EUROPEAN
SOLVENTS INDUSTRY
GROUP

BEST PRACTICE GUIDELINES

Strategies and Techniques for Measuring Solvent Vapour Concentrations in the Work Environment

CONTENTS

Tables

Figures

Foreword

The European Solvents Industry Group (ESIG) provides a single point of contact for information on oxygenated and hydrocarbon solvents in Europe. Through its work with industry and with industry partners, the group promotes best practices in solvent usage, health, safety and environmental protection. Its main aims are to support responsible care in the use of solvents and to provide advocacy on issues affecting the producers of solvents.

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European Solvent Industry Group (ESIG)
www.esig.org

PART 1 Introduction

A wide range of techniques and equipment are available for measuring airborne solvent vapour concentrations. They can help in the process of assessing and controlling exposures to solvent vapours in the workplace, but it is essential that the appropriate equipment is selected, that it is used properly and that the results are interpreted correctly.

Measuring exposures to chemical substances should be carried out as part of an overall programme of health risk assessment to help in the selection and confirmation of effectiveness of appropriate exposure controls. This Guide should be read in conjunction with ESIG Best Practice Guide entitled 'Managing the Health Risks of Solvent Exposure' (Ref 1) which explains the comprehensive framework of regulations that require risks associated with use of chemical substances in the workplace to be assessed and controlled.

1.1 SCOPE AND OBJECTIVES

This guide is intended as a reference for those responsible for providing health and safety advice to employers and their workers who handle solvents as part of their company's operations, including solvents' manufacturers, formulators of products containing solvents, and any companies or professional workers that apply solvent containing products.

it is not intended to be a comprehensive manual on exposure measurement. It is strongly advised that companies without the necessary expertise seek input from a qualified Occupational Hygienist.

This guide aims to help those company's whose workers are potentially exposed to solvents and solvent-containing products to:

- determine if there is personal exposure to solvent vapours during their handling operations for which further control is advised;
- be aware of a tiered approach to implementing a measurement strategy for verification of the level of exposure; provide insight into the various measurement techniques available and when they may be appropriate to be applied to understand sources of solvent emissions, personal exposures and effectiveness of exposure control measures;
- highlight specific aspects of importance in the measurement of complex substances such as hydrocarbon solvents;
- provide an overview on the derivation of limit values for hydrocarbon solvents which are complex substances containing many hydrocarbon species for which there are typically no national limit values available.

Measurement of aerosols/mists which may be generated during certain tasks, e.g. spraying, or the result of condensation from a heated process, and potentially relevant for those solvents with low vapour pressures are not addressed.

PART 2 Why are measurements required?

Measurement of airborne solvent vapour concentrations may be required for a number of reasons, including to:

- help assess possible health risks resulting from work activities
- confirm effectiveness of measures in place to control airborne emissions, including those specified in any REACH Exposure Scenarios (ES) attached to the solvent suppliers SDS
- determine compliance with relevant exposure limit values
- assess the effect of changes in materials, procedures or controls
- determine which work tasks give rise to the most exposure
- investigate complaints concerning alleged health effects, or odour complaints which are not necessarily associated with health effects
- reassure workers who may be exposed to solvents
- support emergency response
- comply with specific legal requirements

PART 3 Exposure limit values

Employers are expected to assess the risks associated with handling solvents used in their operations including taking account of the requirements set out in any supplied REACH Exposure Scenario (ES) relevant to their specific use. In assessing the risks it is important to ensure that exposure to solvent vapour concentrations in the workplace are within any applicable limit values, known generically as Occupational Exposure Limits (OELs). ESIG Best Practice Guideline (BPG) Managing the Health Risks of Solvent Exposure (Ref 1) provides more information on assessing solvent risks and the details included within REACH ES. Here we take a closer look at OELs as they relate to solvents.

3.1 OCCUPATIONAL EXPOSURE LIMITS (OEL's)

A number of individual solvents have been assigned Occupational Exposure Limit values by national or regulatory bodies such as the European Union[1] (EU), national governments (e.g UK Health and Safety Executive (HSE) Workplace Exposure Limits (WELs), and German Ausschuss für Gefahrstoffe (AGS) Values and independent organisations such as the American Conference of Governmental Industrial Hygienists (ACGIH) which sets TLV's (Threshold Limit Values) that are used widely around the world. Where official values do not exist, supplier recommended values may be available.

OELs are typically defined as vapour concentrations for a substance/product below which workers may be repeatedly exposed, day after day, without adverse health effects. They generally refer to 8-hour time-weighted average (TWA) concentrations. Some solvents also have short-term exposure limits (STELs) that represent the allowable concentration over 10-15 minute periods. For substances without STELs, it is suggested that such excursions should not normally exceed 2-5 times the 8-hour TWA limit value, averaged over a 10-15 minute period (Ref 2, Ref 3). If the TWA and STEL values assigned for solvents are observed no adverse health effects are expected.

Measuring exposures to solvent vapours is complicated by the fact that many of the hydrocarbon solvents are complex substances containing numerous individual hydrocarbon species. However, as most of the hydrocarbon solvent constituents have similar toxicological properties (Ref 4) and therefore similar health effects, the compositional variability can be managed on a generic basis. Thus for these complex substances, it is helpful that a single occupational exposure limit value is available (or derived) against which to compare personal exposures. Methodologies have been developed to support the setting of limit values for these complex substances. (See Section 3.2).

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[1] Recommendations for EU indicative/binding limit values are proposed by The Scientific Committee on Occupational Exposure Limits (SCOEL) recently replaced by the Committee for Risk Assessment (RAC)

3.2. OELs FOR OXYGENATED AND HYDROCARBON SOLVENTS

OELs have been established for the majority of oxygenated solvents by official bodies. Unlike hydrocarbon solvents these are single substances.

Conversely many hydrocarbon solvents (HCS) do not have official limit values as they are highly refined petroleum fractions containing numerous individual hydrocarbon species. For this reason the Hydrocarbon Solvents Producers Association (HSPA) has developed a methodology based on the Reciprocal Calculation Procedure (RCP) for assigning limit values to commercial hydrocarbon solvents in order to provide users with a simple and practical means of evaluating exposure to these products. Using average compositional data for each HCS registered under REACH, the RCP has been applied to generate a limit value for each substance and included within the key data for HSCs presented in an overview document, Hydrocarbon Solvents registered under REACH – key data[2]. This may be used as a guide where the actual composition for the HCS is unknown, or no value is available from the supplier. The approach is outlined in Section 3.3.

3.3. RECIPROCAL CALCULATION PROCEDURE (RCP)

The HSPA RCP based approach is outlined below and a detailed description has been published in the scientific literature (Ref 5) up-dated to take account of additional information that has become available over the last few years via the REACH process (Ref 6).

To arrive at a single limit value the RCP may be applied to individual constituents in a mixture that have similar toxicological effects. For example, the typical effects of many HCS include irritancy and depression of the central nervous system. In this case the following formula may be applied.

$$FR_a/L_a + FR_b/L_b + FR_c/L_c + \ldots\ldots = 1/L_{\text{Mixture}}$$

Where FRa is the vapour phase mole or liquid mass fraction of constituent a in the mixture and La is the limit value for constituent a (in ppm or mg/m^3), etc. Using this formula, a combined limit value for the mixture ($1/L_{\text{Mixture}}$) is generated. For HCS with narrow boiling point ranges, each individual constituent is present in the liquid phase at approximately similar ratios as would be expected in the vapour phase.

In the RCP approach, guidance limit values have been derived for groups of similar hydrocarbon solvents based on detailed hazard assessment of their toxicological properties. These are known as Group Guidance Values (GGV) that together cover all the constituents of HCSs. Using these GGVs, a recommended limit value can be calculated for any mixed HCS using the above formula. A list of the HSPA Group Guidance Values (GGVs) and also Substance-Specific Values (SSVs) for use in the Hydrocarbon Solvent RCP Calculation is given in Appendix 1.

The RCP calculation will normally be undertaken by the solvent manufacturer or supplier, an example is given in Table 1. The GGV's used in Table 1 are those recommended following the recent review undertaken to take account of new information that has become available as a result of the REACH process (Ref6). ESIG has developed tools which help the user apply the RCP methodology, by means of a calculator which is available via the ESIG website[3].

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[2] www.esig.org/wp-content/uploads/2018/08/HCS-key-data-2018_07_23-Final.pdf
[3] www.esig.org/regulatory/oel/

Table 1: RCP OEL calculation for regular white spirit in the EU

Constituent	RCP Hydrocarbon Group	GGV or SSV (mg/m^3)	Liquid Mass Fraction (Fr_a)[a]	Reciprocal Calculation[b]
C8 aliphatics	C5-C8 aliphatics	1400	0.02	1.43×10^{-5}
C9 aliphatics	C9-C15 aliphatics	1050	0.14	0.00013
C10-C15 aliphatics	C9-C15 aliphatics	1050	0.652	0.00062
Toluene	NA[c]	192	0.001	$5.2 \times 10^{-6\,-}$
Xylene	NA	221	0.006	$2.715 \times ^{10-5}$
C9 trimethylbenzene isomers	C9-C15 aromatics	100	0.18	0.0018
Naphthalene	NA	52	0.006	0.0001154
Diethylbenzenes	NA	28	0.015	0.000536
Sum				0.00325

[a] Mass fraction in liquid phase divided by 100%. [b] (Fr_a/OEL_a). [c]NA = not available

Based on the calculations shown in Table 1:

- $1/OEL_{complex} = 0.00325$
- $OEL_{complex} = 307.7$ mg/m^3 (rounded down to 300 mg/m^3 based on the ACGIH rounding rules - Appendix 1)

An important advantage of using the HSPA limit values is that exposure to a mixed HCS can be assessed against a single value in the same way that a pure oxygenated solvent would be assessed (e.g. assessment of exposure to methyl ethyl ketone - a common solvent in industrial adhesives).

The RCP methodology can also be used to generate a limit value for a solvent blend. In this case, it is important to take account of varying vapour pressure values for each solvent in the blend which may impact the mass fraction in the vapour phase, compared to the liquid phase and influence the calculation of the limit value for the blend (Ref 6).

3.4. WHERE TO FIND RELEVANT OELs

Relevant OELs for the components of a marketed product are required to be listed in Section 8 of the supplier's SDS. Here the supplier will list any relevant national limit values that apply in the country of sale. In addition, values recommended by the supplier may be provided where no national value is available, such as for a complex hydrocarbon solvent (see Section 3.3). In case of any questions, clarification should be sought from the supplier.

The exposure assessment for a mixture of a hydrocarbon solvent together with, for example, an oxygenated solvent which have independent health effects should be carried out separately against their individual limit values.

Additional information on the health effects of solvents is provided in ESIG Best Practice Guide 'Managing the Health Risks of Solvent Exposure' (Ref 1).

3.5. DERIVED NO EFFECT LIMIT (DNEL) VALUES VERSUS OELs

The European Union (EU) REACH regulation requires that an evaluation of the hazard and risk of exposure to a chemical or chemical safety assessment (CSA) must be performed for substances/chemicals that are manufactured or imported into Europe at levels greater than 10 tons/year. In order to assess risk of exposure in the CSA, a DNEL is calculated. The DNEL is considered to be an exposure level for threshold end points, which should not be exceeded. Separate DNELs are calculated to address duration of exposure (acute and long-term), exposure routes (inhalation, dermal and oral), type of adverse effect (systemic and local) and type of exposure population (worker and consumer). The inhalation DNEL for workers is most analogous to an OEL for HCSs. The DNEL is calculated based on a selected dose descriptor (quantitative estimate of the exposure without adverse effects or NOAEC) and assessment factors (used to quantify the extent of uncertainty inherent with the selected dose descriptor). The European Chemical Agency (ECHA) has provided guidance on the derivation of DNELs (Ref 7). For HCSs, worker inhalation DNEL derivation relies on animal or human data where a NOAEC can be derived. Where the NOAEC is derived from animal data, it is modified (for example, to account for differences in exposure duration such as 6 hours in animal studies compared to an 8-hour work day for humans) to develop a human-relevant point of departure (POD).

Whilst the RCP-derived OEL is analogous to a worker DNEL for HCSs, it is typically calculated differently. Unlike the DNEL, which is based on actual toxicity data, the RCP method relies primarily on existing regulatory OELs for constituents of complex HCSs. In other words, the RCP-derived OEL takes the individual constituents (and their limit values which were likely derived from toxicity testing on these individual constituents) into account while the DNEL is often based on actual toxicity data on the complex substance. Since individual regulatory OELs are developed by regulatory agencies and thus in general inherently more conservative, it is not surprising that DNELs often tend to be higher than those that would be derived using the RCP method.

Where possible, with respect to the worker inhalation DNELs for single constituent solvents such as MEK, MIBK and n-Hexane , the DNELs are simply the existing EU Indicative OEL Value (iOELv).

DNEL values are applied for the demonstration of safe use of a substance as part of the Chemical Safety Assessment carried out by the Manufacturer/Importer under REACH. Whilst OELs are limit values applied by users of a substance as part of their local workplace risk assessment required under national legislation implemented in accordance with the Chemical Agents Directive (CAD).

3.6. ASSESSING EXPOSURE TO A MIXTURE OF SIMILAR SOLVENT TYPES (E.G. HYDROCARBON SOLVENTS)

If using a mixture of HCS which have similar ill health effects a good starting point for a risk assessment is to measure the total hydrocarbon vapour value for the mixture as a whole, and assess this against the HCS in the mixture with the lowest limit value as a simple, conservative approach. As such, this is recommended in particular when carrying out measurement as part of the basic exposure characterisation initial workplace assessment.

Alternatively, the additive effect procedure with the following formular can be used to assess exposure compliance against the mixture as a whole:

$$C1/L1 + C2/L2 + C3/L3 + \ldots\ldots = <1 \text{ (equivalent to the limit value for the mixture)}$$

Where C1 is the concentration of Constituent 1 in the atmosphere and L1 is the OEL constituent 1 (in the same units (ppm or mg/m^3*). The airborne concentration of the individual constituents need to be measured as separate values.*

3.7. ASSESSING EXPOSURE TO A MIXTURE OF DIFFERING SOLVENT TYPES

If using a mixture of solvent types, e.g. a HCS, an Alcohol (e.g. ethanol) or Glycol ether (e.g. Butyldiglycol), the ill health effects may not be additive. In this case, they may be measured and assessed individually for comparison against their individual limit values. In case of interferences impacting real time/direct reading technology, collection/indirect methods with separate laboratory analysis may be the most appropriate choice to assure greater accuracy of results (refer to Section 6).

3.8. UNITS OF MEASUREMENT

It should be noted that direct reading instruments typically measure vapour concentrations in ppm, whilst most solvents have Limit Values expressed in mg/m^3. It is necessary to know the Molecular Weight (MW) of the substances being measured in order to convert ppm into mg/m^3 or vice versa. The calculation method to convert between the two units has been provided in Appendix 4.
There are also several online tools with built in molecular weight databases to convert these units. A good example is the SKC conversion calculator (http://www.skcinc.com/catalog/infopage.php?id=9000).

PART 4 Developing a measurement strategy

The following simplified flow chart provides an overview of the steps involved in developing a measurement strategy following a tiered approach including:

1. Basic exposure characterisation of the workplace including indicative personal exposure measurements;
2. Personal exposure measurement - Screening compliance test against Exposure Limit Value; and
3. Personal exposure measurement – Detailed compliance test against Exposure Limit Value.

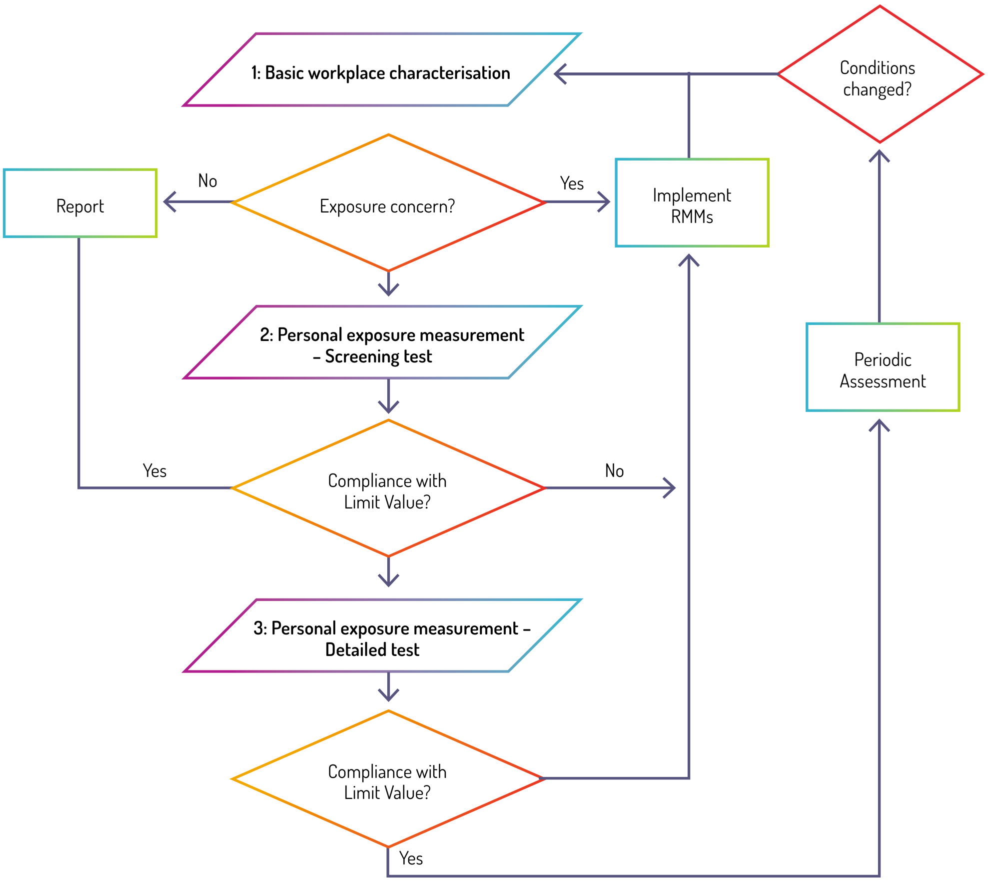

Figure 1: Overview Measurement Strategy – Simplified Flow Chart

It is imperative to assure competent support in the implementation of these steps. Step 1 requires oversight by a Health and Safety professional as a minimum with input from specialist advisers as needed, such as Occupational Hygienist, Toxicologist, Occupational Physician. Steps 2 and 3 require oversight by an experienced Occupational Hygienist.

The first step is to carry out a basic characterisation of exposure to solvent vapours in the workplace prior to considering whether any exposure measurements are needed. In this step the solvents handled need to be identified as well as any relevant workplace factors such as the processes and tasks involving potential for exposure and (groups of) workers who may be exposed.

Elements to consider are:

- Identifying the solvents used including their hazards, OEL values and physical properties impacting exposure potential such as volatility. Once the products have been identified these details can be obtained from the relevant Safety Data Sheets (SDS) or substance/ product suppliers;
- Gaining a general overview of the workplace and its layout, the tasks carried out and the control measures in place;
- Identifying the operators with potential for exposure and considering how the processes vary, perhaps from shift to shift and operator to operator, and how this might affect exposures;
- Carrying out walk-through surveys with direct-reading instruments to help identify sources of vapour emissions and to help to assess the effectiveness of existing control measures, also checking prescribed actions to ensure controls are well maintained and applied as intended. The use of a visualisation technique such as 'smoke tube' to illustrate air movement can be extremely valuable in determining effectiveness of existing controls for limiting/dispersing vapour emissions;
- Reviewing existing exposure measurement results, measurements from comparable installations or work processes to help determine potential exposures.
- Dialogue with operators to identify non-routine tasks or other tasks not readily apparent.

Following completion of the basic characterisation, if no exposure concern is identified then the outcome of the assessment should be recorded. If exposure concern is identified due to ineffective risk management measures, then measures to assure the effectiveness of existing controls should be implemented and, if relevant, apply further low cost measures not requiring capital expenditure such as procedural controls, including keeping lids on containers, prompt and effective spillage clean up, cleaning/storage of personal protective equipment.

If there is uncertainty on the effectiveness of controls and whether or not there is exposure concern, a decision is needed on whether to perform measurement to collect more detailed data on exposure. In this case, it is necessary initially to determine the scope and goal of the assessment, e.g. whether it is to help identify the source of emission/effectiveness of controls, to check compliance against an Exposure Limit Value, or a combination. Based on this a measurement strategy can be developed that includes one or several sampling methods and a range of activities and jobs.

To assess exposure the workforce involved needs to be assigned to groups with more or less the same activities (known as Similar Exposure Groups) to ensure an effective and efficient sampling strategy. The choice of the sampling method will be decided by several factors, including the kind of solvent(s) involved and whether full shift or short term Time Weighted Average (TWA) personal exposures are of interest for comparison with an Exposure Limit Value, or rather identifying the sources of exposure, such as peaks of exposure within a task or job.

In some cases a combination of measurement methods may be needed. For example, to check if additional control measures are necessary for compliance with an Exposure Limit Value using a method to determine TWA exposure, or to identify at what part of the process/activities controls can be most effectively implemented, in which case real time sampling may be appropriate that provides insight to the peaks.

When measuring to check compliance with Exposure Limit Values the measurement strategy should take into account relevant standards such as EN689: 'Workplace exposure - Measurement of exposure by inhalation to chemical agents - Strategy for testing compliance with occupational exposure limit values' (Ref 15). This follows the steps given in the simplified flow chart shown in Figure 1, starting with an initial limited (screening) number of samples which, if all are below a certain percentage of the Exposure Limit Value is sufficient to demonstrate compliance. If not, then further samples are required including validation of the workers within the defined Similar Exposure Groups (SEG). A programme of routine measurements may be needed if exposures are close to the Exposure Limit Value for ongoing demonstration of compliance. **It is imperative that implementation of personal exposure measurement for testing compliance is carried out by an experienced Occupational Hygienist to assure collection of robust sampling data and appropriate analysis.**

Further advice is also available in other technical guidance such as BOHS/NVA: Testing Compliance with Occupational Exposure Limits for Airborne Substances (Ref 14).

Refer to Sections 5 for 'General requirements for measurements' and 6 for 'Types of measurement methods'. Section 3 provides details on Exposure Limit Values for solvents and Section 7 includes an overview of Risk Management Measures.

PART 5 General requirements for measurement

The results of measurements to airborne vapour concentrations may form the basis of significant decisions on possible health risks, compliance with regulations and investment in control measures. As such, it is important that they are undertaken in a structured and meaningful way. This Section sets out the aspects that should be taken into account. Further details on the various measurement methods mentioned is given in Section 6.

5.1. WHAT COMPONENTS SHOULD BE MEASURED?

Solvents often constitute one or more components of a formulated product. Relevant information on the solvent(s) used and the applicable limit values should be provided in Section 8 of the supplier's safety data sheet (SDS). If not, the supplier should be contacted for further information.

5.2. WHERE SHOULD MEASUREMENTS BE MADE?

To demonstrate that exposure does not exceed the appropriate limit value, the sample collected should be representative of the air that people breathe, known as personal exposure monitoring. Measurements should be taken as near as possible to the workers breathing zone (usually in front of and within 30 centimetres of the nose and mouth, although closer is even better).

Measurements may be taken at fixed points in the workplace to assess the effectiveness of exposure control measures (see Section 9) or key sources of vapour emission. Results of fixed position or area monitoring are rarely indicative of personal exposure but may be useful as screening measurements to indicate potential exposure concern.

5.3. HOW DO VAPOUR LEVELS VARY?

Generally, solvent vapour levels will vary substantially both within a working shift (e.g. caused by different tasks) but also between workers and over time (caused by other factors like behaviour or environmental factors like temperature). An example of a shift exposure pattern is shown in Figure 2. Measurement programmes need to take account variation both between workers and over time.

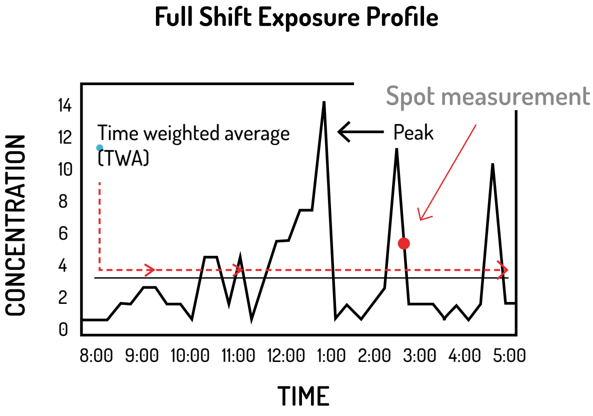
Full Shift Exposure Profile

Figure 2: Example of vapour exposure pattern over a working shift

5.4. WHAT TYPES OF MEASUREMENTS CAN BE MADE?

There are 3 basic types of measurement of airborne concentrations:

- 'Spot' measurements.
- Measurement of the average concentration over a given time period, which may be short or long term, known as the Time Weighted Average (TWA).
- Continuous measurement of concentration at a single location or as a personal monitor in the worker's breathing area.

5.4.1. Spot measurements

These are measurements taken over a short time period (e.g. a few minutes) at a single point in the workplace (which may include the breathing zone of a worker). Also known as 'grab sampling'. They give a rough indication of the concentration at a particular time and location and are indicated on Figure 2 by the red spot. Measurement with a (hand held) Chemical Indicator Device or Photo-Ionisation Detector are common examples.

5.4.2. Short or Long Term Time Weighted Average (TWA) measurements

This measurement period may be the whole of the time period (e.g. covering a whole work shift (known as long term), or the duration of a specific work activity or task (known as short term), or a compilation of consecutive shorter measurements. These measurements, which, once adjusted for duration of exposure, are represented by the red dotted TWA line shown in Figure 2. TWA measurements are particularly useful for measuring personal exposure by sampling air from the breathing zone of a worker. The results can be compared directly with relevant exposure limit values. Although the figure is an illustration from a real-time sampler, common examples of TWA measurements are those obtained by drawing air through a sorbent tube with a pump or via diffusion on to a badge with a sorbent pad. After the sample has been collected the sorbent tube/badge is sent to a suitable laboratory for analysis. An advantage of such measurement methods is that they allow a large range of separate substances to be analysed in the sample and evaluated in the assessment.

5.4.3. Continuous measurement

These provide a continuous measurement of the concentration at a particular time and location as indicated by the black continuous line on Figure 2. Measurement with an electronic photo-ionisation detector (PID) is a common example. These devices generaly assess the concentration to a large range of volatile organic compounds. Some allow assessment of a specific group of substances like aromatics, or have the option to use seperators that allow assessment of one specific substance.

5.5. WHEN TO MEASURE AND HOW LONG FOR?

Measurements for comparison with Exposure Limit Values should be representative of the whole period of 'typical' work activities during which exposure would be expected to occur. The measurements need to confirm that:

- TWA exposure for the whole work shift is below appropriate Exposure Limit Values.
- Exposures during short term tasks are within any Short Term Exposure Limits (STEL) and excursion rules.

In defining a measurement strategy for checking regulatory compliance account should be taken of latest advice including potential for between and within worker variations, numbers of samples required to support statistical analysis (Ref 14, Ref 15). Specialist advice from an experienced Occupational Hygienist is needed to manage such a programme of compliance measurement.

Measurements taken for other reasons, for example to identify vapour emission sources or for confined space entry, are generally taken over much shorter periods using 'spot' measurement techniques. Identifying that a work area or confined space is clean and free of solvents simply means it is safe to enter at that point in time. It does not mean it will remain free of solvents.

Direct reading or real time measurements may also be used as a means to help identify potential high exposures during certain tasks as they occur and assist in targeting any need for further exposure control and/or need for more sophisticated measurement techniques to quantify exposure.

5.6. USING DIRECT READING INSTRUMENTS TO ESTIMATE AIR CONCENTRATIONS

It should be noted that direct reading instruments tend to measure vapour concentrations in ppm, whilst most solvents have Exposure Limit Values expressed in mg/m^3 (refer to Section 3.8).
Direct reading instruments can either be used for measuring spot sampling of air concentrations (hand held) or for personal monitoring if available as a dosimeter with data logging capabilities. Some of the hand held devices provide the opportunity to measure specific components using separator tubes but these have limited capacity so care should be taken to make sure no overloading occurs and with interpretation of results.

The use of direct reading instruments can be extremely valuable in helping to identify emission sources and general airborne levels in the workplace in addition to being used to provide an indication of personal exposure. Further details are given in Section 6.

PART 6 Types of measurement methods

Measurement methods can be broadly subdivided as shown below in Figure 3.

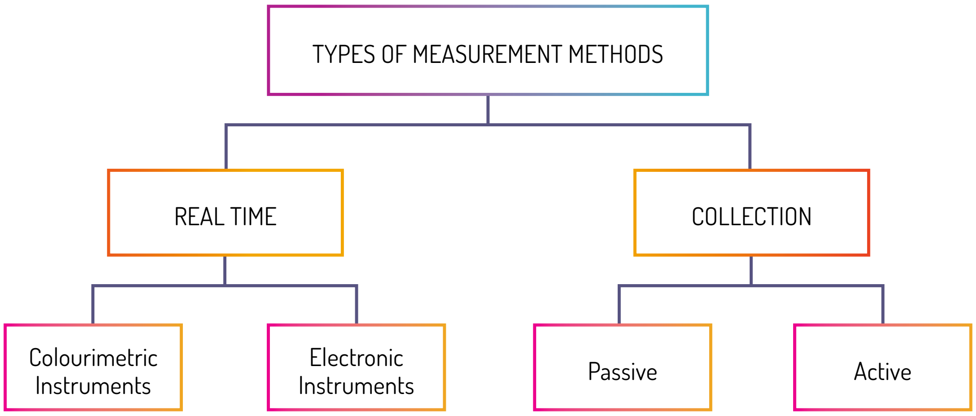

Figure 3: Types of Measurement Methods

These methods have differing levels of accuracy, ease of use and cost that need to be taken into consideration. An overview of each of these methods is given in this section with tips in relation to their application to solvents. In addition, a list of the practical steps in the use of selected methods in Appendix 2 (including: Real Time methods - Chemical Indicator Tubes and Photo-ionisation Detectors; Collection methods - Active and Passive).

6.1. REAL TIME (DIRECT) MEASUREMENT METHODS

Direct measurement methods are those that provide the result immediately. They range from the relatively simple, for example colourimetric techniques, to more complex electronic instruments. Electronic instruments often have the capability to provide continuous reading of airborne concentrations.

6.1.1. Colourimetric Instruments

a. Chemical Indicator Tubes (CIT)

CIT's provide a simple, rapid and inexpensive method for estimating airborne concentrations. A measured volume of air is drawn through the indicator device, for example using a small hand-held pump.

The amount of air sampled during each sample 'stroke' is pre-determined by the sampling pump design and tailored to the tube type, the substance being measured, and the sensitivity required. The length of the resulting 'reactant' stain produced along the axis of the tube is directly related to the concentration of the substance vapour being measured in the atmosphere over the time period during which the measurement is carried out (e.g. 1 minute). The sample volume needed for greater sensitivity for some compounds will demand a longer sample time e.g. 10 minutes or more. A minor calculation may be also required to obtain the final concentration and should be specified in the user instructions.

They are available for many HCS, oxygenated solvents and hydrocarbon mixtures. The length of a coloured stain produced in the tube is related to the concentration of the solvent being measured in the test atmosphere. Although they have an accuracy of typically +/- 25%, they are particularly useful for conducting initial screening measurements to determine whether more detailed investigations are required or for periodic checks to confirm that controls remain effective.

These 'spot check' indicator tubes are a simple and cheap option, but if significant numbers of measurements are needed costs can quickly escalate. The time required to take measurements should also be considered. Measurement time is often about 1-2 minutes per measurement but some vapours/tubes require a larger volume of air to be sampled and a single measurement can take much longer e.g. 10-15 minutes.

b. Other Colourimetric Instruments

Although CIT's are very popular there are variations of this detection principle used in other instruments. Examples of these are:

- Chemical Cassette Indicators e.g. Dräger Chip Measurement System (CMS): This is a good screening tool. It uses a handheld electronic pumping system to sample the vapour into a chemical cassette. Any colour change is measured by the inbuilt optical detection system and a result is displayed once the measurement is complete. Measurement time is similar to that of CITs.
- Dosimeter colour/chemical indicator tubes. These are available for some solvents from manufacturers such as GasTec and Drager. They use a pump to draw air through the tube over extended periods and can be used for personal exposure TWA monitoring. Again, this is a good screening tool.

6.1.2. Electronic Instruments

Electronic methods for chemical analysis are well established. In more recent years these methods have seen extensive development in the area of low level detection (ppm and ppb) of gases and vapours, including more sophisticated ways of recording the measurement data. (Ref 16, Ref 17)

A variety of portable, self-contained direct reading instruments are available to measure total solvent vapour concentrations based on techniques such as photo-ionisation detection (PID), flame ionisation detection (FID), infrared (IR) and even electronic versions of CITs using an optical reader. These are useful for tracing sources of emissions and leaks, measuring the solvent vapour levels present, following the movement and dispersal of vapours in air, testing the atmosphere in confined spaces, and so on. They are the method of choice where continuous or repeated measurements are needed and where solvent specificity is not critical. Some of these instruments are small enough to be clipped to clothing or a body strap and incorporate data logging capability, making them suitable for personal monitoring. The importance of following the manufacturers guidance and instructions is emphasised as these devices require periodic calibration and performance integrity checks.

PID monitors have become very popular and a wide choice of instruments and features are available. The operating principle uses an ultraviolet lamp for which the chemical vapour detection and range (ppm to % v/v levels) are dependent on the energy of the UV lamp. The most common UV source used in these devices is the 10.6eV lamp but there are different energy lamps so it is important to know the performance characteristics and limitations of any device used. Manufacturers will usually publish a list of correction factors which will allow a reading on the instrument to be converted to the solvent of interest. Knowing the lamp strength and the ionization energy (sometimes called ionization potential) for your chemical of concern is important. In general, a chemical with ionization energy lower than that of the lamp photons can be measured.

The PID detector is fast and sensitive but users should be aware that humidity can greatly affect the readings. Additionally, the vast majority of PIDs are not chemical specific so mixtures of gases/vapours that all give a detector response will not allow the selective detection of an individual component. That said, a few popular hydrocarbon substances have been investigated by the equipment manufacturers so that conversion factors to give a 'ppm' value for the complex substance as a whole are available for some common solvents e.g. White Spirit (referred to as Mineral Spirits)[4]

Flame Ionisation Detectors are used mainly in fixed installations supporting continuous measurement. Infrared Detectors can measure to ppm levels, but these are limited in availability and more typically used by specialist personnel.

Electronic instruments are also normally available for hire.

6.1.3. Air Flow Indicator/Smoke Tube

A useful method not involving measurement/quantification of the vapour itself, is the visualisation of air movement and hence the movement of vapours associated with a task. For example, this can bring valuable insight into the effectiveness of ventilation controls to move vapours away from a worker's breathing zone, or to identify potential stagnant air where vapours may accumulate. This, together with the results from spot measurements using direct reading instruments can assist in decisions on the need to improve controls without any need for carrying out personal exposure measurement.

6.2. COLLECTION (INDIRECT) MEASUREMENT METHODS

Collection (also known as Indirect) measurement techniques typically involve adsorption of the vapour on to a collection medium, such as charcoal, and subsequent desorption and analysis in a laboratory to provide the average concentration over the sample period. There are two general methods of collecting the sample, either using a pump to draw a measured volume of air through a sorbent medium (active), or via diffusion (passive). Examples of such measurement methods for solvents are given in Appendix 2.

A significant benefit for complex hydrocarbon solvents of collection measurement methodologies is the ability to analyse the sample via laboratory analysis, typically using a GC-FID (Gas Chromatography-FID) or GC-MS (GC-Mass Spectrometry), and separate out all the component substances. The airborne concentration can then be reported for the individual components of concern for comparison against specific OELs, and the concentrations of all the component substances summed to generate a single concentration for the Total Hydrocarbons present for comparison with the Exposure Limit Value for the mixture as a whole, if available. Airborne concentrations are also given in mg/m^3 the units typically applied to complex hydrocarbon solvents for which the Molecular Weight may not be readily available for conversion to ppm.

It is very important to be fully conversant with the sampling method and, wherever possible, select a validated method. The complexity related to the sample method and the various factors to be considered may require specialist equipment, skills and experience. The advice and/or services of a qualified occupational hygienist/analytical specialist is advised.

6.2.1. Active and Passive Methods

Such techniques are either 'active' in which a pump is used to draw a measured volume of air through a small glass or metal tube containing a sorbent material, or 'passive', in which the sample is collected by a process of natural diffusion without the need for a sample pump. Passive sampling has become increasingly popular for reasons of convenience and cost.

The solvent vapour captured on the sorbent is subsequently desorbed, analysed in a laboratory and the average concentration of solvent vapour over the sampling period calculated. Both methods are suitable for personal sampling.

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[4] Re-named under the HCS naming convension as: Hydrocarbons, C9-C12, n-alkanes, isoalkanes, cyclics, aromatics (2-25%)

These techniques are suitable when initial screening measurements using colorimetric and electronic instruments indicates more detailed/accurate monitoring is required. Although these methods are generally robust and seen as the gold standard for exposure measurement, it is important to be aware that in some situations (e.g. extreme environmental conditions) the suitability of the method should still be checked.

6.2.2. Sample analysis

For indirect sampling it is necessary to send the samples to a laboratory for analysis. In selecting a laboratory it is highly recommended that the laboratory meets appropriate quality assurance criteria, refer to Section 6.2.3.

It is helpful to discuss the planned measurement details with the laboratory in advance of collecting the samples, to check for/confirm specific method requirements.

Analysis is typically done using GC-FID or GC-MS.

The laboratory consolidates all the many individual hydrocarbon components) to generate a Total Hydrocarbon Value for comparison with the relevant HCS limit value. Individual component peaks for constituents of concern, e.g. n-hexane, can also be identified for comparison with the substance specific limit value.

6.2.3. Laboratory Analysis

The analysis of the samples collected on to sorbent materials by active or passive methods should be undertaken by laboratories meeting appropriate quality control/assurance requirements using validated methods. As a minimum the laboratory should:

- Meet ISO 17025: 'General Requirements for the Competence of Testing and Calibration Laboratories' (Ref 8)
- Be accredited to perform the specific analysis by a recognized organization such as the American Industrial Hygiene Association (AIHA) or a national government accreditation scheme such as UKAS (UK) (Ref 9), German DAkkS (Ref 10) and Cofrac (France) (Ref 11)
- Participate in an external quality assurance proficiency-testing scheme for comparison of performance against a standard and with other laboratories for the analyte of interest. International Standards relevant to proficiency testing include ISO/IEC 17043: 'Conformity assessment – General requirements for proficiency testing' (Ref 12) and ISO 13528: 'Statistical methods for use in proficiency testing for interlaboratory comparisons' (Ref 13).

6.3. ADVANTAGES, DISADVANTAGES AND FACTORS IN THE SELECTION OF MEASUREMENT METHODS

6.3.1. Overview of advantages and disadvantages

All the available measurement methods have their applications, advantages and disadvantages as outlined in Table 2 below.

Table 2: Available measurement methods: Their application, advantages and disadvantages

TECHNIQUE	APPLICATIONS	ADVANTAGES	DISADVANTAGES
ALCOHOLS			
Colourimetric Instruments	confined space entry identifying high exposure tasks personal (screening) / area monitoring	easier to use and minimal training quick response often within about a minute lower cost & minimal maintenance small/compact no separate laboratory analysis	many potential interferents some colour changes can be difficult to read variable & lower level of accuracy (+/-25%) do not normally measure TWA but some exceptions
Electronic instruments	confined space entry identifying emission sources determining exposure variation (profiles) identifying high exposure tasks personal (screening) /area/continuous monitoring	easier to use and minimal training, unless data logging capability is applied very quick response and often have data recording accuracy often better than colour indicating devices warning alarms - often user adjustable no separate laboratory analysis	interference possible higher cost regular maintenance and function /bump check required can be bulky and may require regular battery recharge need to consider intrinsic safety of equipment for flammable atmospheres some instruments have humidity impacts that can be significant some instruments have non-specific detectors that cannot distinguish one chemical from another

TECHNIQUE	APPLICATIONS	ADVANTAGES	DISADVANTAGES
COLLECTION			
Active sampling	Personal/area monitoring identifying specific contaminants present	more accurate small, lightweight versions available able to measure individual components can determine short term (<15min) & long term (8hr TWA) exposure many validated methods available	results not immediately available high cost per sample higher competency/more experience required various checks required, including sample flow do not give real-time variation need to consider intrinsic safety of sampling pumps for flammable atmospheres
Passive sampling	Personal/area monitoring identifying contaminants present	more accurate easy to use, small, lightweight with no pump needed able to measure individual components particularly useful for 8 hour TWA measurements many validated methods & uptake rates available no electronic component, hence intrinsic safety considerations not needed	results not immediately available validated method required high cost per sample higher competency/more experience required limitations for short-term sampling (e.g. 15min or less) do not give real-time variation

6.3.2. Overview of factors relevant when selecting an air measurement method

The following provides an overview of the factors to be taken into account prior to selecting an air measurement method for any particular application:

- *Accuracy* – Closeness of measurement result to the actual concentration present
- *Sensitivity* – Quantity of material that must be present in the air to get a response
- *Cost* – The expense associated with the hire or purchase of equipment or supplies, as well as any associated laboratory analysis costs for indirect methods
- *Ease of use* – How much training is required to accurately conduct the test and how difficult it is to operate the associated equipment
- *Calibration* – What checks are required to verify that an electronic instrument is performing acceptably at the concentration(s) of interest
- *Validation* – is the method validated and accepted by, for example, regulators.
- *Bump test/check* - A test done more frequently than calibration on direct reading electronic instruments, typically just before the measurement, to provide confidence the instrument is responding to the target gas/vapour
- *Interferences/specificity* – Will the techniques react to substances other than the compound of interest (cause a colour change or give a meter response)? Interferents may cause an overestimation or underestimation of the amount of material present in the air
- *Exposure metric of interest* – The concentration of contaminants can vary significantly from minute to minute over the course of a day; depending on the purpose of the sampling different metrics of exposure may be of interest, e.g. the average exposure over a specified period is required for comparison with limit values
- *Size & weight of equipment* – Important for monitoring where the equipment is attached to the individual
- *Warning alarm*s – For direct reading electronic devices, an audible/visual warning may be desirable to alert personnel that higher than acceptable concentrations are present
- *Immediacy of results* – immediate (direct reading instruments) versus delayed results (indirect techniques)

Great care needs to be taken over the selection of measurement methods and the interpretation of the results. The methods selected must be appropriate for the solvents present and used in such a way as to provide meaningful results. If in any doubt, it is best to check with equipment suppliers or obtain advice from an expert in Occupational Hygiene.

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5. Occupational Hygiene experts can be identified via their national associations, see: ioha.net/member-organisations/.

PART 7 Risk management measure/exposure control options

If the conclusions resulting from the measurement results indicate that improvements in exposure control are necessary, a number of possible approaches are available to minimise solvent exposure in the workplace following the hierarchy of control:

1. Eliminate or substitute the substance for a safer alternative, e.g. solvent with a lower hazard profile, higher Exposure Limit Value, lower volatility.
2. Enclose the process so that the solvent does not escape.
3. Extract emissions of the substance near the source:
    - Local exhaust ventilation – to remove vapour close to its point of release, and either absorb onto a collection medium or transfer for release at a safe location.
4. General or dilution ventilation – to adequately dilute any released vapours and directed so as to carry vapour away from working areas.
5. Workplace arrangements e.g. to segregate areas with higher potential vapour levels and minimise the number of people exposed.
6. Procedures – to minimise vapour production and release, e.g. keep lids on containers, clear up spillages promptly.
7. Personal Protective Equipment (PPE) such as gloves, coveralls and a respirator. PPE must fit the wearer.

Although exposure to vapour can be reduced by the use of respiratory protective equipment (RPE), this is normally regarded as the least preferable choice. It is only acceptable where vapour control systems are unable to provide adequate levels of health protection, as a secondary line of defence or as a temporary measure while control systems are being installed. Respiratory protection is commonly used for maintenance work or emergency situations such as spills.

It should be appreciated that RPE may not give completely effective protection, and its use requires a formal programme of equipment selection, training, fit testing and maintenance. In addition, national legal requirements might exist which regulate the use of respiratory protection, e.g. wearing time.

Absorption of solvents via skin contact can be prevented by the use of impermeable protective clothing such as chemical resistant gloves. Another ESIG Guide provides additional information on glove selection for solvents and their use (Ref 18).

It is recommended to seek specialist advice, e.g. from an Occupational Hygienist, in the selection, use and maintenance of all control measures.

In addition to protection of workers, effective control of vapour can have the added benefit of generating cost-savings such as reducing solvent usage and wastage, reducing waste solvent disposal costs and reducing time spent on cleaning up spills.

PART 8 Key messages

8. 1. EXPOSURE LIMIT VALUES

- Many HCS are complex substances containing numerous individual HC species for which there are no limit values available. As most HCS have similar toxicological properties and therefore similar health effects, the compositional variability can be managed on a generic basis. As a conservative approach the total concentration of HCS may be compared to the lowest OEL of the individual components. Alternatively, the RCP methodology can be used to derive a single limit value for the complex substance simplifying their measurement and assessment to demonstrate safe use. Section 3.
- The RCP methodology can also be used to generate a limit value for a solvent blend. In this case, it is important to take account of varying vapour pressure values for each solvent in the blend. This may impact the mass fraction in the vapour phase compared to the liquid phase, and influence the calculation of the limit value for the blend.
- Exposure Limit values calculated by using the RCP methodology for the HCS registered under REACH see overview document, Hydrocarbon Solvents registered under REACH – key data . These have been derived based on average compositional data[6]. For specific values actual compositional data should be applied available from the Supplier.
- Exposure Limit Values have been established for most Oxygenated Solvents by official bodies, examples are included in Oxygenated Solvents registered under REACH – key data[7].
- DNEL values are applied for the demonstration of safe use of a substance as part of the Chemical Safety Assessment carried out by the Manufacturer/Importer under REACH. Whilst OELs are limit values applied by users of a substance as part of their local workplace risk assessment required under national legislation implemented in accordance with the Chemical Agents Directive (CAD). An outline of the differences in their basis is given in Section 3.5.

8.2. WORKPLACE ASSESSMENT

- There are many reasons for measuring solvent vapour concentrations in the workplace, beyond assuring compliance with an exposure limit value. Section 2.
- The results of measurements to airborne vapour concentrations may form the basis of significant decisions on possible health risks, compliance with regulations and investment in control measures. As such, it is important that they are undertaken in a structured and meaningful way.
- Developing a measurement strategy should take a tiered approach, starting with a workplace assessment to help characterise the basic exposures, including: identifying the substances handled, their hazards and associated limit values; obtaining a general overview of the workplace and its layout, the tasks carried out and the control measures in place and their effectiveness; identifying the workers with potential for exposure and considering how the processes vary, perhaps from shift to shift and operator to operator, and how this might affect exposures. Sections 4 and 5.
- The use of an airflow indicator (e.g. ‘smoke’ tube) to help visualise air/vapour movement, together with the

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[6] www.esig.org/wp-content/uploads/2018/08/HCS-key-data-2018_07_23-Final.pdf

[7] www.esig.org/wp-content/uploads/2018/08/OSPA_REACHkeydata_20180718-1.pdf

results from spot measurements or equipment with integrated data-logging capability using real time/direct reading instruments can inform decisions on vapour emission sources, peak exposures together with the associated tasks and hence any need to improve controls without carrying out more sophisticated personal exposure measurements.

- If it is decided that personal exposure sampling to confirm compliance with an Exposure Limit Value is needed, the workforce should first be organised into groups of workers with similar exposures (SEG), i.e. groups with similar job exposure profiles who perform similar tasks involving potential exposure to the same substances. An exposure measurement strategy meeting the requirements of EN689 (Ref 15) should be implemented under the supervision of a qualified Occupational Hygienist. Section 4.
- For a mixture of solvents that do not have similar toxicological effects, the ill-health effects are not additive. Therefore, the single compounds need to be measured and assessed separately against their individual limit values, assuming there are no interferences between the solvents impacting the measurement technique. Section 3.7.
- Always take account of the hierarchy of control when selecting or reviewing risk management measures. All controls should be subject to regular inspection and maintenance to assure their ongoing effectiveness. Section 7.
- For regulatory compliance, it is necessary to take account of Risk Management Measures given in supplier REACH Exposure Scenarios in addition to confirming exposures are within national limit values.
- This guidance focuses on airborne exposure to solvent vapours, a workplace risk assessment should also take account of potential for exposure via skin contact.

8.3. EXPOSURE MEASUREMENT TECHNIQUES

- Colourimetric techniques such as Chemical Indicator Tubes provide a simple, rapid and inexpensive method for evaluating airborne vapour concentrations.
- A variety of portable electronic direct reading instruments are available and useful for, e.g. tracing sources of emissions and leaks, measuring the solvent vapour levels present, following the movement and dispersal of vapours in air, testing the atmosphere in confined spaces.
- Real time instruments are available that are small enough to be used as personal samplers. Some incorporate data logging capability, making them suitable for personal monitoring for longer periods (e.g. extended tasks or full shifts). They provide information on TWA exposure as well as exposure patterns (e.g. peaks).
- Direct reading instruments measure the total vapour in the atmosphere to give one total hydrocarbon value, typically reported in ppm, whilst limit values for complex HCS are typically given in mg/m^3. To allow for ready conversion between mg/m^3 and ppm conversion calculations are given in Appendix 4.
- Collection (Indirect) measurement techniques typically involve adsorption of the vapour on to a collection medium, such as charcoal, and subsequent desorption and analysis by GC-FID or GC-MS. The gas chromatogram identifies the many components of a complex HCS as separate peaks which are consolidated to generate a single total hydrocarbon value for direct comparison with the RCP limit value for the substance. It is also possible to identify concentration peaks for certain specific components of concern, e.g. n-hexane, which can be separately compared against its own limit value. Section 6.2.2.
- Collection measurement techniques typically have greater specificity and accuracy compared to real time (direct) measurement methods and are considered the gold standard for measuring personal exposure for

verifying regulatory compliance against exposure limit values with associated statistical analysis.

- All the available measurement methods have their applications, advantages and disadvantages which are captured in Table 2.

Some key DO's and DO NOT's when measuring airborne vapour concentrations are given in Table 3 below.

Table 3: Do's and Don'ts when measuring airborne solvent vapour concentrations

DO	DO NOT
DO use simple direct reading techniques to determine approximate concentrations of contaminants in work areas and identify priorities for more detailed investigations.	DO NOT base exposure control investment decisions or compliance testing on a few direct reading measurements taken very close to the source of the vapour unless the results really reflect the concentrations workers are being exposed to.
DO use techniques which provide data representative of personal exposure where the air is collected from as near to the mouth/nose (breathing zone) as possible, when collecting data to determine compliance with OELs.	DO NOT allow suggestions for 'further measurements' to delay the introduction of improved controls, when it is clear that these are necessary.
DO ensure that those conducting measurements have received sufficient training to understand the capabilities and limitations of the techniques used.	DO NOT assume that expensive electronic instruments have to be used; simple, inexpensive techniques are often adequate.
DO repeat measurements if significant changes occur to materials, processes or work patterns.	DO NOT forget that help and advice is available from solvent suppliers and equipment manufacturers.
DO seek advice from suppliers or qualified consultants if additional information is needed to make decisions.	DO NOT assume this is always correct for your situation - a sense check is useful and be willing to question and seek further advice.
DO use 'gold standard' collection (indirect) measurement techniques when verification of compliance with a limit value is required together with statistical analysis	DO NOT implement collection (indirect) measurement techniques without the necessary expertise to develop and implement a suitable measurement strategy.

PART 9 Acronyms/glossary

DAkkS: DAkkS is the national accreditation body for the Federal Republic of Germany. Pursuant to Regulation (EC) No. 765/2008 and the Accreditation Body Act (AkkStelleG), it acts in the public interest and as the sole provider of accreditations in Germany.

ESIG: European Solvents Industry Group

Exposure Limit Value/Limit Value: a generic term cover all types of occupational exposure limit whether set by regulatory authorities, scientific bobies or trade organisations or individual suppliers. See also OEL.

Exposure Scenario (ES): An exposure scenario is the set of conditions that describe how a substance being registered under REACH is manufactured or used during its life-cycle and how the manufacturer or importer controls, or recommends others to control, exposures to the substance by humans and the environment. It is relevant for hazardous substance manufactured/imported at greater than 10 tonnes/year.

GC-FID: Gas Chromatography/Flame Ionisation Detector

GC-MS: Gas Chromatography/Mass Spectrometry

GGV: Group Guidance Value. Guidance limit values derived for groups of similar hydrocarbon solvents based on detailed hazard assessment of their toxicological properties.

HRA: Health Risk Assessment. The identification of health hazards in the work place and subsequent assessment of risk to health, taking account of existing control measures. Where appropriate, the need for further measures to control exposure is identified.

HSE: Health and Safety Executive

HSPA: Hydrocarbon Solvents Producers Association. Part of ESIG

Independent effect (mixtures): Where no synergistic or additive effects are known or considered likely, the constituents can be regarded as acting independently.

IR: Infra-red

iOELv: Indicative Occupational Exposure Limit Value. Set by the European Union

ISO: International Standards Organisation

LDL: Lower Detection Limit. The lowest airborne concentration that the measurement method can detect.

MAK: Maximum Concentration Values in the Workplace. The German system for setting exposure limits to airborne chemicals.

MDHS: Methods for the Determination of Hazardous Substances, UK HSE

MW: Molecular Weight

NOAEC: No observed adverse effect concentration

NVA: Nederlandse Vereniging voor Arbeidshygiene

OEL: Occupational Exposure Limit. This is the general term for the airborne concentration of a chemical judged to be adequate to protect against adverse health effects when compared to a standard reference period. Two time periods are normally used, long term (8 hours) and short term (15 minutes). It should be noted that in some countries different types of OEL may be set which may require achievement of exposure levels as far below the OEL as reasonably practicable, e.g. the UK Workplace Exposure Limit (WEL). It is recommended that fuller definitions of national, regulatory OELs should be sought within the country of use.

OSPA: Oxygenated Solvents Producers Association. Part of ESIG

PID: Photo-Ionisation Detector

PPB: Parts per billion

PPM: Parts per million.

RCP: Reciprocal Calculation Procedure. Applied to harmonise the approach to setting limit values for complex hydrocarbon solvents.

REACH: Registration, Evaluation and Authorisation of Chemicals, EU Regulation

SEG: Similar Exposure Group. “A group of workers having the same general exposure profile for an agent because of the similarity of the materials and processes with which they work, and the similarity of the way they perform the task(s).” This definition by Mulhausen and Damiano (2006)

Synergistic effect (mixtures): The overall effect is considerably greater than the sum of the individual effects. This may arise from the mutual enhancement of the effects of the constituents of the mixture or because one substance potentiates another, causing it to act in a way which it would not do alone

SDS: Safety Data Sheet. A legal requirement for all classified chemical substances for supply, including: information on the main health, safety and environmental hazards; how to protect against them in normal usage and in emergency situations; OELs; handling, storage and transport; spills and disposal advice; regulatory information such as classification and labelling; toxicity and environmental information

SSV: Substance Specific Value. Identified for certain substances when applying the Reciprocal Calculation Procedure for complex hydrocarbon solvents

STEL: Short Term Exposure Limit, reference period normally 15 minutes

TLV: Threshold Limit Values. The ACGIH system for setting exposure limits to airborne chemicals

TWA: Time Weighted Average. The normal method for calculating how much airborne chemical a worker has been exposed to. Often measured over an 8-hour working day. And can also be a reference to the airborne concentration at which a worker may be exposed (e.g. 8-hour TWA)

UKAS: United Kingdom Accreditation Service. The UK’s National Accreditation Body, responsible for determining, in the public interest, the technical competence and integrity of organisations such as those offering testing, calibration and certification services

Validated Method: A method that meets certain specifications which are demonstrated by examination and provision of objective evidence that the particular requirements for a specific intended use are fulfilled

WEL: Workplace Exposure Limit, UK OEL

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APPENDIX 1

Group Guidance Values (GGV)/Substance-Specific Values (SSV) for the Hydrocarbon Solvent RCP Calculation

The following table provides the Group Guidance Values (GGV) and Substance-Specific Values (SSV) identified for the relevant hydrocarbon groups (Ref 6).

Hydrocarbon Solvent Constituent Group	Proposed Group Guidance/ Substance Specific alue (mg/m^3)	Constituents with EU OELs (mg/m^3)
C5-C8 Aliphatics	1400	Pentane (all isomers) – 2950 Hexane (all isomers)[1] – 1760 Heptane (all isomers) – 1640 Octane (all isomers) – 1401 Cyclopentane – 1720 Cyclohexane – 350 Methylcyclohexane – 1610
C9-C15 Aliphatics[2]	1050	Use SSV
C7-C8 aromatics[3]	Use SSV	Use SSV
C9-C15 Aromatics[4]	100	Cumene – 50 Indene – 24 Biphenyl – 1.3
DO seek advice from suppliers or qualified consultants if additional information is needed to make decisions.		DO NOT assume this is always correct for your situation - a sense check is useful and be willing to question and seek further advice.

1. Except n-hexane.
2. Because of their very low vapour pressures, constituents with carbon numbers > C15 do not contribute significantly to overall vapour exposure. However, the potential for aerosol exposure must be considered.
3. Group eliminated in favour of adopting existing national regulatory values as SSVs.
4. Because of their higher boiling points, aromatics with more than 2 rings are not commonly found at more than trace levels in hydrocarbon solvents.

Hydrocarbon Solvent Constituent Group	Proposed Group Guidance/ Substance Specific Value (mg/m^3)	Constituents with EU OELs (mg/m^3)
SUBSTANCES WITH SUBSTANCE SPECIFIC VALUES - SSV		
	EU-OEL	ACGIH TLV
n-hexane	72	176
Toluene	192	75
Xylene -all isomers	221	434
Ethylbenzene	88	87
Naphthalene	52	52
Diethyl/Triethyl benzene	28	No value

ACGIH Rounding Rules	Example	
OEL < 100 mg/m^3	Nearest 25	92 mg/m^3 x 100 mg/m^3
OEL = 100 - 600 mg/m^3	Nearest 50	423 mg/m^3 x 400 mg/m^3
OEL > 600 mg/m^3	Nearest 200	705 mg/m^3 x 800 mg/m^3

APPENDIX 2

Practical steps involved in implementing selected measurement methods for solvents

Section 5 provides an overview of the various measurement methods relevant for use with solvents. Some practical tips in the application of the main methods applied are given here, including: 1. Chemical Indicator Tubes, 2. Photo-Ionisation Detectors, 3. Sample collection (indirect) methods.

1. CHEMICAL INDICATOR TUBES

Practical use of Chemical Indicator Tubes

1. Check that the hand pump is functioning correctly (i.e. it is leak-tight), using the procedures detailed in the manufacturer's instructions. This should include any extension hose used.
2. Select appropriate indicator tubes; check that the tubes are suitable for use (e.g. within their expiry date on box, and can get to the desired limit of detection), compatible with the pump and that they have been correctly stored.
3. Read the instructions provided on the accompanying leaflet. Check the number of pump strokes to be performed (this varies depending on concentration range of interest), and the expected delay or sample time for each stroke. Also check for likely interference(s) and airborne vapour concentration limitations.
4. Break the ends off the indicator tube according to the manufacturer's instructions, and insert the tube firmly into the pump inlet aperture. Ensure the tube is inserted in the correct direction. There is typically an arrow on the tube that should be pointed towards the hand-pump when inserted.
5. Draw the prescribed volume of workplace air through the tube by operating the pump for the set number of strokes, allowing the required sampling time between each stroke for the gas to be drawn through the tube and react with the media.
6. Read off the length of stain obtained against the concentration scale markings on the outside of the tube. The reading is the furthest point along the color change. If the leading edge is diagonal or diffuse, use the average of the minimum and maximum values. When the demarcation of the color change layer is pale (the color appears to be fading instead of stopping), read the value at the middle point between the dark layer end and the pale layer end. Read the tube immediately as the stain may fade or spread. Record all values.
7. You should seek the tube manufacturer's guidance on disposal.

Note:

Each tube comes with a specific information sheet describing the tube and how it is to be used e.g. how many pump strokes, interferences, temperature and humidity impacts. These instructions must be carefully followed. If there is any doubt speak to the tube manufacturer.

Table 4: CITs: Advantages, Limitations, Application to Solvents

Advantages	General Limitations	Application to Solvents
• Easy to use • Minimal training required • Portable • No laboratory analysis necessary • No on-site calibration required • Immediate results • Low cost	• Precision and accuracy is relatively low with ±25% being typical value. • Be alert to interferences from other substances present which may impact results. • Temperature and/or humidity correction may be needed. Using the hand-pump and tubes outside their respective operating temperature ranges may cause the pump to leak or result in inaccurate measurements	• Some tubes are designed and calibrated for the solvents mixture as a whole. But watch out for cross reactions causing errors in the analysis. • Solvents with final boiling points greater than 200°C (e.g. glycol ethers) do not readily volatilise due to their low vapour pressure. They will only give rise to significant airborne concentrations when used at elevated temperatures. • To help account for low precision and accuracy, use tubes with the first scalemark equal to/or below 50% of the OEL. • Tubes with the first scale mark near or greater than the OEL can still be useful as a practical tool to identify potentially excessive exposures.

2. PHOTO-IONISATION DETECTORS

Practical use of Photo-Ionisation Detectors

1. Be conversant with the instrument manufacturers guidance and instructions.
2. Understand the locations where PID measurenemts will be made. Where high humidity exists, condensation of water vapour on the PID sensor can impact responses. Condensation typically occurs when a PID is brought from a cool, dry indoor environment to a warm, humid outdoor environment. This condition can be minimized by warming the PID to the measurement temperature before entering the humid environment.
3. Inspect unit and accessories for signs of damage or defect.
4. A calibration check (covering zero and its range) is advised prior to use. PIDs are most commonly calibrated with isobutylene (IBE). For best results, use a IBE gas concentration near the expected measurement range. Record the calibration details.
5. A flow integrity check is often advised prior to use and is achieved by temporarily blocking the gas flow into the instrument which should stall the instrument and show a fault condition.
6. Know the calibration basis of the instrument along with any correction factor to be applied to interpet the measured ppm result for the solvent of interest.
7. Allow sufficient time for a reading to be achieved.
8. Note the instrument reading and apply the appropriate conversion factor to give a ppm value of the solvent. Many instruments will have data logging capabilities including the ability to record information in real time with user selectable time intervals. If data capacity allows, then the smallest time interval available is recommended to allow for more detailed interpretation of concentration variation with time.
9. Operate the instrument in clean air following use until the display returns to zero ppm before switching off.

10. Take account of potentially flammable atmospheres and use an intrinsically safe instrument if needed.
11. Many instruments will have user selectable alarm features and the ability to calculate time weighted average readings (e.g. STEL & TWA). The manufacturer should be able to provide the basis of the time averaged calculations.

3. SAMPLE COLLECTION/INDIRECT SAMPLING METHODS

Practical use of active sampling methods

A list of important considerations in the practical application of active methods is given below:

1. The method guidance will typically include information on:
    - sampling media/sorbent
    - permissible flow rates (flow rate range) – typically low flow for measuring solvent vapours
    - air sample volume required (min and max volumes)
    - sampling times
    - sample stability and storage
    - number of blanks
    - potential intererences
    - any environmental considerations (e.g. relating to humidy, ambient temperature)
2. Once the sampling device is assembled (typically a sample pump, tubing, sample tube holder and sorbent tube). The flow rate through the whole assembly is adjusted and checked to ensure that it is set to the required value.
3. For personal sampling the sample device (e.g. sorbent tube & tube holder) should be positioned in the vicinity of the workers breathing zone; this is typically within a 30 cm distance, or closer, of the workers nose/mouth.
4. Consideration should have also been given to the practical aspects of a worker wearing the device without it causing hinderance of any sort to the task. It should be comfortable to wear and any loose tubing should be secured e.g. pinned or taped, to avoid it becoming entangled. The sampling media should not be covered by personal protective equipment (PPE) or other clothing during sampling.
5. Sample pumps may, or may not, be instrinsically safe and certified for use in potentially flammable atmospheres. Awareness of the safety issues, procedures and precautions is important when using any portable battery operated equipment.
6. Once the worker has completed the task and/or the required sampling time has elapsed, the sampling device should be stopped and removed. The flow rate through the sample system should be checked before the sampling assembly is dismantled to verify the flow rate has remained within the acceptable limits from the beginning to the end of the sampling exercise.
7. Samples should be appropriately sealed, stored and labelled.
8. Subsequent storage, packaging and transport to the laboratory for analysis should follow the protocols advised by the analysing laboratory, as well as being consistent with the method guidance (e.g., storge and shipping temperature requirements). A conversation with the analysing laboratory to clarify any points is advised before any sampling exercise is started.
9. A protocol for recording all of the relevant data to enable the calculation of exposure concentrations relating to the task is advised.

Practical use of passive sampling methods

Passive measurement methods involve many of the same considerations listed above for active methods. The major advantage of a passive measurement system is that if does not require the use of a sample pump which greatly simplifies the application. However, passive methods typically have minimum sampling times that must be met for the sampling result to be valid, similar to active methods. All considerations around selecting a valid method, deployment in the sampling task and consultation with the analysing laboratory remain.

APPENDIX 3

Example Collection (Indirect) Measurement Methods for Hydrocarbon Solvents (HCS)

HCS Group	Example Measurement Methods (Seek expert advice)
C5-C8 Aliphatics	BIA 7732 Hydrocarbons, Aliphatic MDHS 72[1], 80[2], 88[3], 96[4]
MDHS 721, 802, 883, 964	BIA 7732 Hydrocarbons, Aliphatic MDHS 72[1], 80[2], 88[3], 96[4]
C9-C15 Aliphatics	BIA 7733 Hydrocarbons, Aromatic MDHS 72[1], 80[2], 88[3], 96[4] NIOSH 1501 Hydrocarbons, Aromatic
Specific Substances	
n-Hexane	BIA 7732 Hydrocarbons, Aliphatic MDHS 72[1], 80[2], 88[3], 96[4] NIOSH 1500 HYDROCARBONS, BP 36°-216 °C
Naphthalene	MDHS 7[21], 80[2], 88[3], 96[4] NIOSH 1501 Hydrocarbons, Aromatic
CEN General methods	CEN 482[5], 689/PrEN689[6], 838[7], 1076[8]

1. **MDHS 72:** Volatile Organic Compounds in air. Laboratory method using pumped solid sorbent tubes, thermal desorption and gas chromatography.
2. **MDHS 80:** Volatile Organic Compounds in air. Laboratory method using diffusive solid sorbent tubes, thermal desorption and gas chromatography.
3. **MDHS 88:** Volatile Organic Compounds in air. Laboratory method using diffusive samplers, solvent desorption and gas chromatography.
4. **MDHS 96**: Volatile Organic Compounds in air. Laboratory method using pumped solid sorbent tubes, solvent desorption and gas chromatography.
5. **CEN482**: Workplace exposure - General requirements for the performance of procedures for the measurement of chemical agents.
6. **CEN689:** 2018. Workplace exposure - Measurement of exposure by inhalation to chemical agents - Strategy for testing compliance with occupational exposure limit values (undergoing final approval – to supercede EN689) (Ref 15).
7. **CEN838:** Workplace Atmospheres - Diffusive samplers for the determination of gases and vapours - Requirements and test methods.
8. **CEN1076:** Workplace exposure - Procedures for measuring gases and vapours using pumped samplers - Requirements and test methods.

APPENDIX 4 Method for Converting between mg/m^3 and ppm

Converting from mg/m^3 to ppm

$$C\ (ppm) = \frac{C\ (mg/m^3)}{Mol.Wt} \times 24.055$$

- C = concentration
- Where 24.055 is the mole volume of an ideal gas at C and 1 atmosphere (760 mm Hg, 101325 Pa, 1.01325 bar).
- Mol. Wt (MW) = Molecular Weight (i.e. the molar mass, in g/mole) is substance specific and should be referenced from chemical suppliers or scientific texts.

Example for Acetone:

$$C\ (ppm) = \frac{500}{58} \times 24.055$$

Molecular Weight of Acetonel = 58 (i.e. the molar mass, in g/mole)

- Assumed concentration = 500 mg/m^3
- Converts to concentration = 207 ppm

Converting from ppm to mg/m^3

$$C\ (mg/m^3) = \frac{C\ (ppm)}{24.055} \times Mol.Wt$$

Example for Hydrocarbons, C10, Aromatics, >1% Naphthalene:

$$C\ (mg^3) = \frac{100\ (ppm)}{24.055} \times 134$$

- Molecular Weight of Hydrocarbons, C10, Aromatics, >1% Napthalene = 134 (i.e. the molar mass, in g/mole)
- Assumed concentration = 100 ppm
- Converts to concentration = 557 mg/m^3

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