

Comprehensive Experience for Indoor Air Quality Assessment: A Review on the Determination of Volatile Organic Compounds (VOCs)

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Abstract

Volatile Organic Compounds (VOCs) are toxic chemicals harmful for the environmental sustainability and human health. Due to the several types of VOCs and the diversity in their physico-chemical properties, it is difficult to develop standard methods for sampling and analysis. The majority of methods depend on the compounds of interest and the required duration of sampling. Each method is associated with a certain value of specificity and sensitivity. To date, however, no specific method qualifies as being the most accurate. This review reports the most common methods employed in determination of VOCs, based on the international literature.

Keywords: Indoor air quality; VOCs; Analytical techniques

Introduction

Most people spend 70% to 90% of their time indoors. It is this fact, together with the remarkable concentration of several indoor air pollutants and the large number of people exposed to them, which justifies the reasons for considering indoor air pollution among the most significant environmental health risks for building dwellers [1,2]. It is worth noting that indoor pollutants' concentrations may be seven times higher than the relative outdoors ones [3-5]. In addition, it has been found that the increased exposure of humans to indoor air pollutants is mainly due to inhalation of indoor air [6,7]. Due to the above facts, World Health Organisation (WHO) established health-based goals for several indoor air pollutants [8-10].

Volatile Organic Compounds (VOCs) are highly reactive. Example compounds are benzene, toluene, ethylbenzene, m-xylene, o-xylene, p-xylene and styrene, chlorinated hydrocarbons such as dichloromethane, chloroform, methyl chloride, trichlorofluoromethane, tetrachloroethylene and organohalogenes such as p-dichlorobenzene and 1,2,4-trichlorobenzene [11].

World Health Organisation has defined VOCs as the organic compounds with boiling points from approximately 50-100°C up to 240-260°C and vapour saturation pressure greater than 102 kPa at 25°C [12]. Several types of VOCs are toxic-genotoxic, some are fatal for humans, some exhibit irritant and/or odorant properties and some others impose negative consequences for the environment [8-10,13-15].

Additionally, indoor VOCs are extremely diverse and their distribution has been the subject of many studies worldwide since the early 80s. VOCs have been associated with human health problems such as allergies, eye irritation, nose and throat malfunction, tiredness, lack of concentration, vascular-nervous dysfunction, cancer and acute-chronic health pathologies [13,14].

VOCs are man-made or of natural origin. Significant anthropogenic sources of VOCs are human activities in crafts, small industry and petrochemistry, as well as, the vehicular emissions [16]. Natural origins of VOCs include wetlands, forests, oceans and volcanoes with estimated global biogenic emission rating around 1150Tg/yr [15,17].

Building materials have been acknowledged as significant sources of VOCs indoors. There is evidence, from a variety of investigations and systematic studies, that building materials can also affect transport and removal of indoor VOCs by absorption and emission [18,19]. It is noteworthy that several household products such as paints, paint strippers and other solvents, wood preservatives, aerosol sprays, cleansers and disinfectants, moth repellents, air fresheners, stored fuels and automotive products, hobby supplies, dry-cleaned clothing, and several indoor combustion sources e.g. cooking fume, incense burning, cigarette smoking etc., contribute to VOCs loading of residential indoor air [11].

Because of their potential harmful effects on human health, much attention has been paid towards the accurate determination of VOCs and many techniques of analysis have been developed for measuring and assessing the intensity of VOCs emissions from indoor materials [14,20].

Studies on Determination of VOCs

European studies on indoor air quality

Addressing the requirements of the new class of knowledge regarding indoor air-quality, the European Commission established the *European Collaborative Action on Urban Air, Indoor Environment and Human Exposure* and for the last 22 years, the *European Collaborative Action ECA "Indoor Air Quality & its Impact on Man"*. ECA has

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been implementing a multidisciplinary collaboration of European scientists with the ultimate goal being the provision of healthy and environmentally sustainable buildings [21].

To accomplish this task, ECA has dealt with all aspects of interactions between indoor environment and air quality, like for example thermal comfort, pollution sources, quality and quantity of chemical and biological indoor pollutants, energy use, and ventilation processes.

Additionally, to provide a broader view on air pollution exposure in urban areas, ECA Steering Committee decided in 1999, to place more emphasis on the links between indoor and outdoor air quality and to outline its work under a wider title, namely “*Urban Air, Indoor Environment and Human Exposure*”. The main focus of this renewed activity was the assessment of the urban indoor air pollution exposure. This was considered as part of the environmental health risk assessment under the view of the special considerations needed for urban and indoor air quality management. The new approach was supported by the activities of the *Joint Research Centre’s Institute for Health and Consumer Protection* in Ispra (Italy) which dealt with the Physical and the Chemical Exposures (Table 1).

ECA report no 6 in 1989 [22] titled as *Strategy for sampling chemical substances in indoor air*, addressed issues regarding the in-field analysis of chemical compounds in indoor air. The report discussed questions of when, for what period of time, how often and where, samples should be taken for determining chemicals in indoor air. It was divided into two parts. In the first part, detailed discussion took place on the dynamics of the indoor environment and the objectives of indoor pollution measurements. In addition, general rules were derived for an optimal strategy to answer the aforementioned questions.

In the second part, the general rules were applied to those pollutants or pollutant classes which were and are still considered being of major importance. Finally, specific recommendations were provided [21]. It is noteworthy that the ECA report paid much attention on the dependence of their concentration levels in parameters such as temperature and relative humidity which affect the emission characteristics of their major sources indoors and change according to the sampling strategy applied (Table 2).

The major sampling strategies for chemical substances in indoor air have been discussed in ECA report no 6 (1989) [22], but more specific guidance for the development of sampling strategies for volatile organic compounds (VOCs) was provided by ECA report no 14 (1995) [23]. This study reported the general considerations which highlighted the sampling objectives of indoor VOC measurements, the numerous sources of VOCs and their emission characteristics, the dynamic character of indoor pollution induced by VOCs, and the interpretation of VOC measurements in relation to health and comfort. It is worth noting that, these considerations are a prerequisite for the development of sampling strategies.

In this report, the discussion on the elements of sampling strategies for VOCs included the type and number of buildings and spaces in which air samples should be taken, the types and status of sources in these spaces, the environmental conditions before and during sampling, the position of the sampler in the selected spaces, the sampling duration, the time and frequency, sampling and analytical methods, and quality control and assurance (Table 3) [23].

In order to achieve a common practice for a standardised procedure in analysing VOCs, an inter-laboratory comparison has been conducted using three materials. The agreement among laboratories was assessed

| Report's Code | Report's Title |
|---------------|---|
| ECA 27 | Harmonisation framework for indoor products labelling schemes in the EU (2012). |
| ECA 26 | Impact of Ozone initiated Terpene Chemistry on Indoor Air Quality and Human Health (2007). |
| ECA 25 | Strategies to determine and control the contributions of indoor air pollution to total inhalation exposure (STRATEX) (2006). |
| ECA 24 | Harmonisation of indoor material emissions labelling systems in the EU (2005). |
| ECA 23 | Ventilation, good indoor air quality and rational use of energy (2003). |
| ECA 22 | Risk assessment in relation to indoor air quality (2000). |
| ECA 21 | European Inter-laboratory Comparison on VOCs emitted from building materials and products (1999). |
| ECA 20 | Sensory evaluation of indoor air quality (1999). |
| ECA 19 | Total Volatile Organic Compounds (TVOC) in Indoor Air Quality Investigations (1997). |
| ECA 18 | Evaluation of VOC emissions from building products (1996). |
| ECA 17 | Indoor Air Quality and the use of Energy in Buildings (1996). |
| ECA 16 | Determination of VOCs emitted from indoor materials and products; second interlaboratory comparison of small chamber measurements (1995). |
| ECA 15 | Radon in indoor air (1995). |
| ECA 14 | Sampling strategies for volatile organic compounds (VOCs) in indoor air (1995). |
| ECA 13 | Determination of VOCs emitted from indoor materials and products. Interlaboratory comparison of small chamber measurements (1993). |
| ECA 12 | Biological particles in indoor environments (1993). |
| ECA 11 | Guidelines for ventilation requirements in buildings (1992). |
| ECA 10 | Effects of indoor air pollution on human health (1991). |
| ECA 9 | Project inventory 2nd updated edition (1991). |
| ECA 8 | Guideline for the characterization of volatile organic compounds emitted from indoor materials and products using small test chambers (1991). |
| ECA 7 | Indoor air pollution by formaldehyde in European countries (1991). |
| ECA 6 | Strategy for sampling chemical substances in indoor air (1989). |
| ECA 5 | Project Inventory (1989). |
| ECA 4 | Sick building syndrome a practical guide (1989). |
| ECA 3 | Indoor pollution by NO ₂ in European countries (1989). |
| ECA 2 | Formaldehyde emission from wood based materials: guideline for the determination of steady state concentrations in test chambers (1989). |
| ECA 1 | Radon in indoor air (1988). |

Table 1. Indoor air quality assessment reports supported by the activities of the Joint Research Centre’s Institute for Health & Consumer Protection [21].

| Parameter | Objective of measurement | |
|--|--------------------------------|--|
| | <i>Average concentration</i> | <i>Maximum concentration</i> |
| Ambient temperature | normal conditions | normal conditions |
| Relative humidity | normal conditions | normal conditions |
| Ventilation status before sampling during sampling | normal normal | no ventilation: doors and windows closed no ventilation: doors and windows closed |
| Occupancy | normal activity | maximum occupancy |
| Source status | normal use | heavy use ^a |
| Sampling location | centre of room at 1-2 m height | close to activity |
| Time of sampling | anytime | during activity |
| Duration of sampling | 5-14 days | 30-60 min |
| Minimum number of samples ^b for orientation | 1 | 1 |
| for control of compliance | 2 | 3 |

Table 2. Recommended conditions for VOCs sampling in the air of public buildings and private homes (adopted and modified from ECA report no 6, 1989 [22]).
a. Attention has to be paid to instructions and warnings for the use of products to avoid potential health damage. In case of combustion sources, temperature and humidity will rise in such experiments. Beware also of rising carbon monoxide concentrations. b. Duplicates are desirable.

by tests that characterised the emission of VOCs from indoor materials and products via small chamber testing (ECA report no 13 1993) [24]. The twenty participating laboratories reached the following main results: a. Chambers of different materials (glass and stainless steel) and of widely different capacity (0.035 to 1475 L) appeared equally suitable. b. The repeatability of duplicate measurements (including sampling) within each laboratory was good. c. The test with a known n-dodecane source showed, for most laboratories, an unexpected and yet unexplained discrepancy. d. The inter-laboratory agreement appeared reasonable (coefficient of variation 26-42%) when testing a PVC tile, but for a wax the scattering was very high [24].

The results also showed unacceptable inter-laboratory discrepancies in the case of a thin layer fast decreasing source. For this reason, a second inter-laboratory comparison was subsequently organised and in order to improve the agreement and the design incorporated additionally: i) control of the chamber air velocity, ii) control of the source layer thickness and iii) adoption of both dilution and sink mathematical models. The concentrations of 2-(2-butoxyethoxy)-ethanol and of the two Texanol isomers emitted from a water-based paint had to be determined over 13 days to derive to the initial emission factor [25]. The results of the 18 participating laboratories from 10 countries showed that the preparation of the paint sample contributed markedly to the variance, because of differences in the paint film thickness (Table 4).

The impact of the chamber itself on the results, if any, was less evident; in fact, a satisfactory agreement of the results has been obtained with chambers of widely different features (capacity range 35 cm³ to 1.5 m³) [25]. Despite the use of calibration solutions prepared from the same batch of pure compounds, the analysis of the compound concentrations contributed markedly to the variance, as confirmed by the results of an analytical comparison carried out in parallel with the main comparison [25]. Model fitting has produced a reasonably good description of the data sets, apparently accounting also for the sink due to chamber wall adsorption.

The maximum ranges of the estimated emission factors, expressed as a ratio of the highest to the smallest reported value, are 52, 9 and 9 for 2-(2-butoxyethoxy)-ethanol, Texanol-1 and Texanol-2 respectively. However, the scattering is markedly reduced if only results obtained with the same GC (Gas Chromatography) detector (FID; flame-

ionisation detector) and paint samples within a narrow thickness range (50.8-70.6 pm) were considered [25].

Accomplishments under the *European Collaborative Action ECA "Indoor Air Quality & its Impact on Man"* were related to ECA (1997) [26] to the background of VOCs analysis. This report discussed thoroughly the association between VOCs and specific effects like sensory, neurotoxic and behavioural effects, and irritation of mucous membranes. The discussion was made in an effort to evaluate the potential of Total Volatile Organic Compounds (TVOC) to serve as an effect indicator [26].

Eighteen laboratories from 10 European countries participated in a 2.5 year research collaboration among 4 research institutes and 4 industrial companies under the VOCEM project entitled "*Further development and validation test chamber method for measuring VOC emissions from building materials and products*" [27]. The scope of this project was to improve the procedure used to measure VOCs emitted from building materials and products in small test chambers. The inter-laboratory comparison included the GC-MS (Gas Chromatography-Mass Spectroscopy) determination of 5 target compounds from carpet, 8 from PVC cushion vinyl and 2 from paint (Table 5), for the first time, chamber recovery (sinks), homogeneity of solid materials and possible contamination during transport were tested [27].

The results showed that the intra-laboratory variance (random errors) was much smaller than the inter-laboratory variance (systematic errors). Causes of the largest inter-laboratory discrepancies were analytical errors, losses of the heaviest compounds due to absorption on the chamber walls and non homogeneity of the materials [27].

Harmonisation of indoor products labelling schemes in the EU, is the subject of the ECA preparatory working group 27 led by the European Commission's Joint Research Centre. An important aspect of the European Commission's policy making process is the field of indoor air quality and associated health effects. The ECA no 27 2012 report [28] describes the outcome of recent activities establishing an EU wide harmonization framework for labelling schemes which consists of core and transitional criteria for testing and evaluation methodologies. Common core criteria are those for which consensus has already been achieved and can be applied, whereas transitional criteria are those for which consensus is still to be reached and these continue to be applied locally during a transitional period [28]. An overview of the existing

| Sorbent | Desorption technique | Compounds sampled | Starting at bp ^a [°C] | Main Advantages and Disadvantages |
|--|----------------------|--|----------------------------------|--|
| Tenax TA | thermal | -most non polar VOCs -slightly polar VOCs -aldehydes>C5 -(acids>C ₃) ^a | > 60 | -low background -well investigated -some decomposition products (benzaldehyde, acetophenone) |
| -low background -well investigated -some decomposition products (benzaldehyde, acetophenone) | thermal | -most non polar VOCs -slightly polar VOCs | > 60 | -low background -reactions of some compounds (i.e. aldehydes, terpenes) |
| Activated carbon | solvent/ thermal | -most non polar VOCs -slightly polar VOCs | > 50 | -high capacity -reactions of some compounds |
| Porapak Q | thermal | -most non polar VOCs -slightly polar VOCs | > 60 | -high background -low thermal stability |
| Porapak S or R,N | thermal | -VOCs incl. moderately polar terpenes | > 40 | -high background -low thermal stability |
| Organic molecular sieves (e.g., Carboxen 563,564, Carbosieve S-III) | thermal | -polar and non polar VOCs | > -80 | -water absorption |

a. Can be used

b. Boiling point (mainly low recoveries)

Table 3: Solid sorbents used to collect VOCs (adopted and modified from ECA report no 14, 1995 [23]).

standards for indoor products emission testing was reported.

The comparability of results obtained with the existing emission test procedures can be checked with round robin tests where a building product (possibly showing homogeneous emissions) is selected and distributed to several laboratories for analyses. Test based on the existing ISO standards (recently organized round robin tests) 16000-3 (2001), -6 (2004), -9 (2006) and -11 (2006) [29-32] showed that typically an uncertainty of around 20% for VOCs and formaldehyde can be expected [28]. For compounds emitted at low concentration levels (e.g. below 20 µg/m³), for polar compounds like glycols or some aldehydes, or for tested products presenting inhomogeneous emissions, uncertainties at a level of 40% can be found [33]. Non-polar and stable compounds like alkanes or aromatics exhibit the highest reproducibility.

Studies of the U.S. Environmental Protection Agency (U.S.-EPA) on indoor air quality

The U.S. Environmental Protection Agency (U.S.-EPA) provided technical aspects of updated information to assist in evaluating EPA's updated and expanded vapour intrusion database and to support finalisation of EPA's vapour intrusion guidance. For this purpose, background Indoor Air Concentrations of VOCs in North American residences from 1990–2005 were reported [34].

A total of 18 residential background indoor air quality studies were evaluated and considered for inclusion in the statistical analyses regarding VOCs concentration. Most of these studies were conducted in urban or suburban settings, although 7 of the 18 studies also included some residences in rural settings. The studies collectively reported statistics regarding the distribution of concentrations of more than 40 VOCs in thousands of indoor air samples collected in residences (Figure 1). The collective data spanned more than two decades, from 1981 to 2005. The study sample sizes varied from about 10 to 2,000 samples, although most of the studies reported 50 to 500 samples. Information regarding each of the 18 background indoor air studies is provided in Table 6 [34-43].

An assessment of indoor air quality was given in the work published by Weisel [44,45]. A total of 100 homes were surveyed in suburban and rural areas of New Jersey under the constraint to be unaffected by contaminated groundwater or soil. Samples were collected for 24 hours

using a Summa canister sampler placed on the ground floor of the house in an actively used living space other than a kitchen, to minimize collection of compounds emitted during cooking [34].

Another study carried out by the New York State Department of Health (NYSDOH) [46] reported a baseline indoor air quality study. They sampled the indoor air in basements and living spaces from 104 single-family homes heated with fuel oil. Approximately 400 samples were collected between 1997 and 2003. The residences sampled were required to have no past oil spills, no hobbies or home business that regularly use products containing VOCs, and no recent activities using products that contain VOCs (e.g., painting, staining) [34].

Further, two studies reported by Rago et al. [47,48], obtained background indoor air quality in Massachusetts. Indoor air samples were collected during 2004 and 2005 in early spring and late fall (windows closed, heat on) from the first-floor living spaces of 100 residences scattered throughout the state. The samples were collected over a 24-hour period using 6-liter Summa canisters. The participants in the study were predominantly Licensed Site Professionals in Massachusetts, and their residences were located in urban, suburban, and rural areas [34].

Indoor and outdoor air samples were also collected in another study in 75 randomly selected residential houses in Ottawa, Canada, as part of a baseline exposure assessment funded by Health Canada during the winter of 2002 to 2003. Researchers sampled 10 litres of air at a rate of 100 mL/min for 100 minutes using multi-sorbent sampling tubes located in the middle of the living room or family room of the house [34,49].

Furthermore, as part of a program of vapour intrusion mitigation at a site (Redfield) in Denver, Colorado, a total of 375 indoor air samples were collected in 1998 from about 100 residences after installation of sub-slab depressurisation systems. Because these mitigation systems were designed and installed to interrupt the vapour intrusion pathway (and on-going monitoring demonstrated their effectiveness for controlling the subsurface vapours), the interpretation provided was that the indoor air concentrations were representative of background indoor air with no vapour intrusion [34, 50].

Moreover, Sexton et al. [51] measured exposures to VOCs delivered to healthy, non-smoking adults in three Minneapolis/St. Paul metropolitan neighbourhoods with different outdoor VOC profiles.

| Laboratory | Dry weight of paint ^a (mg·cm) ⁻² | Paint thickness ^b (µm) | |
|---------------------------------|--|-----------------------------------|-------------------|
| | | mean | Std. dev. |
| 1 | NR | 46.3 | 6.2 |
| | NR | 40.8 | 6.5 |
| 2 | 15.3 | 89.5 ^c | — |
| | 13.5 | 83.5 ^c | — |
| 3 | 10.8 | 53.0 | 6.5 |
| | 10.1 | 56.1 | 5.4 |
| 4 | 8.2 | 39.1 | 4.7 |
| | 7.4 | SNR | — |
| 5 | 31 | 107 | 15 |
| | 33 | 123 | 16 |
| 6 | 10 | 43.4 | 5.3 |
| | 13 | 65.6 | 9.2 |
| 7 | 17.7 | 58.7 | 3.3 |
| | 17.3 | 50.8 | 3.5 |
| | 15 | 56.9 | 1.6 |
| | 15 | 52.1 | 1.4 |
| 8 | NR | 80.8 | 13.5 |
| | NR | 59.0 | 7.8 |
| 9 | 12.5 | 60.8 | 4.5 |
| | 9.5 | 52.2 | 5.5 |
| 10 | 30 | 103 | 13 |
| | 30 | SNR | — |
| 11 | 51.7 | 56.0 | 5.5 |
| | — | — | — |
| 12 | 8.4 | 65.2 | 8.9 |
| | 9.0 | 65.0 | 4.9 |
| 13 | 10.3 | 68.6 | 2.4 |
| | 10.2 | 60.2 | 2.7 |
| 14 | 11.5 | 69.3 | 4.9 |
| | 11.5 | 64.7 | 4.5 |
| 15 | — | — | — |
| | 28.9 | SNR | — |
| 16 | 21 | S | N |
| | 22 | SNR | R |
| 17 | 12.3 | SNR | — |
| | — | — | — |
| 18 | 26.8 | 70.6 | 18.0 |
| Mean of all runs ^{d,e} | | 18.9 ± 11.6 | — |
| Mean of selected runs | | 12.1 ± 2.9 | 60.5 ^d |

- a. Reported by the participants; NR = not reported.
 b. Measured at the Environment Institute (Ispra) by digital film gauge; SNR = sample not received.
 c. Glass plate, measurement by material profiling technique.
 d. Runs for which the mean paint thickness was in the range between 50.8 and 70.6 µm.
 e. With exception of the two values reported by laboratories ns. 11 and 18, which are outliers.

Table 4. Thickness of the paint samples (adopted and modified from ECA report no 16, 1995 [25]).

They combined indoor air data from the three neighbourhoods and reported statistics for the combined data set [34].

Finally, as part of a multiyear characterisation of a vapour intrusion site (Colorado Department of Transportation Materials Testing Laboratory [CDOT MTL]) in Denver, Colorado, indoor air was sampled in residences after installation of sub-slab depressurisation systems. Over 400 indoor air samples were collected from October 1998 through June 2001 from 21 single-family homes, 8 town homes, and 12 apartment buildings. Only samples with non-detectable levels (at a method detection limit of 0.011 µg/m³) of 1,1-dichloroethylene, the primary groundwater contaminant, were compiled for this characterisation of background indoor air.

This data screening approach effectively excluded any contribution of vapour intrusion to the indoor air in these samples. Most of the

| Material and compound | ECA-IAQ 1 st or 2 nd comparison | | VOCEM Comparison | |
|---------------------------|--|------|---------------------|------|
| | Min-max | mean | Min-max | Mean |
| PVC | | | | |
| phenol | 32-41 | 37 | 29-38 | 33 |
| 1,2,4-trimethylbenzene | 31-36 | 33 | - | - |
| n-decane | 41-47 | 43 | - | - |
| n-undecane | 39-44 | 41 | - | - |
| 2-(2-butoxyethoxy)ethanol | - | - | 22-40 | 29 |
| C7 alkylbenzene | - | - | 23-46 | 37 |
| C8 alkylbenzene-1 | - | - | 50-72 | 63 |
| C8 alkylbenzene-2 | - | - | 46-56 | 52 |
| n-tetradecane | - | - | 38-49 | 44 |
| C9 alkylbenzene | - | - | 62-76 | 70 |
| TXIB | - | - | 78-97 | 86 |
| Σ unidentified compounds | 36-49 | 43 | 36-46 | 40 |
| Paint | | | | |
| 2-(2-butoxyethoxy)ethanol | 100-225 | 135 | - | - |
| 2-(2-butoxyethoxy)ethanol | - | - | 61-105 | 75 |
| Texanol | 66-143 | 99 | 8.2-45 | 27 |
| Σ unidentified compounds | - | - | 60-77 | 66 |
| Carpet | | | | |
| n-decane | - | - | 51-103 | 74 |
| n-undecane | - | - | 10-34 | 23 |
| n-dodecane | - | - | 13-27 | 23 |
| 2-phenoxyethanol | - | - | 87-95 | 91 |
| n-tridecane | - | - | 29-38 | 33 |
| Σ unidentified compounds | - | - | 53-70 | 60 |

Table 5. Summary of result dispersion in the VOCEM comparison on material emission and in the two previous ECA-IAQ comparisons [c.v.% of SERa] (adopted and modified from ECA report no 21, 1999 [27]).

single-family homes sampled had basements, and many also had attached garages [34,52].

As a conclusion of the studies reported from U.S. Environmental Protection Agency (U.S.-EPA), some chemicals, notably the petroleum hydrocarbons benzene, toluene, ethylbenzene and xylene, as well as, the chlorinated hydrocarbons carbon tetrachloride, chloroform, tetrachloroethylene, and others, are frequently detected in background indoor air [34]. Evaluation of the background indoor air concentration summary statistics (i.e., percentiles) suggests that typical background VOC concentrations are log-normally distributed and vary considerably within and among the studies.

This variation can be attributed to differences in the date of the study, sampling methods, geographic settings, and climatic conditions, as well as variations in house air exchange rates, consumer habits, and outdoor air concentrations [34]. The large range of concentrations within and among the studies reviewed supports the use of concentration distributions rather than a single measure of the distribution, as a “typical” value, to characterize background concentrations in indoor air. Time trends in the background indoor air concentration statistics reported in the studies reviewed for this technical report suggest that indoor air quality appears to have been improving over time in the United States and Canada [34].

The indoor air concentrations measured in individual studies

| Reference | Study Location | Sample Dates | Season | No. of Samples | Available Data(Statistics) | Collection Device | Collection Period | Analytical Method ^a |
|--|---------------------------|--------------|----------------------|----------------|---------------------------------------|-------------------------------------|-------------------|--------------------------------|
| Studies included in the compiled summary of statistics (15 studies) | | | | | | | | |
| Weisel (2006) | NJ | 2004–2005 | Varies | 100 | Population Stats (25/50/75/90/95/Max) | Summa canister | 24 hours | EPA TO-15 |
| NYSDOH (2006) | NY | 1997–2003 | All | 400 | Population Stats (25/50/75/90/95/Max) | Summa canister | 2 hours | EPA TO-15 |
| Rago et al. (2004, 2005) | MA | 2004–2005 | Spring, Fall | 100 | Population Stats (25/50/75/90/Max) | Summa canister | 24 hours | EPA TO-15 |
| Zhu et al. (2005) | Ottawa, CA | 2002–2003 | Winter | 75 | Population Stats (50/75/90/Max) | Sorbent tube, active sampler | 1.7 hours | GC/MS |
| Sexton et al. (2004) | Minneapolis, MN | 1999 | Spring, Summer, Fall | 292 | Population Stats (50/90) | Charcoal passive sampler | 48 hours | GC/MS |
| Foster et al. (2002) | Denver, CO | 1998–2001 | All— Quarterly | 427 | Population Stats (25/50/75/90/95/Max) | Summa canister | 24 hours | EPA TO 14/15 SIM |
| Kurtz and Folkes (2005) | Denver, CO | 1998–2001 | All— Quarterly | 282 | Population Stats (50/90/95/Max) | Summa canister | 24 hours | EPA TO 14/15 SIM |
| Van Winkle and Scheff (2001) | Chicago, IL | 1994–1995 | All | 48 | Population Stats (50/90/Max) | Summa canister | 24 hours | EPA TO-14 |
| Clayton et al. (1999) | Midwest States | 1995–1997 | All | 395 | Actual Data (25/50/75/90/95/Max) | Passive sorbent sampler | 6 days | GC/MS |
| Gordon et al. (1999) | AZ | 1995–1997 | All | 185 | Population Stats (50/75/90/Max) | Passive sorbent sampler | 6 days | GC/MS |
| Mukerjee et al. (1997) | Brownsville, TX | 1993 | Spring | 9 | Population Stats (50) | Multi-sorbent active canister | 24 hours | GC/MS |
| Heavner et al. (1996) | Mt. Laurel, NJ | 1992 | Winter | 61 | Population Stats (50/Max) | Active multi-sorbent sampler | 14 hours | GC/MS |
| Heavner et al. (1995) | Columbus, OH | 1991 | Winter | 24 | Population Stats (50/Max) | Multi-sorbent sampler w/ pump | 3 hours | GC/MS |
| Sheldon et al. (1992) | Woodland, CA | 1990 | Summer | 125 | Population Stats (25/50/75/90/Max) | Canister and active sorbent sampler | 24 hours | GC/MS |
| Pre-1990 Studies evaluated but not included in the compiled summary of statistics (3 studies) | | | | | | | | |
| U.S.-EPA (1987a) | Los Angeles, CA (1) | 1984 | Winter, Summer | 111 | Population Stats (25/50/75/90/95/Max) | Tenax | 12 hours | GC/FID |
| | Contra Costa, CA (2) | 1984 | Summer | 68 | Population Stats (25/50/75/90/95/Max) | Tenax | 12 hours | GC/FID |
| U.S.-EPA (1987b) | Elizabeth and Bayonne, NJ | 1981 | Fall | 348 | Population Stats (25/50/75/90/95/Max) | Tenax | 12 hours | GC/FID |

Table 6. Summary of Background Indoor Air Quality Studies (1981–2005) selected for Evaluation (adopted and modified from U.S.-EPA report no 530-R-10-001, 2011 [34]).

a. GC/FID = gas chromatography/ flame ionization detection; GC/MS = gas chromatography/mass spectrometry; SIM = selected ion monitoring.

conducted between 1990 and 2005 and compiled here are considerably lower than those measured during earlier periods. This is a finding that is consistent with other publications [34,49,53,54].

Analysis Techniques on VOCs Determination

Strategy for indoor air sampling

Indoor air concentrations of VOCs are influenced by many factors. In addition to the input rate of the chemicals from their source, concentrations are also influenced by the degree of ventilation in the building and the input rate of other sources inside and near the building.

In order to delineate the indoor air sampling strategy, the major factors that influence the contaminant concentrations in indoor air must be considered. Such factors are the following [55]:

Outdoor air: outdoor air contaminant concentrations will influence to some degree the indoor air concentrations of contaminants. In addition, the particular air exchange rate in which outdoor air replaces indoor air is influenced by a number of factors including proximity to outdoor sources of pollution, meteorology and the topography of the surrounding area.

Indoor air sources: indoor air sources of VOCs are numerous, since VOCs are emitted from a variety of household products and activities of residents. VOCs have been shown to outgas from a large variety of building materials such as pressed-wood products and fibre board, and to be released from a large number of household products such as cleansers, insecticides and solvents, hobby supplies such as paints, glues, etc. and personal products including deodorants, cosmetics, sprays, etc. Cigarette smoke is known to contain many VOCs which may concentrate in indoor air. Factors which influence indoor source strength include usage patterns of occupants, age of emitting material, temperature and relative humidity.

Meteorological factors: meteorological factors influence the penetration and distribution of pollutants into a structure as well as its air exchange rate. Four important parameters to consider include temperature, wind, barometric pressure and moisture.

Air exchange rate: The rate at which outdoor air replenishes indoor air is known as the air exchange rate. The air exchange rate in a building is mainly determined by three processes, including infiltration, natural ventilation and mechanical ventilation.

Location and characteristics of groundwater and soil gas contamination: The concentration level of these contaminants in groundwater is the first important variable. In addition, Henry's Law coefficients provide an indication of their tendency to partition from the groundwater to the air spaces in the overlying soil.

Pollutant depletion mechanisms: VOCs in the indoor air may be removed from the air through a number of mechanisms including atmospheric conversion, in which the compound undergoes a chemical transformation, or adsorption of the volatile onto indoor surfaces.

Features of buildings and surrounding grounds: every building has unique features that influence how contaminants may enter and be distributed through it. Important factors which may influence these parameters include building size (area of building footprint and area of below-grade walls), construction type (slab-on-grade, crawl-space or basement), basement wall construction type (poured concrete or hollow block and number of stories) and the presence of obvious cracks in floors or walls in contact with soil [56]. The type of ground cover

(e.g., grass, pavement, etc.) outside the building may also influence concentrations of VOCs in indoor air. Impermeable ground covers such as pavement may cause vapours to accumulate in these areas.

Successful sampling should yield a representative estimate of contaminant concentrations in the indoor air of the building for the exposure period while the above mentioned factors must be considered because of their influence in airflow and the concentrations of chemicals in the indoor air. As a result, contaminant concentrations are likely to fluctuate to some extent on a continuous basis.

However, certain sampling conditions are not controllable by the investigator whereas others are totally influenced by the activities and actions of the occupants. Ultimately, sampling conditions should be established which will reflect a balance between targeting the questions that need to be answered for that situation and meeting a realistic timetable for the project.

In respect to MADEP [57] methodology for the determination of Air-Phase Petroleum Hydrocarbons (APH), several types of indoor air sampling locations termed "sample location zone categories" are defined. The sampling categories and nomenclature are given in Table 7 [55].

Analytical methods for VOCs' determination

Selection of a sampling method for use in conducting an indoor air study is dependent on the objectives of the study, the contaminants of concern and the required sampling duration. The methodology should be able to detect compounds at ambient levels, generally in the part per trillion (ppt) to part per billion (ppb) range for environmental samples. The methodology should produce results which are accurate and reproducible with a minimum of artifactual and contamination problems and should allow for sampling periods which are representative of occupants' exposure time.

These methodologies range in sophistication from screening methods which use direct-reading instruments with relatively low precision and accuracy to collection methods which are the most precise and accurate. There are also analytical field methods that involve aspects of both the direct reading and collection methodologies. Strictly speaking, direct-reading methods and analytical field methods are all categorized as "analytical methods". Analytical methods incorporate air sampling as well as on-site detection and quantification of chemical compounds. These methods differ from other collection methods that can typically achieve a more sensitive quantification limit. VOCs collection methods involve the concentration or collection of the compound into a container or onto some kind of sorbent material for later analysis.

Each of the above monitoring methods can involve either active or passive sampling techniques. Active sampling involves using a pump to actively pass air through a sorbent cartridge or collection filter or into an air sample container. Passive sampling of VOCs relies on the kinetic energy of gas molecules and diffusion of the gases in an enclosed space onto a sorbent medium. Table 8 summarizes the air monitoring techniques.

As already discussed, there are a variety of techniques that can be used to measure levels of contaminants in indoor air. A number of these techniques have been incorporated into formal methods that have been developed for identification and quantification of pollutants in air. The U.S.-EPA Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air [58,59] (also commonly

| Sample Location Zone Category | Definition |
|-------------------------------|--|
| Zone A | Samples are obtained at vapour entry points into a building (e.g., breach in foundation, sump hole). Samples are used to identify areas of point- source vapour emissions into impacted structures and/or for investigative/health screening purposes; typically, an instantaneous grab sample, though sample volume may need to be metered to avoid overwhelming the analytical system. |
| Zone A-1 | Soil gas samples. Samples are obtained from temporary or permanent subsurface probes; typically an instantaneous grab sample, though sample volume may need to be metered to avoid overwhelming the analytical system. Care must be exercised to avoid short-circuiting the sample pathway by the use of a high sampling vacuum or flow rate. Care must also be exercised to avoid or prevent entrapment of groundwater. |
| Zone B | Samples taken in unoccupied (and unfinished) areas on building levels in contact with the soil. Little personal exposure is expected. This sample could be an instantaneous grab or time integrated sample. |
| Zone C | Samples taken in occupied finished part of the building level in contact with the soil. Some personal exposure could be expected, depending on the extent of the area's use. This should be a time-integrated sample. |
| Zone D | First floor living area. Personal exposure level depends on percentage of time occupied and whether sleeping quarters are located on this level. Time-integrated samples are appropriate. |
| Zone E | Second or higher floors. Occupied during sleeping or other hours. This zone needs to be considered if there is a major contaminant situation, if there is a direct-air connection with the level of entry or if it is occupied by an unusually sensitive receptor. Time-integrated samples are appropriate. |
| Outside/Ambient | Used to assess the influence and impacts of outdoor air quality on indoor air quality. Also can be used as an additional quality control sample because background ambient air concentrations of volatile petroleum hydrocarbons are at well-documented average levels at most locations. Time integrated samples are appropriate. |

Table 7. Sampling categories and nomenclature (adopted and modified from MADEP, 2000 [57]).

| Technique | Example Instrument/Method | Positive Features | Negative Features |
|---------------------------------------|----------------------------|---|--|
| Analytical (Screening) Methods | | | |
| Direct-measuring | Organic vapor analyzer | - On-site detection and quantification | - Low sensitivity |
| | Photo-ionization detector | - Capability of catching concentration excursions | - Low specificity |
| Field/Analytical | Portable gas chromatograph | - On-site detection and quantification - Allows use of simple collection device such as a Tedlar bag - Better detection capability than the direct-measuring techniques | - Usually considered a "screening" method because does not involve identification using a mass spectrometer |
| Collection Methods | | | |
| | Evacuated canisters | - Capability of taking multiple aliquots for analysis | - More expensive than adsorbent tube method - May require special handling to prevent sample deterioration during transport to lab for analysis |
| | Adsorbent media tubes | - Less expensive than evacuated canister method | - May be subject to "breakthrough" problems - May require special handling to prevent sample deterioration during transport to lab for analysis |
| | Passive badge sampler | - Can monitor longer-term period of time - Relatively inexpensive | - Higher humidity can produce erroneous results - Possible back- diffusion off sampling medium - Possible interferences between compounds |

Table 8. Summary of some general air monitoring techniques (adopted and modified from MADEP, 2002 [55]).

referred to as the "TO methods") and the Compendium of Methods for the Determination of Air Pollutants in Indoor Air [60] also commonly referred to as the "IP methods") are the most commonly used methods for indoor air sampling and analyses. The VOC IP methods are essentially the same as the comparable TO methods (e.g., TO-1, TO-2, TO14/15/17, etc.) which have been adapted to the indoor application [55]. In addition, MADEP has recently developed a method for the determination of the volatile fraction of petroleum hydrocarbons in air (e.g., the air-phase petroleum hydrocarbons - APH) [57].

The TO methods (method TO-1 - TO-17) were developed for ambient air studies but can be easily adapted for use in conducting

indoor air studies. In MADEP's experience, Methods TO-1, TO-2, TO-14, TO-15, and TO-17 are the most commonly used TO methods for the sampling and analysis of indoor air impacted by contaminated waste sites. A summary of these most commonly used methods and the types of compounds for which they are appropriate is included in Table 9 [55].

In addition to the U.S.-EPA Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air (TO methods) a number of existing ISO standards for indoor products emission testing are also available. The ISO 16000 series of standards of particular interest are summarized in Table 10.

| List of TO Methods | Description | Types of Compounds Determined |
|---|--|--|
| TO-1 | Tenax GC Adsorption and GC/MS or GC/FID Analysis | Volatile, nonpolar organics (e.g., aromatic hydrocarbons, chlorinated hydrocarbons) having boiling points in the range of 80 °C to 200 °C. |
| TO-2 | Carbon Molecular Sieve Adsorption and GC/MS or GC/FID Analysis | Highly volatile, nonpolar organics (e.g., vinyl chloride, vinylidene chloride, benzene, toluene) having boiling points in the range of -15°C to 120°C. |
| TO-14 | Specially-Prepared Canister and GC/FID/ECD or GC/MS Detection | Volatile, non-polar organics (e.g., toluene, benzene, chlorobenzene). |
| TO-15 | Specially-Prepared Canister and GC/MS Analysis | Volatile, polar and non-polar organics (e.g., methanol, benzene, xylene, nitrobenzene). |
| TO-17 | Multi-Bed Adsorbent Tube Followed by GC/MS | Volatile, polar and non-polar organics (e.g., alcohols, ketones, benzene, toluene, o-xylene, chlorobenzene). |
| MADEP Air-Phase Petroleum Method | | |
| APH | Summa® Passivated Canister; Sampling and C/MS Analysis | Air-phase petroleum hydrocarbon fraction analysis. |
| List of IP Methods | | |
| IP-1A | Stainless Steel Canister | Volatile organics (e.g., aromatic hydrocarbons, chlorinated hydrocarbons) having boiling points in the range of 80°C to 200°C. |
| IP-1B | Solid Adsorbent Tubes | Same as above. |

Table 9. List of sampling and analytical methods applicable to indoor air (adopted and modified from U.S.-EPA, 1984; MADEP, 1999; U.S.-EPA, 1990; MADEP, 2002 [55,58,60,61]).

| Code and year of establishment | Content |
|--------------------------------|--|
| ISO 16000-3 (2001) | Concerning active sampling of formaldehyde and other carbonyl compounds and analysis by liquid chromatography (HPLC). |
| ISO 16000-6 (2004) | Concerning active sampling of VOC on Tenax TA and analysis by gas chromatography. |
| ISO 16000-9 (2006) | Indoor air – Part 9: Determination of volatile organic compounds from building products and furnishing – Emission test chamber method. |
| EN ISO 16000-11 (2006) | Concerning the procedures for sampling, storage and preparation of test specimens. |
| ISO/FDIS 16000-28 (2011) (E) | Concerning determination of odour emissions from building products using test chambers. |
| ISO16000-6 (1989). | Volatile organic compounds in air analysis. |

Table 10. ISO 16000 series of standards for VOCs sampling and determination.

Most of the available analytical methods use either gas chromatography (GC) or high performance liquid chromatography (HPLC) to separate analytes in a mixture of compounds, and then use detectors to identify individual compounds. In GC, the mobile phase is an inert gas, usually helium. The mobile phase is used as a carrier gas to move compounds along the analytical column. Modern GC methods use very long, flexible, capillary columns which provide excellent resolution and speed for the analysis of complex mixtures of chemicals often found in ambient and indoor air samples.

In HPLC, liquids are used as mobile phases that allow an analyst to control the sorption characteristics more precisely. The mobile phase can be polar, for example, acetonitrile, or non-polar, for example hexane. The ability to manipulate the polarity of the mobile phase constitutes a very powerful tool for the analytical chemist and allows for better control over resolution and retention time.

Once a mixture of chemicals has been separated by chromatography, each compound can then be identified by passing the air sample through a detector. Several types of detectors are available to identify and quantify air toxics. The choice of the most appropriate detector depends on the structural characteristics of the compounds being identified and the required detection limits. Ultraviolet (UV) detectors have been used most extensively in HPLC work. However, Infrared (IR) detectors have been used to characterize hydrocarbons, oils and grease [55].

The flame ionization detector (FID) is the most widely used one in air toxics analysis as well as other environmental analyses and responds to most organic compounds. The photoionization detector (PID) is used to provide selectivity in a chemical analysis for compounds that have ionization potentials that fall within certain boundaries. The electron capture detector (ECD) exploits the ability of certain compounds to capture electrons and uses this attribute to provide selectivity and sensitivity. A nitrogen-phosphorus detector (NPD) is a detector that has been optimized to respond to compounds containing nitrogen and phosphorous [55].

Mass spectrometry (MS), especially when coupled with high-resolution gas chromatography (GC/MS) has certain advantages over other detectors like PID and FID that are commonly used in environmental analysis.

One of the most useful features of MS is the generation of a mass spectrum for each individual compound that is unique for each compound and serves as a type of fingerprint of each compound. An important feature of an MS detector, is that it is able to discriminate between compounds that coelute during gas chromatography [55].

Electron Impact (EI) is currently the most commonly used technique for ionizing compounds that elute from GC columns into the ionization chamber of a mass spectrometer. Most of the Toxic Organics (TO) methods use a mass spectrometer as the ultimate detector. Mass spectrometry provides a level of confidence in the identification of

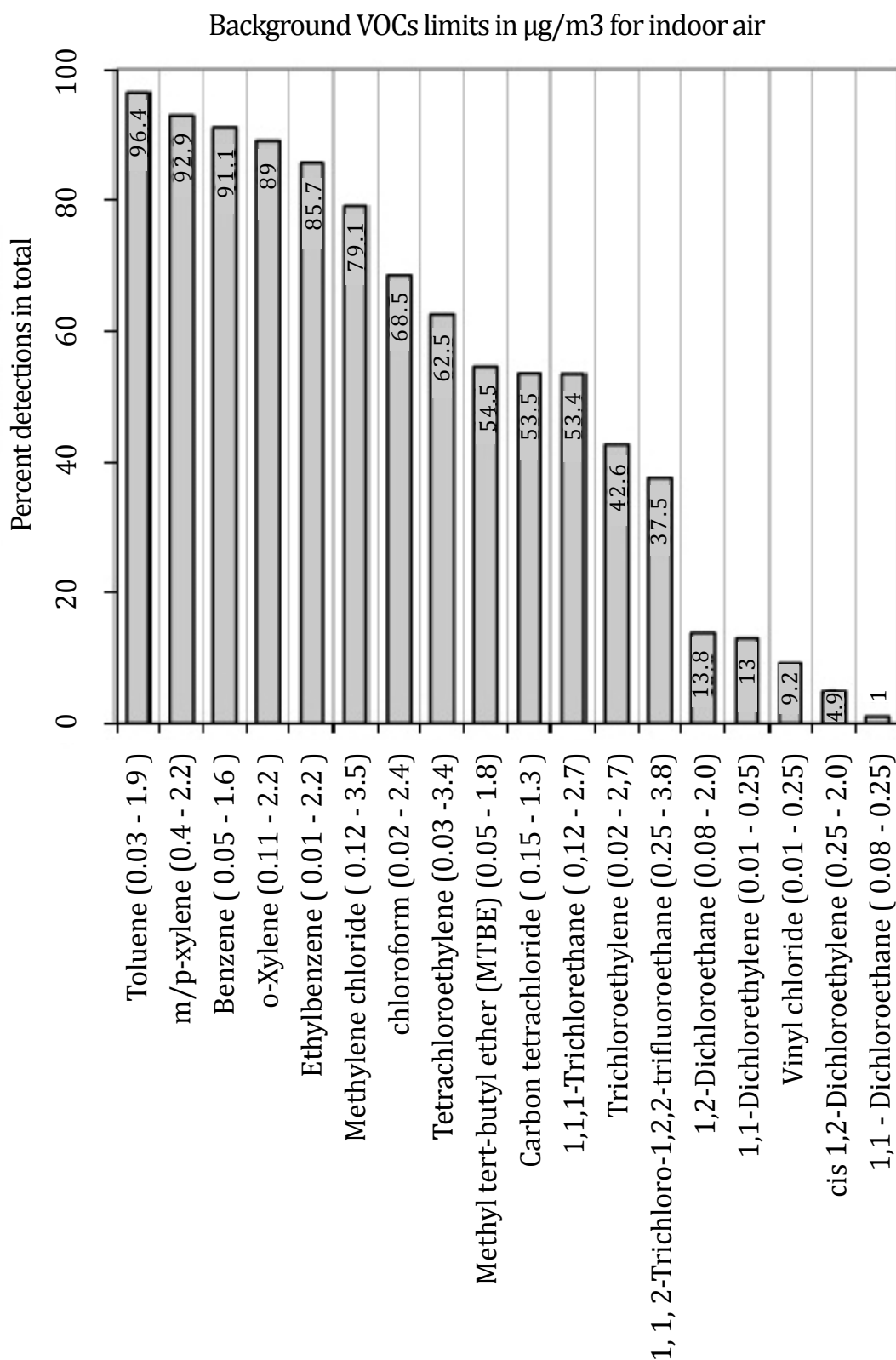


Figure 1. Total percent detections of common VOCs in background indoor air compiled from 15 studies conducted between 1990 and 2005. Range of reporting limits is shown in parentheses (adopted and modified from U.S.-EPA report no 530-R-10-001, 2011 [34]).

unknown analytes that none of the other techniques described here can provide [55].

Conclusion

Indoor Air Quality and VOCs emissions from building and household materials have been a major challenge for scientists, industry and consumers over the last decades. In response to the need for improved consumer protection much research has been conducted regarding VOCs determination in indoor air because of their effects to human health. A series of protocols and methodologies have been developed from national and international research schemes in order to achieve common indoor air sampling strategies and VOCs quantitative analysis.

To accomplish this task, the European Commission established the *European Collaborative Action on Urban Air, Indoor Environment and Human Exposure* and for more than 22 years now the *European Collaborative Action ECA "Indoor Air Quality and its Impact on Man"* has been implementing a multidisciplinary collaboration of European scientists. The result is the establishment of standardized methods regarding the sampling, the analysis, the data handling and the evaluation of the VOCs concentration indoors which have been published in a series of reports.

In parallel, a number of techniques have been incorporated into formal methods that have been developed for identification and quantification of pollutants in the air. The EPA Compendium of Methods referred to as "TO" and "IP" methods corresponding to the quality of ambient and indoor air respectively, are commonly employed to sample and analyze indoor air. Additionally, a number of existing standards for indoor products emission testing are available. The ISO 16000-6, -9 and -11 series of standards are used for VOCs determination indoors.

The selection of the appropriate methodology is a function of the analytes of interest and the required specificity and sensitivity. In addition, the selection of a sampling method is dependent on the objectives of the study, the contaminants of concern and the required sampling duration, while many factors must be considered in order to achieve reliable and reproducible results on indoor air VOCs determination.

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