.23	156 to 170	4 @ 20"		93, 121, 136*, 91
α-pinene	80-56-8			156			
β-pinene	127-91-3			165			
Aldehydes							
Hexanal /caproaldehyde	66-25-1 MN7175000	C ₆ H ₁₂ O	100.16	131	10	1.3	44, 56, 72, 82, 41
Benzaldehyde /benzoic aldehyde	100-52-7 CU4375000	C ₇ H ₁₂ O	106.12	179	1.0	0.1	
Nonanal /pelargonic aldehyde	124-19-6 RA5700000	C ₉ H ₁₈ O	142.24	93	23	3	43, 44, 57, 98, 114
Acetates							
Ethyl acetate /acetic ether	141-78-6 AH5425000	C ₄ H ₈ O ₂	88.1	77	73	9.7	43, 88*, 61, 70, 73, 45
Butyl acetate /acetic acid butyl ester	123-86-4 AF7350000	C ₆ H ₁₂ O ₂	116.16	126	10	1.3	43, 56, 73, 61
Amyl acetate /banana oil	628-63-7 AJ1925000	C ₇ H ₁₄ O ₂	130.18	149	4	0.5	43, 70, 55, 61
Other							
Octamethylcyclotetra-siloxane	556-67-2 GZ4397000	C ₈ H ₂₄ O ₄ Si ₄	296.62	175			281, 282, 283

^a Molecular Weight^b Boiling Point^c Vapour Pressure

*Indicates molecular ion

Table 1.2. Common volatile organic compounds with mass spectral data.

Appendix

Multi-bed sorbent tubes: Other sorbent combinations and instrumentation/conditions shown to be equivalent may be substituted for those listed. In particular, if the compounds of interest are known, specific sorbents and conditions can be chosen that work best for that particular compound(s). The tubes that have been used in NIOSH studies with the Perkin Elmer ATD system are ¼ " stainless steel tubes, and are shown in the figure in the next page:

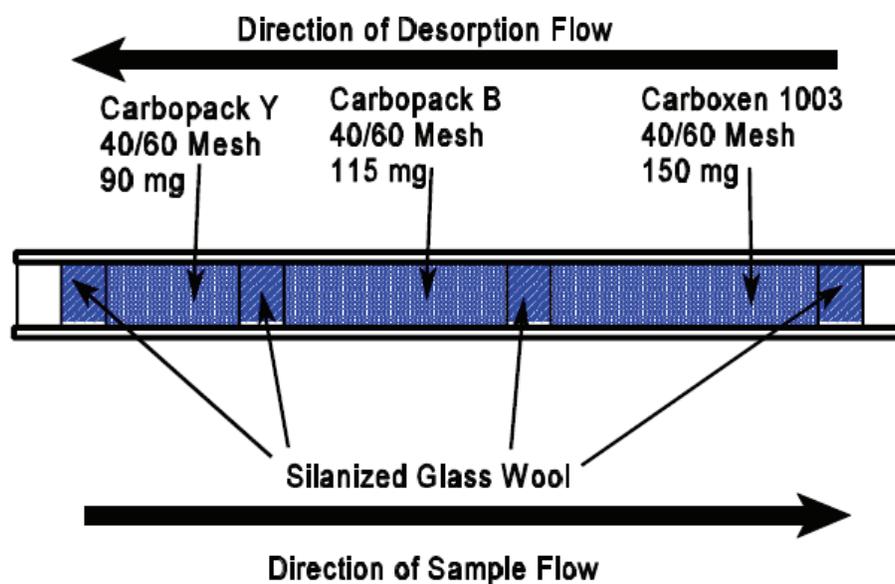


Fig. 1. Carbopack™ and Carboxen™ adsorbents are available from Supelco, Inc.

Preparation of spiked samples: Spiked tubes can be prepared from either liquid or gas bulb standards.

Liquid standards: Stock solutions are prepared by adding known amounts of analytes to 10-mL volumetric flasks containing high purity solvent (carbon disulfide, methanol, toluene). Solvents are chosen based on solubility for the analytes of interest and ability to be separated from the analytes when chromatographed. Highly volatile compounds should be dissolved in a less volatile solvent. For most compounds, carbon disulfide is a good general purpose solvent, although this will interfere with early eluting compounds.

Gas bulb standards: Inject known amounts of organic analytes of interest into a gas bulb of known volume filled with clean air. Prior to closing the bulb, a magnetic stirrer and several glass beads are placed in the bulb to assist in agitation after introduction of the analytes. After injection of all of the analytes of interest into the bulb, warm the bulb to 50 °C and place it on a magnetic stirring plate and stir for several minutes to ensure complete vaporization of the analytes. After the bulb has been stirred and cooled to room temperature, remove aliquots from the bulb with a gas syringe and inject into a sample tube as described below.

Tube spiking Fit a GC injector with a ¼" column adapter. Maintain the injector at 120 °C to assist in vaporization of the injected sample. Attach cleaned thermal desorption tubes to injector with ¼" Swagelok nuts and Teflon ferrules, and adjust helium flow through the injector to 50 mL/min. Attach the sampling tube so that flow direction is the same as for sampling. Take an aliquot of standard solution (gas standards 100 to 500 µL; liquid standards, 0.1 to 2 µL) and inject into the GC injector. Allow to equilibrate for 10 minutes.

Remove tube and analyze by thermal desorption using the same conditions as for field samples.

Instrumentation: Actual media, instrumentation, and conditions used for general screening of unknown environments are as follows: Perkin-Elmer ATD 400 (automated thermal desorption system) interfaced directly to a Hewlett-Packard 5980 gas chromatograph/HP5970 mass selective detector and data system.

ATD conditions:

Tube desorption temperature: 300°C

Tube desorption time: 10 min.

Valve/transfer line temperatures: 150°C

Focusing trap: Carboxen 1000, 60/80 mesh, held at 27°C during tube desorption

Focusing trap desorption temperature: 300°C

Desorption flow: 50-60 mL/min.

Inlet split: off

Outlet split: 20 mL/min.

Helium: 10 PSI

GC conditions:

DB-1 fused silica capillary column, 30 meter, 1- μ m film thickness, 0.25-mm I.D. Temperature program: Initial 35°C for 4 min, ramp to 100°C at 8°/min, then ramp to 300°C at 15°/min, hold 1-5 min.

Run time: 27 min.

MSD conditions:

Transfer line: 280°C

Scan 20-300 amu, EI mode

EMV: set at tuning value

Solvent delay: 0 min for field samples; if a solvent-spiked tube is analyzed, a solvent delay may be necessary to prevent MS shutdown caused by excessive pressure.

Alternative methods may be obtained adapting, for instance, NIOSH Method 1500 (Hydrocarbons b.p. 36 - 216 °C) or NIOSH Method 1501 (Hydrocarbons, aromatic).

Main differences - not fundamentals - may consist in: sorbent choice (charcoal tube), desorption technique (elution with CS₂), sampling time (longer than in workplaces) and other. More important is the possibility of using diffusive (passive) samplers.

5. Passive sampling

The original purpose of the development on passive sampling (based on Fick's laws) is to provide technology at low cost, enabling air quality surveys to be routinely executed at multiple locations within urban and rural areas, industrial sites and forests. This requires the examination of the performance characteristics of the diffusive sampler over long sampling periods, in comparison with established methods, and in practical applications of urban monitoring (Brown et al., 1994; Brown et al., 1999). Several authors proposed the use of different models of diffusive (passive) devices (Brown, 1993; Harper, 2000; Bertoni et al.,

2001; Brown, 2002; Kot-Wasik et al., 2007) conceived for the determination of long-term averaged concentration of some airborne volatile and semi-volatile organic compounds, relevant on the human health protection (VOCs, polycyclic aromatic hydrocarbons and nicotine). The diffusive sampling technique is known to be the cheapest and easiest way to perform extensive sampling campaigns, both in temporal and spatial terms. Moreover, this is the only collection technique allowing the true separation of the vapour phase species from the particle bound fraction (Bertoni et al., 2004; Namiesik et al., 2005).

A lot of different models of passive sampler have been proposed by many researchers; in this chapter we can show only a "classic" sampler (Analyst, developed by the Italian National Research Council, IIA-CNR, Fig. 2 and 3) and a more recent sampler, based on radial diffusion principle (Ring, IIA-CNR, Fig. 4).

All the diffusive samplers have to respect the requirements and test methods according to EN 13528-1, EN 13528-2, EN 13528-3, EN 14412 and EN-ISO 16017-2.

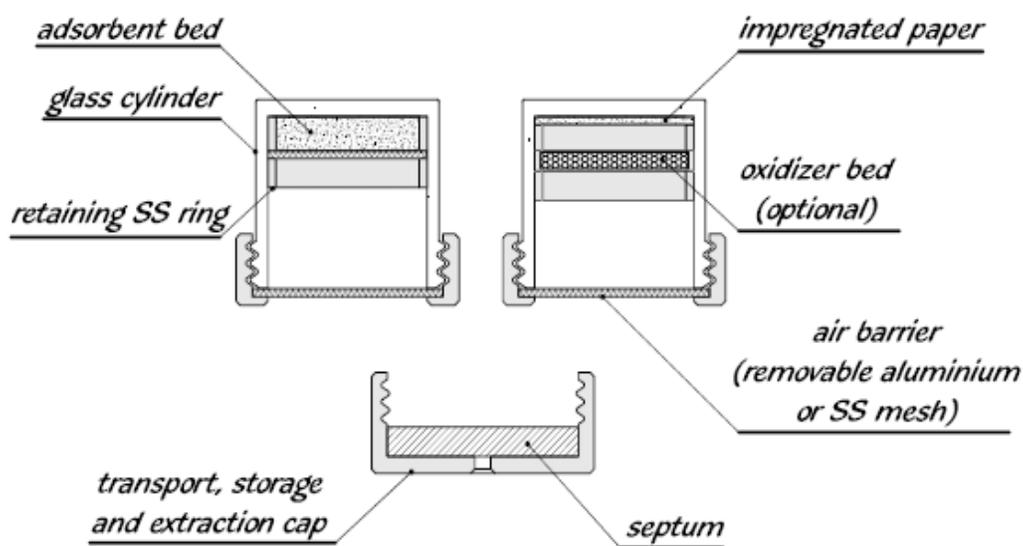


Fig. 2. Analyst sampler scheme

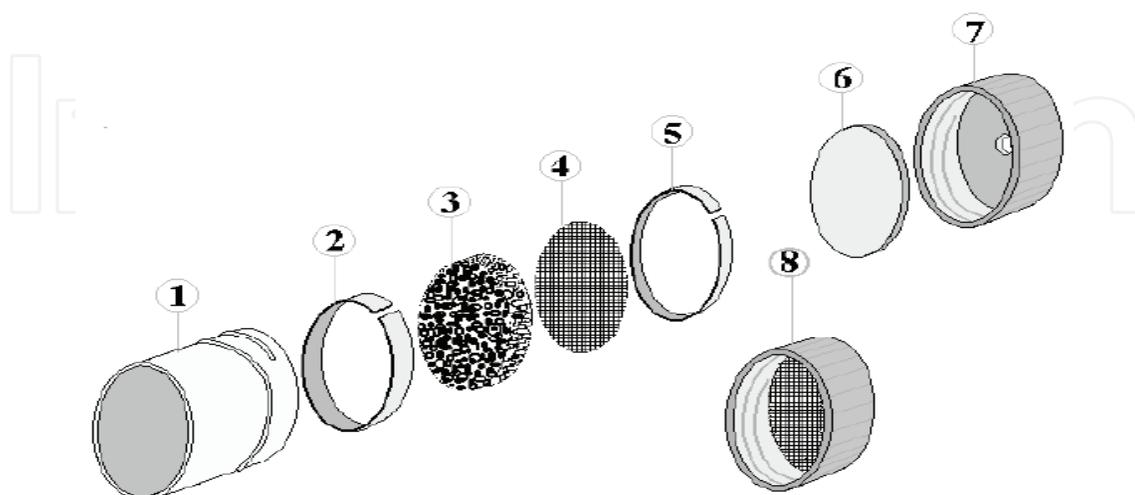


Fig. 3. Scheme of the Analyst : 1: glass cylinder (i.d. = 20 mm); 2 and 5: retaining S.S. rings; 3 adsorbent bed; 4: viewing S.S. ring; 6: Teflon seal; 7: cap; 8: aluminium diffusion cap.

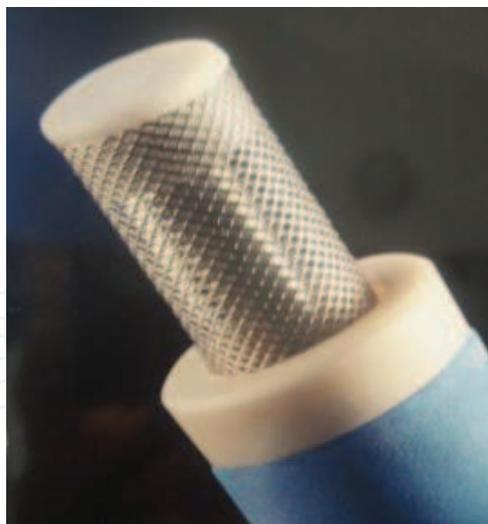


Fig. 4. Diffusive sampler "Ring" (IIA CNR).

6. Data evaluation and exposure risk assessment

Studies have found that home levels of several organics average 2 to 5 times higher indoors than outdoors. During and for several hours immediately after certain activities, such as paint stripping, levels may be 1,000 folds background outdoor levels. Despite direct reading instruments can be used (like the IR used in indoor monitoring shown in Figure 5), as above mentioned, currently it is better to try to obtain very low LODs and LOQs by employing sampling methods as described.

Sometimes they are used Threshold Limit Values (TLVs) that are the guideline values set by the American Conference of Governmental Industrial Hygienists (ACGIH) to minimize workers exposure to hazardous concentrations as much as possible. The TLVs are published yearly for more than 700 chemical substances and physical agents (ACGIH, 2010). This use is incorrect and unauthorized by ACGIH, because the TLVs respect is not a warranty of no health effects, that is on the contrary a fundamental requirement in nonindustrial environment.

No standards have been set for VOCs in non-industrial settings. OSHA regulates formaldehyde, a specific VOC, as a carcinogen. OSHA has adopted a Permissible Exposure Level (PEL) of 0.75 ppm, and an action level of 0.5 ppm. Based upon current information, it is advisable to mitigate formaldehyde that is present at levels higher than 0.1 ppm. Recently the World Health Organization (WHO, 2010) provided health-based guidelines for 55 airborne inorganic and organic compounds for carcinogenic and non-carcinogenic health endpoints. The non-carcinogenic endpoints include development toxicity, reproduction toxicity, respiratory toxicity, neurotoxicity, hepatotoxicity, hematotoxicity, eye/nose/throat irritation, and odor annoyance. The lowest concentration at which effects are observed in humans, animals, and plants was used as a starting point for the non-carcinogenic endpoints. Uncertainty factors determined through scientific judgment in consensus and averaging time were also taken into account in determining the health endpoint for non-carcinogenic compounds. The classification by the international Agency for Research on Cancer (IARC) was used to determine a chemical as a carcinogen. The endpoint of carcinogen was determined by linear extrapolation from the high dose level, which is characteristic of animal experiments or occupation exposure with cancer responses.

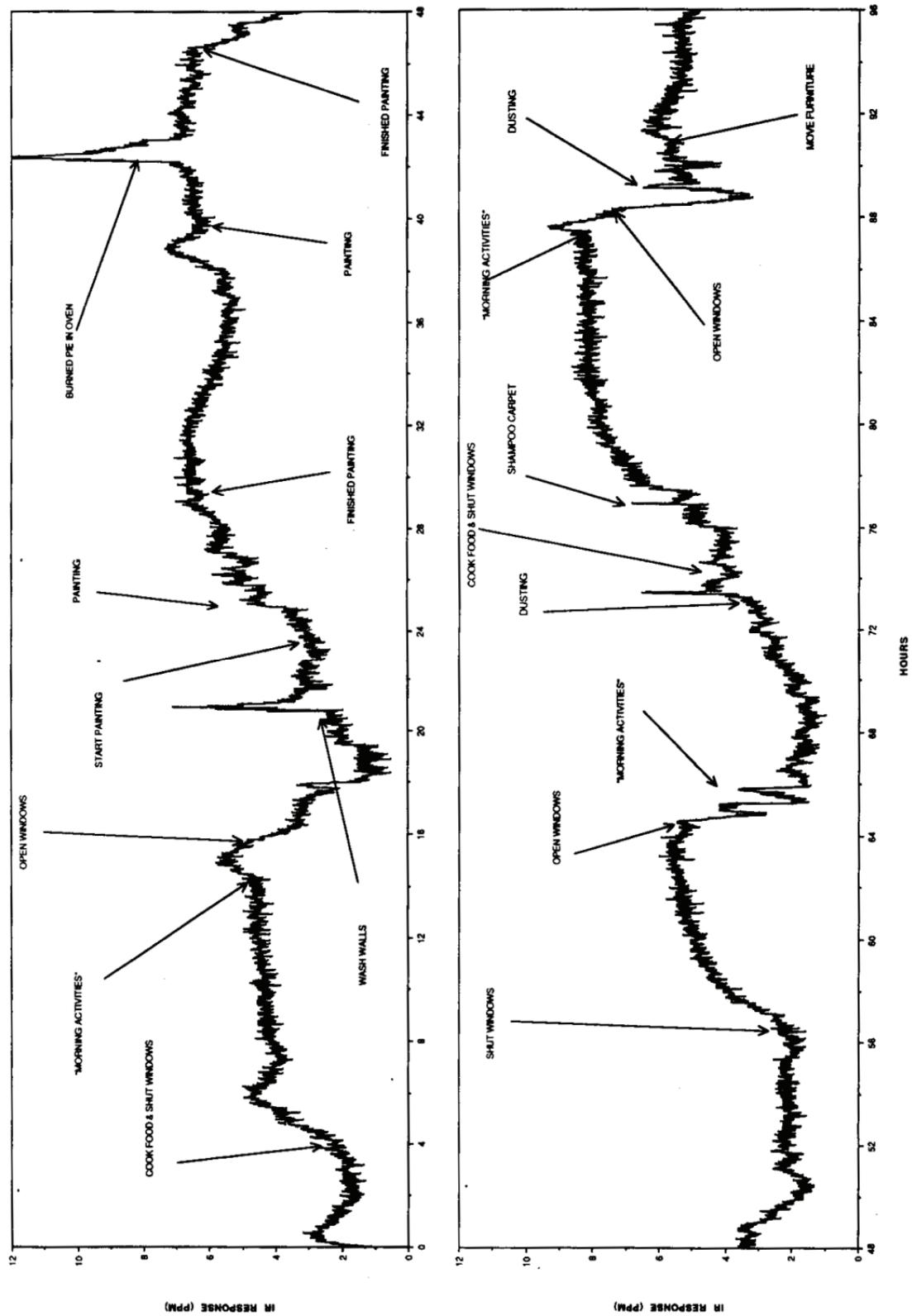


Fig. 5. Variation in indoor VOC levels in house house as detected by an IR instrument. VOC levels are expressed in ppm of equivalent 33% propane/67% butane. Human activities at different times are shown (Clobes et al., 1992).

This objective requires measurements for checking whether specified limit or guideline values are being exceeded. Examples of limit and guideline values (except workplace atmospheres and ambient air) for indoor environments are given in Table 2.1 and 2.2, established by the ad hoc committee of IRK/AOLG of Germany for organic chemicals.

Pollutant	Country	Limit value	Pollutant
Tetrachloroethene	Germany	0.1 mg/m ³	7 days

Table 2.1. Examples of limit values.

Pollutant	Country/Organisation	Guideline Value	Averaging Time
Formaldehyde	Germany	0.12 mg/m ³	not specified
Nitrogen dioxide	Germany	60 µg/m ³ ^a	7 days
Toluene	Germany	0.3 mg/m ³ ^a	not specified
Styrene	Germany	0.03 mg/m ³ ^a	7 days
Dichloromethane	Germany	0.2 mg/m ³ ^a	24 h
TVOC	Germany	0.2 - 0.3 mg/m ³	not specified

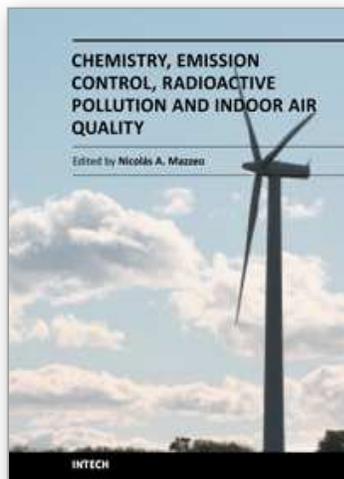
^a Guideline value (RW I-value, "Richtwert I" = guideline value I) aimed at hygienic prevention.

Table 2.2. Examples of guideline values.

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The atmosphere may be our most precious resource. Accordingly, the balance between its use and protection is a high priority for our civilization. While many of us would consider air pollution to be an issue that the modern world has resolved to a greater extent, it still appears to have considerable influence on the global environment. In many countries with ambitious economic growth targets the acceptable levels of air pollution have been transgressed. Serious respiratory disease related problems have been identified with both indoor and outdoor pollution throughout the world. The 25 chapters of this book deal with several air pollution issues grouped into the following sections: a) air pollution chemistry; b) air pollutant emission control; c) radioactive pollution and d) indoor air quality.

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