

EUROPEAN COLLABORATIVE ACTION
INDOOR AIR QUALITY & ITS IMPACT ON MAN

Environment and Quality of Life

Report No 14

**Sampling strategies for volatile
organic compounds (VOCs)
in indoor air**



European Commission
Directorate-General for Science, Research and Development
Joint Research Centre-Environment Institute

EUROPEAN COLLABORATIVE ACTION
INDOOR AIR QUALITY & ITS IMPACT ON MAN
(formerly COST Project 613)

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**Sampling strategies for volatile
organic compounds (VOCs)
in indoor air**

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Abstract

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Sampling strategies for volatile organic compounds (VOCs) in indoor air. Report No 14, EUR 16051 EN
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Strategies for sampling chemical substances in indoor air have been discussed in a previous report of this series (Report No 6). This report gives more specific guidance for the development of sampling strategies for volatile organic compounds (VOCs). The report is divided into three sections:

- a) General considerations which highlight the sampling objectives of indoor VOC measurements, the numerous sources of VOCs and their emission characteristics, the dynamic character of indoor pollution by VOCs, and the interpretation of VOC measurements in relation to health and comfort. These considerations are a prerequisite for the development of sampling strategies.
- b) Discussion of the elements of sampling strategies for VOCs. These elements include the type and number of objects (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, time and frequency, sampling and analytical methods, and quality control and assurance. The common choices of the above mentioned elements are discussed.
- c) Outline of sampling strategies, i.e. selections of the above-mentioned elements, for the more frequent sampling objectives.

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1. INTRODUCTION

A fact which is often overlooked is that the sampling and analysis of indoor pollutants are only the last steps in a process which primarily needs to establish why, where, when and under which environmental conditions an air sample should be analysed. Without a correct answer to these questions, i.e. without an appropriate sampling strategy, the results of indoor pollution measurements are at risk of being misinterpreted or even meaningless. In report no. 6 of this series (ECA, 1989b) strategies for sampling chemical substances in indoor air have been discussed. Following an introduction, the report presents

(a) general considerations regarding sampling strategies for indoor pollutants. It is pointed out that strategies need to be based on a careful definition of the sampling objective and due consideration must be given to the dynamic character of the indoor environment and, hence, of indoor air pollution. This enables a correct choice of the elements of a strategy such as the time of sampling, the sampling duration, frequency and location, and quality assurance;

(b) a short discussion of the sampling of formaldehyde, nitrogen dioxide, suspended particulate matter, asbestos, radon and volatile organic compounds. For each pollutant the discussion involves the impact of the respective sources on the sampling strategy and brief recommendations for climatic, other environmental and sampling conditions appropriate for two measurement objectives, i.e. the determination of average and of maximum indoor concentrations.

Among the pollutants considered in report no. 6, volatile organic compounds (VOCs) are of particular interest for indoor air quality. In fact, VOCs are important because

- of the many individual compounds and the resulting complexity of their mixtures in indoor air;
- the indoor concentrations of many VOCs largely exceed their outdoor concentrations;
- of the toxicological relevance of many VOCs.

As a result, VOC concentrations in indoor air are frequently determined. This report aims at giving more specific guidance than report no. 6 for the development of appropriate sampling strategies for VOCs. The report is divided into three sections:

- General considerations which highlight the definition of VOCs, the sampling objectives of indoor VOC measurements, the numerous sources of VOCs and the large variation in their emission characteristics, and the dynamic character of indoor pollution by VOCs. These considerations are a prerequisite for the development of a sampling strategy.
- Discussion of the elements of the sampling strategy. These elements include considerations concerning the type and number of objects (buildings), the selection of spaces in which the 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, time and frequency, sampling and analytical methods, and quality control and assurance. The common choices of the above mentioned elements and their rationales are outlined.

- Strategies for the more frequent sampling objectives. This third section recommends certain elements discussed in the second section which are appropriate for specific sampling objectives such as the determination of the distribution of concentrations and personal exposures or the testing of compliance with IAQ guidelines.

To some extent, the present report - in particular part of chapter 2 - is a repetition of what has already been outlined in report no. 6 of this series (ECA, 1989b). While such repetition seemed to be justified, it had to be kept at a minimum. Therefore, the reader is asked to refer to this preceding report for details on the general aspects of sampling strategies. In particular, reading the introduction and chapter 2 (general considerations) of report no. 6 is recommended.

2. GENERAL CONSIDERATIONS

Several hundred organic compounds have been detected in indoor air (Berglund et al., 1986) most of which belong to a class called volatile organic compounds (VOCs, see below). They originate from a plethora of sources with very different emission characteristics. Concentrations of organic indoor pollutants vary widely between indoor spaces and may also vary within a single space as a function of location and time. The extent of these variations depends on factors such as the type of indoor space, the emission characteristics of the sources therein (including ongoing activities), occupant behaviour and the ventilation conditions. The large variability of all these factors causes indoor air pollution and human exposure to it to be a highly dynamic process rather than a static phenomenon.

An understanding of this process is a prerequisite for giving a correct answer to the questions of where, when and under which environmental conditions an air sample should be collected, i.e. for designing an appropriate sampling strategy. A prerequisite of equal importance is knowing exactly why to make VOC measurements, i.e. the measurement or sampling objective. If, for example, the objective is to find out whether indoor air pollution contributes to complaints of acute health effects, sampling should be performed under conditions which enable the measurement of peak concentrations to which an occupant may be exposed. This means that sampling should be performed at a location, a certain point in time, for a certain duration and under environmental conditions yielding maximum exposure levels. On the contrary, the assessment of a potential contribution of VOCs to a chronic effect would require the determination of a time integrated average concentration or total exposure.

Following are a definition of VOCs, a short discussion of the sampling objectives, and of various factors rendering indoor air pollution a highly dynamic process.

2.1 Definition of VOCs

Organic indoor air pollutants are usually classified into four broad categories which have been defined by a working group convened by the World Health Organisation (WHO) as shown in Table 1 (WHO, 1989). The definition is based on ranges of boiling points. According to this definition, VOCs are volatile organic compounds which boil between 50 °C and 260 °C. However, no exact limit exists between the four categories. The reason is that in practice, the categories are determined by the methods used to sample organic pollutants from air. The most frequently applied methods are given in the last column of Table 1 (see also section 3.7 of this report). Most of these methods rely on pre-concentration of organic compounds on adsorbents and therefore the type and amount of adsorbent and the sample volume will to a certain extent influence the boiling point range of the trapped compounds. Using combinations of appropriate adsorbents very volatile (VVOCs) and volatile organic compounds (VOCs) can be sampled simultaneously, and, hence the distinction between them may even become redundant.

TABLE 1. Classification of Organic Indoor Pollutants ^A

| Description | Abbreviation | Boiling point range ^B from °C to °C | | Sampling methods typically used in field studies |
|---|--------------|---|---------|--|
| Very volatile organic compounds (incl. gases) | VVOCs | <0 | 50–100 | batch sampling, adsorption on charcoal |
| Volatile organic compounds | VOCs | 50–100 | 240–260 | adsorption on Tenax®, graphitized carbon black or charcoal |
| Semivolatile organic compounds | SVOCs | 240–260 | 380–400 | adsorption on PUF ^C or XAD-2 ^D |
| Organic compounds associated with particulate matter (particulate organic matter) | POM | >380 | | collection on filters |

^A Adapted from WHO (1989)

^B Polar compounds are at the higher side of the range

^C Polyurethane foam

^D Styrene-divinylbenzene copolymer

VOCs typically detected in indoor air belong mostly to 9 groups of compounds as shown in Table 2. Most of the compounds are used as solvents. Formaldehyde and acetaldehyde, although they do not belong to the VOC class according to the definition in Table 1 and are analyzed with a different method, have been included in this report because of their important role as organic indoor air pollutants.

Table 2. Chemical structures of VOCs most frequently detected indoors and typical representatives

| Chemical structure | Frequently detected compounds |
|--------------------------|---|
| alkanes | n-hexane, n-decane |
| cycloalkanes and alkenes | cyclohexane, methyl-cyclohexane |
| aromatic hydrocarbons | benzene, toluene, xylenes, 1,2,4-trimethylbenzene |
| halogenated hydrocarbons | dichloromethane, 1,1,1-trichloroethane, trichloroethene, tetrachloroethene, 1,4-dichlorobenzene |
| terpenes | limonene, alpha-pinene, 3-carene |
| aldehydes | formaldehyde ¹⁾ , acetaldehyde ¹⁾ , hexanal |
| ketones | acetone, methylethylketone |
| alcohols, alkoxyalcohols | isobutanol, ethoxyethanol |
| esters | ethylacetate, butylacetate, ethoxyethylacetate |

¹⁾ no VOC, see text

2.2 Objectives of a study

As already outlined in the introduction the objective of a study has an important impact on the sampling strategy. Among possible objectives, the following play the most important role:

1. Determination of the distribution of VOC concentrations and personal exposures.
2. Measurement in response to health and comfort complaints in buildings.
3. Testing of compliance with IAQ guidelines.
4. Identification of VOC sources.
5. Evaluation of remedial actions.

Each of these objectives requires a proper selection of the various elements constituting the sampling strategy such as type and number of spaces to be included in a study or the sampling method, frequency and duration. The elements of the sampling strategy are discussed in chapter 3 of this document and selections for the above mentioned objectives are suggested in chapter 4.

2.3 The dynamic character of indoor pollution by VOCs and its causes

The dynamic character of indoor air pollution in general has already been described in detail (ECA, 1989b). Indoor air pollution by VOCs is a particularly variable phenomenon: type and concentration of VOCs may change from one indoor space to another and concentrations may vary between different locations within the same space. In addition, there are short and long term variations of VOC concentrations with time. Large short term variations during working hours in offices have been reported by Grot et al. (1990), Wolkoff (1990b) and Ekberg (1993). Seifert et al. (1989) studied the extent of seasonal variations of indoor VOC concentrations averaged over two weeks in homes.

The pronounced dynamics of indoor pollution by VOCs are mainly caused by two factors: (a) the large variety of VOC sources in the indoor environment and the diversity of their emission characteristics, and (b) the wide range of ventilation conditions and air circulation patterns. These two factors are briefly discussed below.

Sources of VOCs

VOCs are emitted from a plethora of sources most of which belong to the following three categories: (a) building related materials, furniture or other inventory - (b) humans as themselves or human activity related sources - (c) outdoor sources, mostly outdoor air pollution by motor vehicles, the contribution of which to indoor air pollution is mediated and modulated by ventilation.

Sources of VOCs have different emission characteristics depending on the above mentioned categories. Emissions from sources of category a) usually are rather constant and change only very slowly with time, whereas emission from sources of category b)

show strong variation with time which may be periodic or episodic. The variability of sources of VOCs and their emissions and its impact on sampling strategy is discussed in more detail in section 3.2.

Ventilation

The ventilation process and the air circulation patterns are also important factors contributing to the dynamic behaviour of indoor air pollution. Ventilation efficiency depends strongly on ventilation type and on the position and shape of the air in- and outlets. Ventilation and air flows are changed by activities of the occupants such as the opening and closing of doors and windows or the operation of mechanical ventilation devices or sun shields. Changes of the outdoor climate around a building (wind speed and direction, temperature) influence also ventilation rates and air flows, in particular in the case of infiltration and natural ventilation. Changes of ventilation and air flow patterns are responsible for variations of indoor concentrations of VOCs as a function of time and space. Moreover mechanical ventilation systems may become indoor sources of VOCs if the air intake is placed near to an outdoor source or if they are not properly maintained.

There are many different types of indoor spaces such as offices, class rooms and other non-industrial workplaces, homes with very different spaces such as living rooms, kitchen, bathrooms, bedrooms and hobby rooms, buildings associated with vehicle use and adjacent to traffic. Many of these spaces have very typical VOC sources such as correction liquids or office equipment in offices, dish washing detergents or cooking in kitchens, and hot water or personal hygiene products in bathrooms. Consequently, indoor air pollution will usually change as one moves from one space to another.

2.4 Interpretation of VOC measurements in relation to health and comfort

It is known from the work environment and has been shown by many investigators that high levels of VOCs can have an impact on human health and comfort. However, the interpretation of VOC measurements in indoor environments in terms of potential effects of VOCs on health and comfort of the occupants is in general a difficult task. The most important difficulty results from a lack of toxicological information on VOCs at indoor concentrations. Although it is known from occupational hygiene that a considerable number of VOCs may cause irritation or other acute effects, these effects have usually been observed at concentrations which are several orders of magnitude higher than those measured in indoor air. For most of the several hundred identified VOCs in indoor air only very limited toxicological information is available and only few air quality guidelines for indoor concentrations of VOCs exist. Also very little information is yet available on effects of mixtures of VOCs usually observed indoors. In addition there are large differences between the sensitivities with which individuals react to VOCs.

It has been suggested (Cain and Cometto-Muniz, 1993) that some apparent "neurotoxic" reactions to atmospheric agents may result secondarily from the distraction or reduced

attention caused by sensory stimulation. In human and animal studies, the irritation thresholds for individual VOCs occur at one to three orders of magnitude higher concentrations than the respective odour thresholds, yet the two threshold levels are closely correlated. Both threshold levels decrease as the length of the carbon chain increases. It is therefore conceivable that in relation to short term health effects the odour detection/intensity of VOCs in indoor air can directly be a useful predictor of non-specific symptoms.

Because of the lack of toxicological information, often concentrations of VOCs are compared in complaint and control houses or sites in order to find out whether a correlation between VOC concentrations and complaints (or specific building characteristics) exists. In this case a difficulty may result if concentrations of many VOCs are compared simultaneously. As pointed out in section 3.1, significant differences between the concentrations of some VOCs may be detected just by chance. Therefore a correct interpretation of the results requires a due consideration of the significance level of the detected differences. On the other hand, because of the dynamic character of indoor VOC pollution (see section 2.3), correlations between VOC concentrations and complaints may be obscured if the measurements of both are not performed simultaneously (Hodgson et al; 1991).

If the impact of VOC pollution on health or comfort of the general population or a specific population group has to be assessed a particular difficulty results from the fact that many VOCs have indoor concentrations with a very skewed non-normal distribution. Particularly the extreme values in the tail of the distribution may be of interest. As outlined in section 3.1, special, stratified study designs may be required in order to achieve sufficient statistical power for a correct assessment of the high end of the VOC concentration distribution.

For all these reasons one should realise, that although VOCs may be a co-factor in the etiology of symptoms or complaints, their measurement in problem building studies will rarely give a clear indication thereof.

3. IMPORTANT ELEMENTS OF A SAMPLING STRATEGY

The elements that determine the study strategy can be derived from the objectives of the study as outlined in section 2.2, in combination with the factors that determine the dynamics of the processes that govern indoor VOC levels as described in section 2.3. Given the limited amount of resources available for a study, decisions have to be made about which indoor environments to study, how many of these environments to include, how often and how long to sample, and under what conditions to sample, which VOCs to determine, which methods to use, what level of quality assurance, etc. Consideration of these questions will be discussed in more detail in the following sections of this chapter.

Other questions that also have to be addressed in developing the sampling strategy are the following:

- Is the study providing answers that are valid for the objectives?
- Are we measuring what we want to measure?
- Are the requirements of precision of the study results met?

Aspects related to quality control and quality assurance will be dealt with in section 3.8.

3.1 Types of indoor environments and sample size

Indoor environments and spaces

There are numerous types of indoor environments that are used by the general public. An indoor environment may be understood to be an entire building or a part of a building which is separated from the rest of the building and independent as far as ventilation and/or air conditioning is concerned. Examples of parts of a building as suggested here are apartments or wings of an office building with a separate ventilation or air conditioning system. Examples of indoor environments are residential buildings, public gathering places such as nursery schools, schools and offices, transportation means such as cars, trains and aeroplanes, recreational vehicles as mobile homes and leisure boats. Each type of indoor environment has different characteristics. Types and number of sources, source use, ventilation, mixing volume, sinks, type of occupants, occupant behaviour and the like can all be different and put a variety of constraints on the study design.

As mentioned in section 2.3 the large variety of VOC sources in the indoor environment and the wide range of ventilation conditions and air circulation patterns are partially interrelated. Some human activities, which frequently represent a source of indoor VOC pollution, are typically performed in a distinct indoor environment such as cooking in homes or use of correction liquids or copying machines in office buildings. Mechanical ventilation is more common in office buildings than in homes. The opposite is true for natural ventilation. Mechanical ventilation systems may become indoor sources of VOCs if the air intake is placed near to an outdoor source or if they are not properly

maintained. The design of a strategy for VOC measurements must therefore be based on a careful consideration of the sources likely to be encountered.

The home is the single most important exposure source due to the substantial amount of time that is spent there by virtually the entire population. Generally more than 50 % of the time is spent in the home, with subgroups like infants, elderly and diseased people spending even more of their time in the home.

Offices and schools are also places where a considerable part of the population gets exposed daily to VOCs during several hours over periods of years.

Basically all children go to school during the period when their bodies are developing and exhibit a relatively higher metabolism than adults. In some countries an increasing incidence of hyper-sensitivity among school children has been observed. Children are therefore considered a special risk group, although it is still not conclusively demonstrated to what extent exposure to VOCs is involved.

Mobile homes, recreational vehicles and boats are objects of particular interest due to the small volume and unfavourable surface area to volume ratio under which people are staying there. Although few people spend prolonged periods of time in recreational indoor environments, concentrations of VOCs may be relatively high.

Sample size

The sample size is an important determinant of the precision of a study. For instance, the precision of the mean value of the VOC level estimated from a sample of homes is given by the standard deviation which usually decreases with the number of samples taken. Thus, when the sample size increases the precision of the estimated sample mean value increases.

Many VOCs, however, have indoor levels with a skewed non-normal distribution, as have many other indoor pollutants. Particularly the extreme values in the tail of the distribution might be of interest to the investigator. A reliable estimate of this part of the distribution might require a large sample size (in the order of a hundred houses or more). Since only few houses will have these extreme indoor levels, the chance of finding such a house in the sample is very small. This can be remedied with pre-existing knowledge of important determinants of indoor VOC levels and their occurrence in the housing stock. Stratification of the sample for these determinants and over-sampling of houses with determinants of high indoor VOC levels will provide a more efficient way of estimating the high end of the distribution. Thus, the number of homes to be sampled can be reduced. When the distribution of the relevant determinants is known and the sample is carefully stratified for these determinants, the complete distribution can be obtained.

In the case of the evaluation of health complaints, two situations can be distinguished. In one situation, there is little information available on which agent(s) might cause the complaint. VOC measurements will then be a kind of 'fishing expedition' where one

collects samples and waits to see which VOC turns up at what concentration. In a given situation a considerable sample size is necessary to obtain a reasonable statistical power for testing whether or not the observed VOC concentrations are extreme compared to a common distribution of indoor VOCs. Special attention should be paid to the problem of multiple comparisons. When 100 individual VOC components in complaint houses are tested versus a set of control houses using a significance level of 5 %, by definition about 5 of these VOCs will have levels that are (statistically) significantly different from the controls, due to chance alone. The chance to find one VOC at levels higher than normal is over 50 %.

In another situation, when a specific single VOC or group of VOCs is suspected to be related to the complaints, or when clear quality guidelines are exceeded, the above mentioned problems are less important. In both situations, however, the needed statistical power (the chance of finding a difference, if it exists, combined with the chance of finding it even if there is no difference) should be given due consideration prior to the measurements (and be communicated in connection with the complaints).

3.2 Types of sources

As outlined in section 2.3, potential indoor VOC sources are mainly related to building materials and furnishings, to human activities (cleaning, painting, gluing, smoking,...) and to outdoor air quality. In addition, VOC emissions can be characterised by both temporal and spatial patterns. Three different types of temporal VOC emission patterns can be distinguished (Seifert and Ullrich, 1987): constant, periodic and episodic. Some sources of VOCs are relatively constant in time (building materials) and others episodic (activity related sources such as consumer or hobby products) with both regular and irregular time patterns. Combustion sources, by contrast, are almost always episodic. Table 3 gathers examples of sources of VOCs, their emission characteristics as regular (R) or irregular (I) and also examples of emitted VOCs.

It is also possible to divide each group of sources into two subgroups depending on whether they are point or distributed sources. Point sources often result from human activities, for example, use of household products or smoking cigarettes while distributed sources include materials such as thermal insulation products with large surface areas, furnishings, floor or wall coverings. The sources resulting from human activities have often an irregular time-pattern and they generate VOC emissions very close to the individuals.

Pollutant concentration gradients (Rodes et al., 1991) may be large in the area nearby a personal activity source (painting, gluing) in comparison to other locations in the same room. This is a very important consideration when deciding the appropriate sampling strategy to determine exposure.

Table 3. Examples of sources of VOCs, their emission characteristics and emitted VOCs

| Sources | Duration ¹⁾ of the emission and its characteristics ²⁾ | | | | Some examples of emitted VOCs |
|---|---|------------------|------------------|------------------|---|
| | conti- nuous ³⁾ | days to weeks | hours to days | mins to hours | |
| Building related materials, furniture or other inventory: | | | | | |
| Carpets | R | | | | solvents, 4-phenyl-cyclohexene |
| Wood products | R | | | | terpenes, aldehydes, wood preservatives |
| Vinyl floor | R | | | | solvents, 2,4,4-trimethyl-1,3-pentanediol diisobutyrate, ethylhexanol |
| Human activity related sources: | | | | | |
| Smoking | | | I | I | aldehydes, benzene, nicotine |
| Cleaning ⁴⁾ | | | I | I | solvents, limonene |
| Painting ⁴⁾ | | I | I | I | solvents, aldehydes |
| Appliances & equipment | | | | I | solvents, aldehydes |
| Sealing & gluing ⁴⁾ | | I | I | I | solvents |
| Outdoor sources: | | | | | |
| Traffic ⁵⁾ | R, I | R, I | R, I | R, I | aromatic hydrocarbons |

1) not considering sink effects

2) R = regular, I = irregular

3) variations of the emission rate over a 24 hour period are small compared to its mean value and are essentially monotonous.

4) emission characteristics depend on volatility of solvents.

5) "emission" to indoor air depends strongly on ventilation habits and on nearby outdoor sources

3.3 Selection of spaces within a building

Within one building different rooms generally have different VOC levels, since sources are not necessarily evenly distributed over all rooms. Transfer of pollutants from one room to the other depends on the air flow pattern in the building. In mechanically ventilated buildings this pattern may be fairly constant over time, whereas in naturally ventilated buildings air flow patterns may change with wind direction, opening or closing of ventilation provisions, windows, external or interior doors.

As the number of samples that can be taken generally is limited, the selection of spaces for sampling becomes necessary. The selection of spaces may be obvious for some study objectives e.g., if complaints are associated with a certain room, or the contribution from a specific interior source of emission is of interest. If the reason for sampling is a specific health complaint, one should also consider the possibility of using the concept of exposure sampling in a pilot study phase of an investigation.

When there is no specific guidance given, the living room and the bedroom should normally be recommended for the sampling of VOCs in a private home investigation. Although bedrooms or other rooms may be considered due to prevalent occupancy, the living room is usually the best single choice if only one space can be selected, since many of the VOC emitting processes take place there. In addition, in most studies on the occurrence of VOCs in homes the air of the living rooms has been analysed and, hence, reference data are available. Whatever room is selected, it should be kept in mind that the sample may be affected by VOCs transferred from other parts of the building. Similar reasoning for the selection of spaces has to be applied also in other types of buildings.

In mechanically ventilated or air-conditioned buildings without specific complaints, it is recommended that the sampling locations are selected carefully to ensure they are representative of the building as a whole or of the studied environment. There should at least be one sample per floor and wing or one sample per unit of rooms supplied by the same HVAC equipment or one sample for each set of rooms with the same activity. It should be considered that a significant difference in the VOC concentration may occur between the incoming air and the air in the room. On the other hand the ventilation system itself has been mentioned as one source of VOC emission.

There is normally a pronounced difference between indoor and outdoor VOC concentrations. To verify this situation and to detect the possible presence of strong external sources at least one sample of outdoor air should be collected in parallel to the indoor sample(s). This will permit a meaningful interpretation of the results, especially with regard to the identification of sources.

3.4 Environmental conditions before and during sampling

The level and homogeneity of the VOC concentration in a room depend on a number of environmental conditions mentioned earlier. Some of these conditions have a direct or indirect influence on source emissions, others influence the dilution and mixing of VOCs in a room and thus have an effect on the results. A few examples may illustrate these effects.

Source emissions may depend on temperature and surface air velocity. Occupants and their activities are sources of VOCs. When there is a strong source in a position far away from windows and doors a concentration gradient may develop. Increasing the ventilation by opening a window decreases the VOC concentration. On the other hand, if the room is mechanically ventilated the increase of the ventilation rate may improve

mixing in addition to reducing the average VOC concentration. The presence of large temperature gradients in a room may affect mixing and hence the spatial distribution of VOCs. It should also be taken into consideration that the occupants' behaviour and activities, including the sampling activity itself, may affect the sampling result. The results of the determination of VOCs in indoor air depend on the environmental conditions before and during sampling, and as they may be affected as described above, it is necessary to consider and specify these conditions before the measurement.

To what extent the environmental conditions before sampling and during sampling influence the final result of an indoor air analysis depends on the sampling duration (see section 3.6). The longer the sampling duration the less important becomes the influence of the conditions before sampling, and the more important are the conditions during sampling and vice versa. Thus, conditions before sampling will usually have a negligible influence on a sample taken over a fortnight whereas they will strongly determine the result of a grab sample taken during a few minutes.

In this context it is important to note that although some of the environmental conditions such as ventilation rate, occupancy and occupant activity may change instantaneously, the influence of this change on the VOC concentration is usually not instantaneous. Assuming that an activity is started which causes a continuous emission of VOCs and the ventilation rate is n air changes per hour, then only $t = 3/n$ ¹⁾ hours after the beginning of the activity 95 % of the steady state or maximum concentration is reached (assuming complete mixing). Similarly, it takes $3/n'$ hours after a change of the ventilation rate from a value of n to a new value of n' air changes per hour to approach the new steady state concentration c' by 95 % of the difference between c' and the starting value c .

For most sampling objectives one of the following three conditions is appropriate:

Normal conditions

Normal conditions of occupancy, activity of occupants, ventilation, temperature and humidity are considered those which would have governed at the measurement location and time if no sampling would have been performed. This includes also changes of these conditions during longer sampling periods if they would have occurred without sampling.

Sampling under such conditions is appropriate if the frequency distribution of indoor concentrations of VOCs is to be determined to obtain a picture of the normal living conditions of the population, e.g., in studies aimed at characterising the exposure of the general population. The duration of sampling is addressed in section 3.6.

1) exactly: $t = \frac{-\ln(1-0.95)}{n}$; $-\ln 0.05 = 2.9957 \approx 3$

Conditions of maximum VOC concentrations

Due to the large variability in the indoor environment it is difficult to know when you are sampling under conditions of maximum VOC concentrations. This is particularly true for short sampling periods. Therefore, longer sampling periods would be preferable. On the other hand, an activity causing a high emission only during a short period of time e.g. one hour once a week may not be detected if longer sampling intervals are being used and other sources contribute as well to the emission.

Collecting information on the maximum concentration of VOCs is especially appropriate, if the possibility of acute effects such as sensory irritation has to be evaluated. To obtain these maximum concentrations, ventilation may be reduced and/or parameters such as temperature and relative humidity may be adjusted to obtain the maximum emission. However, to avoid unrealistic situations and false interpretation of the results the indoor climate during sampling should be kept within the normally accepted range of comfort (ISO, 1984).

Controlled (pre-determined) conditions

For special sampling objectives conditions are required which are pre-determined and cannot be influenced by the investigator. There are two major examples for such a situation.

One is the case when a measured concentration has to be tested for compliance with an existing air quality guideline. If boundary conditions have been specified together with the guideline, the investigator is bound to these specifications.

The second example is linked to the first and applies to mitigation measures. If the success of such measures has to be evaluated it is important that VOC measurements are performed under identical conditions before and after mitigation has taken place.

3.5 Position of the sampler

Pollutant concentrations in a room are often not homogeneous (see section 2.3), e.g. because there is insufficient mixing. Local concentration gradients due to activity dependant emissions, uneven heating, low ventilation efficiency, windows, etc. are normal situations. In addition, most VOCs are emitted from point sources and a strong source will cause a concentration gradient in the vicinity of the source, e.g., an office machine, a moth ball or a solvent used in hobby works (Rodes et al., 1991). Therefore the position of a sampler may influence the outcome of a measurement. The choice of the most appropriate position(s) depends on the objective of a measurement. Two positions normally satisfy the requirements of most measurement objectives:

Breathing zone position

Most measurement objectives (e.g. objectives 1, 2, 3 described in section 2.2) require the determination of VOC concentrations in a position where air is normally inhaled by people. In the following this position will be called "breathing zone position". It is typically a position at 1- 1.5 m above the floor level (other levels may be required in a day care centre) at the centre area of a room, at the centre of the table in a dining room, at the centre of a sitting area in a living room or about 30-50 cm above the head end of the bed(s) in a sleeping room. In a kitchen this position may be either at 1.2-1.7 meter above floor level in the centre or at the main working position. Personal sampling as used in the work environment should be considered for some of the objectives as the best option.

Source position

The identification of a source which is suspected to make an important and/or unwanted contribution to indoor air pollution by VOCs requires a different choice of the sampling position. Source identification is a two step procedure. The source has first to be located, e.g. by an informed guess or by means of a portable monitor like a photoionization detector. Then a sample is taken as near as possible to the centre of the emitting orifice or surface area. In the following this position will be called "source position". In order to confirm that the source has been correctly located and/or to estimate the contribution of the source to the indoor concentration of VOCs, the sample taken in the source position may be compared to a sample taken in the breathing zone position. If the suspected source is a nearly flat surface, the use of a portable micro emission cell (FLEC) would allow the in-site measurement of its VOC emission rate (Wolkoff et al., 1991). Alternatively, it may be possible to remove part of the suspected source for testing in the laboratory after the air sampling has been completed. (If neither option is possible, laboratory tests of identical materials or products may provide useful information about the source emission.)

Particular objectives may require sampling in positions other than those described above. In order to test whether concentration gradients of VOCs may be related to air quality complaints in places where people frequently move between different locations, it may be required to take samples in several locations and heights above floor level (Noma et al., 1988). The possibility of certain samplers being influenced by the occupants during sampling has to be borne in mind. In more complex sampling situations appropriate measurement or monitoring techniques may be available from experience in the work environment.

3.6 Sampling duration, time and frequency

The sampling duration depends clearly on the objectives, but it is also tightly linked to the sensitivity of the analytical method, the stability of the samples and the breakthrough volumes of the compound(s) of interest on the particular sorbent. These factors have to some extent to govern the decisions on sampling parameters. Factors belonging to the sampling methods are discussed in more detail in section 3.7.

It has to be taken into account that short-term sampling may lead to a loss of sensitivity whereas during long-term sampling some pollutants of interest may not be quantitatively collected (see section 3.7).

Sampling duration is a very important factor to be considered if health effects are suspected to be related to indoor air quality. It has to be taken into account that short-term sampling easily leads to a misrepresentation of a "true" average value due to the selected time for sampling. On the other hand long-term sampling leads to a loss of information on the temporal variation of the concentration and in particular on peak concentrations.

Short-term samples (up to about 60 min) should preferably be taken when peak concentrations are suspected and likely to be the cause of any adverse effect. Consecutive short-term sampling can be appropriate for information on fluctuation of concentrations, when the emission of a pollutant source is expected to vary considerably over time.

Long-term sampling (from several hours to a few weeks) is suitable to assess average air pollutant concentrations. It is especially appropriate for indoor air quality investigations when chronic effects are involved.

When the objective is the evaluation of compliance with an indoor air quality guideline, the sampling duration must be in accordance with that applied in defining the reference value.

If short-term sampling is carried out, human activities giving rise to VOC emissions and the environmental conditions before and during sampling must be carefully considered (see section 3.4). Many factors can influence the level of VOCs: time of day, season, ventilation status, occupation and human activities. To investigate the potential influence of indoor VOCs on complaints, data collected via a questionnaire can be very useful. For instance, if complaints occur under certain circumstances e.g. daily, weekly, with a seasonal pattern, the sampling time should be chosen accordingly.

Concerning the sampling frequency, a single sample is rarely sufficient to assess indoor air quality. For practical reasons and considering the likely limitation of the budget and manpower available, the number of samples will generally remain small. However, it should be borne in mind that the range of uncertainty of a result is inversely proportional to the square root of the number of samples. Two sampling periods (summer and winter) should be considered if important seasonal variations may be expected.

3.7 Sampling and analytical methods

Measurements of VOCs are usually subdivided into a sampling and an analytical step, of which the sampling is carried out in the indoor environment. The method of enrichment of VOCs on solid sorbents with subsequent thermal or liquid desorption is widespread. A gas chromatograph coupled to a mass spectrometer or another detection device is

required for proper identification of individual VOCs. Some of the VOCs, e.g. low molecular weight aldehydes, are preferably derivatised during or after sampling and the derivatives are analysed with gas chromatography (GC) or high performance liquid chromatography (HPLC). In this chapter only the sampling and essentials of desorption techniques are addressed. For information on analytical techniques including selection of chromatographic columns, detection techniques, etc., the reader is referred to textbooks of environmental organic analysis.

Principles of VOC sampling

The choice of the sampling method depends on the objective of an investigation, the VOCs of interest, and on the available money and manpower. A significant disturbance of the indoor environment while collecting the samples such as increased air circulation or different behaviour of the occupants, must be avoided, otherwise this could lead to biased analytical results. Even sampling itself, whether by active or passive means, requires some intervention which may in certain situations affect the results.

In the following, the main points to be considered in the selection of an appropriate method are discussed. In most cases an enrichment step is necessary to determine VOCs in indoor air.

Active sampling means the use of a pump for drawing a specified volume of the air to be sampled through an adsorbent tube with a specified, usually low air flowrate. Some sampling pumps allow the collection of long term average samples intermittently, or sampling at a very low air flowrate. However, the equipment is rather expensive, and has to be checked and validated for stability of air flow and volume. Noise from the sampling pump can be disturbing during longterm sampling and is therefore an important parameter for pump selection. There is a wide range of adsorbents available for active sampling as discussed below. Active sampling is usually performed when short-term averages are needed (Crump and Madany, 1993). Short-term samples are preferred when increased or variable concentrations are to be expected and time resolution is needed (Wolkoff, 1990b).

Grab sampling using Summa®-polished stainless steel or aluminium canisters allows for sampling very short periods of time (down to 10-30 seconds). However, evacuated canisters can also be used for time integrated sampling over minutes to days using a suitable flow restrictive inlet. The VOCs are enriched afterwards in the laboratory. However, the sensitivity of this technique limits its use for indoor air studies since fairly high concentrations are required.

Passive samplers (Seifert, 1987) consist of adsorbents normally contained in a thin tube. The cross section of the tube and the distance between the opening of the tube and the adsorbent surface determines the sampling rate of the passive sampler. Passive samplers are fairly inexpensive, light weight, simple to operate and can be mounted almost everywhere or carried on a person for personal monitoring. Distribution of the samplers by mail (without visiting the study site) together with instructions on how to expose and

return them, is possible under appropriate conditions. These samplers are suitable for long term average measurements in large scale studies (Seifert et al., 1989). However, the choice of solid sorbents is limited. The sampling rate of each compound of interest has to be known or estimated accurately enough. Although sampling rates generally are provided by the manufacturers, it is recommended to determine the sampling rates by exposing the sampler to test mixtures with known concentrations under controlled conditions in the laboratory. If the sampling rate of a substance is not known, estimates can be obtained using published diffusion coefficients of the analyte in air (Lugg, 1968).

Other detection techniques: Gas detector tubes (e.g. Dräger®, Gastek®, Kitagawa®) are available for many VOCs and are simple to use. However, they have rather low sensitivities and are subject to many interferences which give rise to erroneous results. Most of these tubes are not designed for the concentration range generally encountered indoors.

Adsorbents

The selection of the adsorbent is an essential part of the measurement and sampling strategy. Therefore adsorbents have to be selected very carefully. An overview of the available solid sorbents for sampling VOCs is given in Table A in Appendix 1. Only adsorbents, which are commonly used in indoor and/or ambient air studies are included. Although there are more adsorbents, some of which may be even more suitable for VOC measurements, these are not included since they have not been sufficiently evaluated. Most adsorbents listed in the table are used for active sampling. Several of them may also be used for passive sampling, although they have not yet been evaluated for this purpose.

Tubes which contain two or more adsorbents to retain a broad range of VOCs are commercially available. Despite some advantages of such mixed sorbent tubes, several disadvantages are known. The sorbents in the same tube differ in their optimal desorption temperature and high humidity may also cause problems, especially when an adsorbent for polar compounds is included.

In selecting a sorbent, the recoveries of different VOCs have to be considered. The recovery depends on the breakthrough volume, chemical reactions of the sampled compounds on the sorbent and the desorption efficiency. Breakthrough volumes depend on temperature and may be influenced by specific displacement effects (Rothweiler et al., 1990).

Continuous monitoring

As an alternative to in-field trapping of pollutants with subsequent laboratory analysis, continuous monitoring may be used. Continuous monitoring gives instantaneous information about variations or fluctuations of VOC concentrations. Two types of instruments are being used: continuous direct reading instruments like the photo-ionisation detector or continuous intermittent reading instruments like the non-methane total hydrocarbon monitor. These monitoring instruments are usually

non-selective, but some are sensitive to VVOCs. The technique is useful for measuring relative variations of known and constant mixtures of VOCs, but only in rare cases for determining the concentration. Semi-selective monitoring instruments such as the photo acoustic detector are expensive, and therefore rarely used in larger indoor air studies. When using continuous monitors the sampling strategy in terms of sampler location must be carefully considered as would be the case when using other types of monitors.

3.8 Quality control and quality assurance

There is a tendency, due to financial constraints, to evaluate the indoor air quality in a room based on a minimum number of measurements and very frequently the quality of the generated data remains insufficient for any kind of statistical analysis. There are however some features that have to be fulfilled as a minimum requirement. Any protocol for a measurement has to give information on the quality control performed. At least 10 % of samples taken should be duplicated. Blanks and field blanks have to be analysed in conjunction with the samples. The use of standards (internal and external), and avoidance of contaminants and losses during sampling and storage must also be documented.

Quality control and quality assurance (QC/QA) constitute an integral and important part of the entire sampling strategy and sampling management. Generally, the rules applied to occupational and outdoor ambient air measurements should be followed for indoor measurements. The extent of QC/QA work will heavily depend on the sampling objective and other related factors given below. Where methods or guidelines already are available these should be applied (Thorsen and Mølhave, 1987; VDI, 1991; HSE, 1992).

Some of the salient features to be considered with regard to QC/QA of VOC measurements are: definition of the sampling and data quality objectives and design criteria for sampling, sampling media, sampling location and chemical analysis.

The quality control already begins at the definition and establishment of the sampling objective (Thorsen and Mølhave, 1987). In addition, the data quality objective should be decided depending on the sampling objective (Keith, 1990).

The choice of sampling parameters such as time, duration and location of sampling, are all closely related to the choice of the sorbent and the sampling technique. Many pitfalls may be associated with sampling (Knöppel, 1992; Wolkoff, 1994). One example is the depletion of VOCs in the vicinity of a passive sampler at low air velocities resulting in an underestimate of the bulk air concentrations (De Bortoli et al., 1989).

The quality of the analytical results depends mainly on internal laboratory control, but it is equally important to know potential artefact formation in the sampling or in the analytical system (Wolkoff, 1994). It is strongly recommended that a quality routine and a scheme of reporting total instrumental performance is applied on a continuous basis. In addition, active participation in international intercomparisons and round robin tests

are strongly recommended. Where available certified reference materials should be used for quality control. For more details see also Table 5 in report nr. 6 of this series (ECA, 1989b) and Wolkoff (1990b).

3.9 Additional information

Indoor VOC concentrations are strongly influenced by static characteristics related to building structure and design and by dynamic features (activities, ventilation, ...). To develop an appropriate sampling strategy and to ease the interpretation of the analytical results, it is recommended to collect additional information as outlined in Table 4 .

Table 4: Useful additional information for VOC measurements

| Building characteristics | Inventory of sources * |
|--|--|
| <ul style="list-style-type: none"> - type (flat, detached or attached house) - age - building use, occupant & activity pattern - building design (compartmentation) - building materials - insulation materials - type of ventilation - maintenance of installations - conditions of temperature & humidity - recent renovations or modifications carried out or planned at short term - ventilation rate | <ul style="list-style-type: none"> - sources of energy - interior panels and decorations - furniture - household & consumer products - tobacco smoke - animals - plants - specific treatments (termicides...) - environment (outdoor & immediate proximity of sources of pollution) |
| Specific characteristics of complaints | Occupant characteristics |
| <ul style="list-style-type: none"> - complaint pattern - occurrence of complaints related to: <ul style="list-style-type: none"> • a particular activity • a particular day or time in a day • a particular room - size of the complaining population: <ul style="list-style-type: none"> • all the occupants • isolated occupants | <ul style="list-style-type: none"> - number, age, sex of persons - number of smokers and non smokers - time spent in each micro environment |

* other than building materials

In the investigation of problem buildings even more extensive information like that outlined in ECA report No. 4 (1989a) should be considered.

The additional information allows for an evaluation of several factors that are most likely to be important in solving a given problem. Questionnaires are needed to collect additional information on the characteristics of each environment studied and the time-activity patterns of the occupants. If the objective is the determination of the potential influence of VOCs on complaints, information on symptoms may also be obtained by means of a questionnaire (ECA, 1989a). The data collected via a questionnaire can be considered at several stages:

prior to sampling: for example, to guide the choice of a representative building stock related to the objective (distribution of VOCs in buildings of a certain type of construction, with a certain type of ventilation ...);

in an intermediate stage to lead the measurements: for instance, if a complaint occurs under certain circumstances, the sampling will be performed under comparable conditions. Data concerning building design features and potential sources may also indicate the possibility of migration of some pollutants such as might occur with integrated parking garages or integrated shops (dry-cleaning, printing ...). In this case the information sometimes leads to the choice of specific compounds or chemical families to be determined and, therefore, of the strategy of sampling and analysis;

in the interpretation of the analytical results; if the objective is the assessment of exposure of the occupants in a given micro environment, the knowledge of the time spent by the individual in the respective area is needed. Extreme values may sometimes be explained by information on any event which has occurred during or prior to sampling (e.g., renovation work, changes of the building layout or of the ventilation system) or by a particular building feature (e.g., integrated garages or shops).

4. GUIDANCE FOR SPECIFIC SAMPLING OBJECTIVES

The following sections 4.1 to 4.5 present guidance for sampling VOCs in indoor environments in order to achieve the five objectives mentioned in section 2.2. Each study is unique. Therefore, all recommendations given in the following sections have to be fairly general. The aim is to present some specific considerations connected to these objectives that should be observed in setting up a study. It should also be noted that for each of the objectives discussed below more research is needed firstly to understand some of the problems encountered in VOC measurements, secondly to be able to give more firm guidance on what to do in specific situations.

4.1 Determination of the distribution of VOC concentrations and personal exposures

Personal exposure to VOCs will take place indoors, as well as outdoors. Moreover, some VOCs may enter the body via other routes than inhalation, e.g. through ingestion (food, drinking water) and through the skin. One should realise that measurements of VOCs indoors may only represent part of the population exposure, albeit a major part in many instances. Personal exposure through air is a function of the concentration, C_i , of the specific compound in the locations (often defined as micro environment) visited by a person and the time, t_i , spent in each of these locations. Personal exposure can be measured directly, or estimated indirectly. In the direct way, people carry a personal sampler during their normal daily activities. Thus, the sampler automatically integrates exposure while it is carried through the different micro environments.

In the indirect mode, micro environment concentrations are determined by placing stationary samplers/measurement devices in a number of micro environments (e.g. living room, bedroom, school/workplace, outdoors) and by (simultaneously) measuring or estimating the time spent in these micro environments (e.g. by diaries, or by using existing time-activity data). From these data, the integrated personal exposure can be calculated by summing the products of concentration and time over all micro-environments. Determination of the distribution of concentrations and indirect estimation of the distribution of personal exposures are therefore often very similar activities. Since a report on the latter (COST 613/2, 1991) is already available, the remainder of this section will deal with the determination of the distribution of indoor concentrations.

Purpose

The concentration distribution of VOCs may be investigated for a number of purposes. Firstly, to assess the contribution of an indoor micro environment to personal exposure. Determining the pollutant distribution and comparing the results with distributions in other micro environments will help identify and quantify the major routes of personal exposure. Secondly, the evaluation of health complaints; this requires a reference database for comparison purposes. Thirdly, the surveillance of time-trends of indoor VOC levels which may require repeated (over 5 or 10 year intervals) determinations of the

concentration distribution in indoor environments, to assess the impact of changes in the use of indoor sources, or properties of the buildings.

In general, the determination of concentration distributions will have a public health perspective. This means that the concentration measurements should be performed in a way that is relevant to the possible health effects of the pollutants under study. This is an important complicating factor in the design of a measurement strategy, since several hundreds of VOCs have been identified in indoor air, and for most of these only very limited information is available of their possible health effects. Some VOCs observed indoors are known or suspected carcinogens, while others may have neurotoxic effects after prolonged exposures at high concentrations. This would call for long-term average concentration measurements. On the other hand, many VOCs are known irritants at elevated concentrations, usually at short-term peak concentrations, which would call for a high resolution in time.

When surveillance and monitoring of trends is the objective this poses additional constraints on the study design. Now the required power to detect changes in the distributions over time has also to be taken into account. Usually, the power needed to detect changes in the average VOC levels over time of the order of 5-10 % will require a substantial number of homes to be sampled.

Designs

The different requirements (sampling duration, number of houses) in combination with financial and logistic restraints call for a multi-tier approach (multi-layer). Each tier can be tuned to specific aspects of the objectives. Thus, in one tier the differences between different rooms in a house can be studied in a few houses, for instance using a technique with high time resolution. The variation over different seasons can be studied by repeated measurements in another limited number of houses, by time-integrated techniques. Based on the results of studies in such tiers, an optimal strategy can be derived for a large scale survey of pollutant concentrations in the general housing stock. In this survey only relatively cheap techniques will have to be employed in only one room (usually the living room or activity room). By combining the results from the other tiers in the study the findings can be generalised to the general housing stock. Special studies can be added to focus on groups of homes that are of special interest. These could be newly-built houses with relatively high impact of VOC emission from building materials, or (experimental) energy-efficient houses with low ventilation rates, or specific building materials.

Selection of houses to be sampled

To determine the distribution of concentrations in the general housing stock, a random sample of houses has to be selected in some way. Several procedures exist to obtain a random sample, depending on national or local conditions (e.g. based on national census, municipal records, postal code, random digit telephone dialling, and the like) (Cox et al., 1988). Usually one or more of these strategies, tuned to local conditions, are in use by

national statistical offices and polling bureaux. The use of a true random sample of the housing stock poses logistical problems since the selected houses are distributed over the whole country, or over the area of interest. A more efficient staged approach is the technique of cluster sampling. In this technique, first a random sample of cities is selected, from which a random sample of houses is selected. In this way, there is no need to travel to cities that were not originally selected. An additional stage or cluster could be made by selecting neighbourhoods in the selected cities, before taking a random sample from these neighbourhoods. This would also limit travel within the selected cities.

When geographical differences in type of construction, age distribution of houses, ventilation regime, presence of sources, outdoor VOC levels, etc. are not important, it may not be necessary to take a random sample of the general housing stock. In that case it might suffice to study one or a few selected cities, that are convenient to investigate. Such an approach was used a.o. in the Netherlands, where houses were randomly selected from two independent samples: pre-war inner-city houses in one city, and post-war homes in another. In these samples comparable VOC distributions were found (Lebret et al., 1986).

Selecting random samples of the housing stock may not always be the most cost-effective way to obtain information on the distribution, particularly on the high concentrations, when pre-existing knowledge of important determinants of indoor VOC levels and their occurrence in the housing stock is available. Stratification of the sample by these determinants and over sampling of houses with determinants of high indoor VOC levels will provide a more efficient way of estimating the high end of the distribution. Thus, the number of homes to be sampled can be reduced. When the distribution of the relevant determinants is known and the sample is carefully stratified on these determinants, the complete distribution can be obtained (Pellizzari et al., 1987; Ryan et al., 1988).

Sampling method

In a survey-type design the sampling method should be inexpensive, robust and provide time-integrated samples. Passive samplers are very well suited for this purpose as demonstrated by Seifert et al. (1989) and by Brown and Crump (1993), but active sampling with low flows may also be an option; although the required pumps are more expensive, the possibility of using automated systems may keep costs within acceptable limits.

Sorbents should be suited for long storage before and after sampling.

Position of the sampler

Since the study will usually have a public health perspective, the appropriate position of the samplers is at breathing height in such a way that the occupants are not hindered in their normal daily activity.

Location

If only a single room is sampled, it is usually the living room or activity room though sometimes, it may be the bedroom. If the determination of exposure is the goal of the measurement other rooms may be considered depending on the magnitude of the product $C_i \times t_i$ expected in micro-environment i . The same exposure may result from short-term exposure to high concentration or long-term exposure to low concentration. For survey type studies a pilot phase may be desirable. The sampler is located in such a way that it is not affected by a single source or by incomplete mixing of fresh air (away from doors, windows or ventilation ducts).

Sampling duration

The samples should be collected over a period of time comprising most of the common household activities that affect IAQ. Depending on the type of sampler durations of several days up to two weeks are often used. Longer durations will dilute peak concentration from an occasional source, shorter duration's might miss the impact of consumer products that are used once a week or less. Given the duration of the sampling, the equipment should be unobtrusive to the occupants.

Environmental conditions before and during sampling

The conditions before sampling are of limited interest when the objective is to assess the distribution of concentrations, and when the sampling duration is long enough (e.g., more than 12 hours). Conditions during sampling should be registered by diaries or by questionnaire at the end of the sampling period. This information can be used in explaining the occurrence of outliers or unexpected values.

Ancillary information

Ancillary information is as such not necessary to collect for the determination of the concentration distribution. It can, however, be used in statistical analyses of the data to assess the impacts of sources, or other factors affecting the VOC levels. It should be kept in mind that spurious findings are likely to occur when several hundred of VOCs are statistically analysed for associations with several tens of potential independent variables. Factor analysis can be a helpful tool to reduce the number of associations to be tested (Lebret et al., 1986).

Reference material

The distribution of indoor VOCs have been studied in several countries using different strategies. The results of these studies were summarised by WHO (1989). It appears that these distributions do not differ much between countries. However, it is not clear to what extent concentration distributions have changed since the mid- eighties when the data were generated.

4.2 Measurements in response to health and comfort complaints in buildings

Background

The common health and comfort complaints encountered in indoor environments are mucosal irritation in eyes, upper and lower airways, effects mediated by the central nervous system (CNS) such as headache, generalised lethargy and tiredness leading to poor concentration, and the perception of malodour (ECA, 1989a). These complaints appear spontaneously, usually within a short time after exposure. However, the possibility of chronic effects due to a long-term VOC exposure cannot be ruled out at present. Effects of indoor air pollution on human health have been discussed in ECA report No. 10 of this series (ECA, 1991). The approach has been to discuss categories of adverse health effects and describe the relevant indoor exposures which may give rise to these health effects.

The objective of VOC measurements in the field should be the identification of possible associations between the complaint rate and the peak or time-integrated concentrations or exposures measured during the period of complaint.

Measurements are costly and therefore they should be carefully planned to obtain maximum information. It is advisable to begin an investigation with a walk-through inspection to obtain information of the indoor air quality (Valbjørn et al., 1990), e.g. recognisable odours or irritants arising from specific materials, products or activities.

Approach

The sampling strategy should rely on information of the complaint pattern observed from the use of questionnaires or based on observed health effects. If the complaint occurs during an activity, like laser printing or after cleaning, sampling should be carried out before and during the event to establish peak concentrations or exposures, i.e. short-term sampling. If certain sources are suspected and their emission patterns have been identified it is possible to design a sampling strategy taking into account microenvironmental factors.

Preliminary VOC measurements in locations with strong complaints may be made in order to assess whether high concentrations of known irritants or neurotoxic substances are present, which could explain the complaints occurring (ECA, 1991).

If no such concentrations can be detected, as is often the case, samples should be taken in a limited number (about a total of 10) of microenvironments with both high and low complaints. Statistical considerations of the variance of the measured concentrations will then allow for the estimation of the number of samples which would be necessary in order to detect an association between VOCs and complaints at a desired level of confidence. On the basis of the resulting numbers of samples, the severity of the complaints, and the budget available, an informed decision can be taken on whether or not further VOC measurements are reasonable and needed.

As mentioned in chapter 2 the sampling strategy should depend upon the type of health or comfort effect reported. It appears relevant to monitor peak concentrations or exposure for acute effects like mucous membrane irritation, i.e. effects or discomfort which disappear if there is no more exposure. If, in a study, VOC measurements are combined with a questionnaire enquiry of symptoms of acute effects, VOC measurements and compilation of questionnaires should be performed simultaneously (Hodgson et al., 1991).

It is not necessarily the concentration of VOCs that creates the problem. The gradients rather than the levels of concentration have been suggested as the reason for complaints (Noma et al., 1988; Rodes et al., 1991). Long-term sampling, providing time-integrated concentrations, appears to be the most relevant strategy for chronic effects. If the complaint is malodour one should try to identify potential sources and sample accordingly. If the problem cannot be assigned to a specific activity or material, sampling should be performed during conditions of minimum ventilation.

If a building or location in a building differs from a similar building with regard to complaint rate, measurements should be performed in both places under identical conditions also taking into account the environmental conditions prior to and during the event. In the case of job-related complaints sampling should provide a time-integrated concentration representative of this job activity and possibly enable comparison with other job type situations under similar environmental conditions.

It is in some cases required to bring suspected materials or office equipment to the laboratory for further investigations (Brown et al., 1993; Wolkoff, 1990a), e.g. by head space analysis. It may sometimes be useful to carry out more detailed investigations to identify unknown compounds, undertake odour assessment or provide information on which VOCs to measure, like acids, aldehydes or odorous VOCs.

4.3 Testing of compliance with indoor air quality guidelines

While there are legally enforceable standards established for outdoor air, no such standards exist for the indoor air in non-occupational environments. In some countries guideline values are used, which represent a less stringent means of regulating indoor air quality and thus identify situations where measures to reduce concentrations of pollutants may be of benefit to the occupants. Very few sets of guideline values applicable to the indoor air exist. The most authoritative guidelines have been published by the World Health Organization. Although the WHO Air Quality Guidelines (WHO, 1987) have not been established specifically for indoor air they may also be used for the evaluation of indoor air quality. The set comprises guideline values for about 10 volatile organic compounds.

Besides WHO, some countries have published guideline values for volatile organic compounds other than formaldehyde, among them Canada for acrolein, acetaldehyde and the sum of these two and formaldehyde (HWC, 1987), Norway for total volatile organic compounds (Helsedirektoratet, 1990) and Germany for tetrachloroethene (Anonymous, 1990).

A common feature of all published indoor air quality guideline values is the fact that only limited instruction has been provided about the way of testing compliance with these values.

While sampling intervals have been defined in some cases (WHO, 1987; Anonymous, 1990), nothing has been fixed, e.g., in terms of sampling frequency or environmental conditions before and during sampling.

Under these conditions, the test for compliance of VOC concentrations with existing guideline values can only be carried out taking into account the principles which are outlined in this report. Special care has to be taken to avoid sampling conditions outside the range of what is generally tolerable (with regard to temperature, relative humidity and ventilation status). In addition, it is highly recommended to incorporate measures to ensure good quality control and minimise overall uncertainty in the results e.g. the use of duplicate samples.

4.4 Identification of VOC sources

A visual walk-through inspection should give indications of potential sources, like building materials, office equipment or information about cleaning and maintenance routines. A general knowledge of material emission characteristics and of odour sources should assist the identification of potential VOC sources. It is important to make sure that all potential emission sources have been identified and thoroughly considered prior to the design of the sampling strategy. There are six basic approaches for the identification of potential VOC sources:

1. Field measurements combined with principal component analysis or other non-linear regression programs (Lebret et al., 1986; Daisey et al., 1993).
2. Measurements at selected locations near potential emitting materials and comparison with measurements in the centre of the room (Seifert and Ullrich, 1987).
3. Use of a portable detector pointing at suspected sources (Gammage and Matthews, 1988; Gammage et al., 1989).
4. Use of a portable micro emission cell to be placed on planar surfaces (Wolkoff et al., 1991)..
5. Head space analysis of selected building materials/consumer products. Possibly, a comparison with a measurement of room air samples can be carried out (Wolkoff, 1990a).
6. The picnic method - evaluation of the immediately perceived air quality by a trained panel (Fanger et al., 1988).

Field sampling of VOCs is one method of identifying emission sources. Thorough material knowledge about emission characteristics is required. Factor analysis techniques can provide information about common VOC origins (Daisey et al., 1993). The variation of the sample duration and frequency may provide further information about the emission characteristics (Seifert and Ullrich, 1987). If the emission is activity dependent, like handling of carbonless copy paper, use of an office machine, cooking, passive environmental (breathing zone) or personal samples can be collected with and without the activity going on.

The sampling may be performed close to a suspected source like a painted wall, new furniture or office equipment. If the measurements take place under steady state conditions the observation of concentration gradients should give indications of potential sources. This approach, however, has not been reported to be successful using long-term sampling. Alternatively, emission sources may be located using a portable detector (photoionization detector) directed toward a suspected emitting source and compared with the concentration measured in the centre of the location.

A portable micro emission cell, where the material itself becomes an integral part (bottom) of the cell, can conveniently be applied in field sampling of planar surfaces (Wolkoff et al., 1991) providing qualitative and quantitative emission data of the material surface. By comparison with an average sample taken in the middle of the room the strength of the source may be estimated.

Sometimes it is preferable to bring suspected emitting sources like materials or consumer products to the laboratory (Brown et al., 1993) for an emission or head space analysis using GC/MS and/or GC-sniffing techniques, in particular when the complaint is malodour (Wolkoff, 1990a). Many malodourants are present in low concentrations (ppb-ppt) and still produce an odour problem because of their low odour thresholds. Consequently, they are difficult to measure without prior knowledge of the VOCs of interest. Source identification may also be performed in some cases in conjunction with evaluation of the immediately perceived air quality by a trained panel (Fanger et al., 1988).

4.5 Evaluation of remedial actions

Remedial actions considered primarily in this paragraph are modifications to a building, its systems or equipment aimed at reducing indoor air pollution by VOCs. Usually such remedial actions will consist of either the removal or modification of the source or improvement to the ventilation conditions.

Remedial actions may also aim at elimination or modification of sources of odour or other indoor pollutants such as SVOCs, POM (see Table 1), suspended particulate matter or biological particles, or at improving the indoor climate. Such remedial actions are considered to the extent that VOCs have been identified and are used as indicators of

their effectiveness. An example of such a remedial action is the elimination of fungi which produce characteristic VOCs.

Obviously, the most important feature of VOC measurements aimed at evaluating the effectiveness of remedial actions is that VOC samples have to be collected before and after the remedial actions under identical or as much the same conditions as possible. This implies that the sampling strategy has to be established before the pre-remedial measurements. The elements of the sampling strategy should be chosen in such a way that the success or failure of the remedial actions is demonstrated as clearly as possible by the results of the VOC measurements.

Following are recommendations for the selection of the important elements of the sampling strategy. For most elements it is not possible to consider all of the many different situations requiring remedial actions and assessment of their efficiency by VOC measurements. Therefore the above mentioned general rules are applied to some typical situations as examples of how to select the elements of the sampling strategy.

Indoor environments and sample size

Air samples should in principle be collected in each indoor environment in which a remedial action is taken. If the same action is taken in a number of identical buildings or independent parts of buildings (see section 3.1), for economical reasons, VOC measurements may be performed only in a subset of them. However, investigators should be aware that the "same" action may yield largely varying results for unexpected reasons such as human errors or unexpected inhomogeneity of materials. In any case a minimum of three or 10 % of the sites concerned (whatever is more) should be selected randomly. Measurements at additional sites should be performed after the remedial action if the measured mean VOC concentrations are near to the maximum admissible or target concentrations aimed at by the remedial action, e.g. if the upper limit of the 95% confidence interval of the measured mean concentrations are higher than the target concentrations.

Selection of the status of VOC sources

The status of VOC sources can only be selected for those sources dependent on human activities such as smoking, cleaning or hobby activities or on human interaction such as equipment or appliances that emit only or predominantly during use. The selection of their status depends on the type of source and the objective for the evaluation of remedial action. Two types of evaluation are briefly considered:

- (a) The aim of the remedial action has been to modify or remove an activity related source of VOCs. The evaluation of success of this type of action is simplified if other VOC sources are reduced to a minimum during the VOC measurements.
- (b) The aim of the remedial action concerns modification of ventilation rates, efficiencies or the introduction of pollutant barriers into a space. In this case all sources should be active which may contribute to the unwanted VOC concentrations or exposures.

Whether the activity of the sources should be normal or as high as reasonably possible depends on the aim of the remedial action i. e. whether it was intended to reduce average or peak concentrations.

Selection of spaces within an indoor environment

For the selection of spaces within an indoor environment similar rationales hold as for the selection of the indoor environments themselves. All spaces in which a remedial action has been taken or which should benefit from a remedial action should in principle be included in the VOC measurement program. If the same remedial action is applied to a number of identical spaces (e.g., offices) in a building VOC measurements may be performed in only part of them applying the same rationale as for the selection of indoor environments.

If a source is removed or modified which, although polluting several spaces, causes highest pollutant levels in a distinct space, VOC measurements in this space may be sufficient. An example may be an attached garage from which VOCs are diffusing to a one family house. If a lock is introduced in order to reduce diffusion, VOC measurements in the space communicating with the garage will be sufficient in order to evaluate the efficiency of this remedial action. Another example is the installation of a mechanical exhaust in a kitchen to reduce pollution from a gas cooking appliance. In this case VOC measurements in the kitchen may be sufficient but the investigator should be aware of secondary effects such as the possible reduced effectiveness of flues venting appliances in adjacent rooms.

Environmental conditions before and during sampling

Temperature, humidity and ventilation conditions are selected following the two general rules outlined above, i.e. as much the same conditions as possible for the pre- and post-mitigation measurements and focusing as clearly as possible on the success or failure of the remedial actions as mentioned above and in section 3.4.

Position of the sampler

In case the remedial action involves modifying or removing a source of VOCs, the source position as defined in section 3.5 is appropriate for assessing the result of the remedial action. However, the breathing zone position will be more appropriate if the remedial action is intended to significantly reduce occupant exposure to a VOC which may have other possible sources in the environment.

If the remedial action is aimed at improving the ventilation efficiency at least two sampling positions in a space should be selected which before the remedial action yield the largest VOC concentrations. For other remedial actions the breathing zone position (see section 3.5) should be considered.

Sampling duration, time and frequency

For the selection of these parameters the type and objective of the remedial action has to be taken into consideration.

Short term sampling (see section 3.6) is appropriate for assessing the effect of source modification (with sampling in source position, see section 3.5) or for other remedial actions if they are aimed at reducing peak concentrations of VOCs. Long term sampling is appropriate if the remedial action is aimed at reducing average concentrations or exposures.

In case of actions aimed at reducing peak concentrations sampling has to be performed at a time when highest VOC concentrations are expected, whereas the sampling time is not critical in case of actions aimed at reducing average concentrations. For the assessment of remedial actions which require the use of products (e.g. a glue for the installation of a different type of flooring material) with short term VOC emissions which may interfere with the measurement of the target VOCs (emitted by the removed material), post-action sampling should be performed after decay of this emission. Sampling after the remedial action may be required at more than one time if the decay time is not sufficiently well known.

The number of samples per measurement location depends on the selection of the source and environmental conditions and of the sampling time(s). If only one set of these conditions has to be selected, one duplicate sample will in general be sufficient, otherwise one duplicate sample for each set of conditions will be required.

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APPENDIX 1: SOLID ADSORBENTS USED TO COLLECT VOCs

An overview of the available solid sorbents for sampling of VOCs is given in Table A. Only adsorbents which are commonly used in indoor and/or ambient air studies are included. Although there are more adsorbents, some of which may be even more suitable for VOC measurements, these are not included since they have not been investigated sufficiently. Most adsorbents listed in the table are used for active sampling. Several of them may also be used for passive sampling, although they have not yet been well investigated for this purpose.

In selecting a sorbent the recoveries of VOCs have to be considered. The recovery depends on the breakthrough volume, chemical reactions of the sampled compounds on the sorbent and the desorption efficiency. Breakthrough volumes depend on temperature and may be influenced by specific displacement effects.

Table A: Solid sorbents used to collect VOCs

| Sorbent | Desorption technique | Compounds Sampled | Starting at bp** [°C] | Main Advantages and Disadvantages |
|---|----------------------|---|-----------------------|--|
| Tenax TA | thermal | - most non-polar VOCs - terpenes - slightly polar VOCs - aldehydes >C5 - (acids >C ₃) * | > 60 | -low background -well investigated -some decomposition products (benzaldehyde, acetophenone) |
| Carbotrap | 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 adsorption |

* can be used (mainly low recoveries)

** boiling point

Pollutants are desorbed from solid sorbents either thermally or by means of a solvent. Solvent desorption leads to a loss of sensitivity due to dilution. For non-reactive compounds this loss of sensitivity may be overcome by desorption at increased temperatures with a high boiling solvent (e.g. benzyl alcohol) into a small gas-tight vial. Headspace vapours are directly injected onto a GC column. However, as most solid sorbents have a limited adsorption strength they are used in combination with thermal elution, where the whole sample is available for a single analysis. Several thermal desorption units are commercially available, most of which allow cryofocusing of the desorbed compounds before injection into the GC column. Thermal desorption has to be performed using an inert carrier gas, e.g. helium. The connection of the desorption unit and the GC column should be made of an inert material, e.g. deactivated fused silica, to avoid chemical reactions. Analysis takes place after cryofocussing of the sample using high-resolution GC in combination with flame ionization detection (FID), electron capture detection (ECD) or mass spectrometry (MS).

Humidity may interfere either with sorbent sampling or with GC analysis. During sampling it may reduce the breakthrough volumes of polar compounds and it may even lead to chemical reactions. If water is retained, clogging of the cryotrap is possible during thermal desorption. In the case of desorption with a nonpolar solvent, water may prevent good contact with the solvent. In some cases, high humidity and/or the addition of polar compounds may also improve desorption for some chemicals.

All adsorbents have limitations. Rarely, one adsorbent is best suitable for all VOCs of interest. Therefore, in practice, adsorbents are often only moderately suitable for some VOCs of interest. Therefore, for some objectives, it is advisable to use more than one sorbent or sampling method to obtain reliable results. Whatever method is used, it is crucial to know, which VOCs cannot be determined or may be artifacts.

For some compounds or compound classes specific methods are required. In table B a small selection of specific methods used in indoor air studies can be found. Experience with some of these is only scarce.

Table B: Sampling and analytical techniques for specific classes of VOCs for which the methods indicated in Table A are not appropriate.

| VOC class | Sampling medium | Treatment | Separation technique | Detection |
|---------------|---|------------------------------|----------------------|----------------------------|
| Aldehydes | acidified DNPH (cartridge, filter, liquid) | extraction, direct injection | HPLC, (HRGC) | HPLC: UV, DAD HRGC: FID |
| Amines | acidified solvent; coated filters | derivatisation | HPLC, (HRGC) | HPLC: UV; HRGC: FID |
| Organic acids | alkaline solvent (0.02n KOH) | derivatisation | HRGC | FID, ECD |
| Isocyanates | 1-(2-Methoxyphenyl)-piperazine coated filters | extraction | HPLC | ELCD |

(): limited use

DAD: Diode array detector

DNPH: 2, 4-Dinitrophenylhydrazine

ECD: Electron capture detector

ELCD: Electrochemical detector

FID: Flame ionisation detector

HPLC: High performance liquid chromatography

HRGC: High resolution gas chromatography

UV: Ultraviolet detector

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European Commission

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Strategies for sampling chemical substances in indoor air have been discussed in a previous report in this series (Report No 6). This report gives more specific guidance for the development of sampling strategies for volatile organic compounds (VOCs). The report is divided into three sections:

- (a) General considerations which highlight the sampling objectives of indoor VOC measurements, the numerous sources of VOCs and their emission characteristics, the dynamic character of indoor pollution by VOCs, and the interpretation of VOC measurements in relation to health and comfort. These considerations are a prerequisite for the development of sampling strategies.
- (b) Discussion of the elements of sampling strategies for VOCs. These elements include the type and number of objects (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. The common choices of the above-mentioned elements are discussed.
- (c) Outline of sampling strategies, i.e. selections of the abovementioned elements, for the more frequent sampling objectives.

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