

**Economic and Social Council**Distr.: General  
4 October 2016

Original: English

**Economic Commission for Europe**Executive Body for the Convention on Long-range  
Transboundary Air Pollution**Working Group on Strategies and Review****Fifty-fourth session**

Geneva, 13 and 14 December 2016

Item 3 of the provisional agenda

**Progress in the implementation of the 2016–2017 workplan****Draft guidelines for estimation and measurement of  
emissions of volatile organic compounds\*\*****Prepared by the Task Force on Techno-economic issues***Summary*

The 2012 amendments to the Protocol to Abate Acidification, Eutrophication and Ground-level Ozone (Gothenburg Protocol) to the Convention on Long-range Transboundary Air Pollution not only introduce commitments for Parties to reduce emissions of volatile organic compounds (VOCs), but also mandatory emission limit values for different activities in annexes VI and XI to the Protocol and the establishment of solvent management plans for activities using solvents covered by annex VI. The present document provides guidelines to measure VOCs emissions, develop solvent management plans and calculate emissions. It corresponds to the requirement in annex VI to the amended Protocol that “methods of calculation will be reflected in the guidance adopted by the Executive Body”.

The draft guidelines are being presented to the Working Group in accordance with the mandate provided by the Executive Body (see ECE/EB.AIR/135, annex). The Working Group considered an earlier version of the guidelines at its thirty-third session (Geneva, 15–17 December 2015). They have subsequently been updated, following comments received from Belarus and the ad hoc drafting group established at the request of the Working Group at that session. It is expected that a final draft, incorporating any comments made by the Working Group at its present session, will then be submitted to the Executive Body for the Convention for adoption at its thirty-sixth session (Geneva, 15–16 December 2016).

\*\* The present document is being issued without formal editing.



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## List of abbreviations and acronyms

API	American Petroleum Institute
BAT	best available techniques
BREF	BAT reference documents
BTEX	benzene, toluene, ethylbenzene and xylenes
C	carbon
CEN	European Committee for Standardization
CH <sub>4</sub>	methane
C <sub>3</sub> H <sub>8</sub>	propane
CO <sub>2</sub>	carbon dioxide
CONCAWE	European Petroleum Refiners Association
E	emission
ELV	emission limit value
ELVc	emission limit value in waste gas
ELVf	fugitive emission limit value
FID	flame ionization detector
FR	response factor
FTIR	Fourier transform infrared absorption
g	grams
GC	gas chromatography
IR	infrared
ISO	International Organization for Standardization
K	Kelvin
Kg	kilogram
KPa	kilopascal
M	atomic molar mass in grams per mole (g/mol)
m <sup>2</sup>	square metre
m <sup>3</sup>	cubic metre
mc	mass of carbon in a VOC
mg	milligram
Mg	megagram
MPE	maximum permitted emissions
NDIR	non-dispersive infrared

NIOSH	National Institute for Occupational Safety and Health (United States of America)
Nm <sup>3</sup>	normal cubic metre
O	oxygen
OSHA	Occupational Safety and Health Administration (United States)
ppm	parts per million per volume
QA/QC	quality assurance/quality control
SMP	solvent management plan
STP	standard temperature and pressure
TOC	total organic carbon
TVOC	total volatile organic compounds
USEPA	United States Environmental Protection Agency
UV	ultraviolet
VOCs	volatile organic compounds

## I. Context and aim of the guidelines

1. The 2012 amendments to the Protocol to Abate Acidification, Eutrophication and Ground-level Ozone (Gothenburg Protocol) not only introduce commitments for the reduction of emissions of volatile organic compounds (VOCs) by Parties but also mandatory emission limit values (ELVs) for different activities in annexes VI and XI to the Protocol and the establishment of solvent management plans for activities using solvents covered by annex VI.

2. According to paragraph 4 of annex VI, the following requirements shall be satisfied:

(a) Emissions shall be monitored in all cases via measurements or through calculations achieving at least the same accuracy. Compliance with ELVs shall be verified through continuous or discontinuous measurements, type approval, or any other technically sound method. For the emissions in waste gases, in case of continuous measurements, compliance with the ELVs is achieved if the validated daily emission average does not exceed the ELVs. In case of discontinuous measurements or other appropriate determination procedures, compliance with the ELVs is achieved if the average of all the readings or other procedures within one monitoring exercise does not exceed the limit values. The inaccuracy of the measurement methods may be taken into account for verification purposes. The fugitive and total ELVs apply as annual averages;<sup>1</sup>

(b) The concentrations of air pollutants in gas-carrying ducts shall be measured in a representative way. Monitoring of relevant polluting substances and measurements of process parameters, as well as the quality assurance of automated systems and the reference measurements to calibrate those systems, shall be carried out in accordance with European Committee for Standardization (CEN) standards. If CEN standards are not available, International Organization for Standardization (ISO) standards, national or international standards which will ensure the provision of data of an equivalent scientific quality shall apply.

3. This document provides guidelines to measure VOCs emissions, develop solvent management plans and calculate emissions. It corresponds to the requirement set by annex VI to the Gothenburg Protocol, as amended, which stipulates that “emissions shall be monitored in all cases via measurements or through calculations achieving at least the same accuracy”, noting that “methods of calculation will be reflected in the guidance adopted by the Executive Body”, with the ultimate goal of facilitating the ratification and implementation of the amended Protocol.

## II. Types of emission limit values implemented for volatile organic compounds in annex VI

4. VOCs emissions may be discharged in the atmosphere through stacks (emissions from waste gases) or not through stacks (fugitive emissions). Annex VI<sup>2</sup> considers ELVs for waste gases containing VOCs and for fugitive VOCs emissions but also total ELVs considering both types of the emissions.

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<sup>1</sup> Fugitive emissions as well as total emissions can be determined with a solvent management plan, distracting the yearly output of solvents from the yearly input. The solvent management plan is carried out during the year of operation (see chapter IV).

<sup>2</sup> The references throughout this document correspond to the Gothenburg Protocol, as amended.

5. Waste gases are defined in annex VI as follows: “**Waste gas**” means the final gaseous discharge containing VOCs or other pollutants from a stack or from emission abatement equipment into air. The volumetric flow rates shall be expressed in cubic meters per hour ( $\text{m}^3/\text{h}$ ) at standard conditions.<sup>3</sup>

6. Fugitive emissions are defined as follows: “**Fugitive emission**” means any emission, not in waste gases, of VOCs into air, soil and water as well as, unless otherwise stated, solvents contained in any product; this includes uncaptured emissions of VOCs released to the outside environment via windows, doors, vents and similar openings. Fugitive emissions may be calculated on the basis of a solvent management plan.

7. In a plant, total VOCs emissions include those from waste gases and fugitive emissions: “**Total emission of VOCs**” means the sum of fugitive emission of VOCs and emission of VOCs in waste gases.

8. Three types of ELVs are defined in annex VI:

(a) “**Emission limit value**” (ELV)<sup>4</sup> means the maximum quantity of VOCs (except methane) emitted from an installation which is not to be exceeded during normal operation. For waste gases, it is expressed in terms of mass of VOCs per volume of waste gases (expressed in milligrams of carbon (C) per cubic meter ( $\text{mg C}/\text{m}^3$ ) unless specified otherwise), assuming standard conditions for temperature and pressure for dry gas. Gas volumes that are added to the waste gas for cooling or dilution purposes shall not be considered when determining the mass concentration of the pollutant in the waste gases;<sup>5</sup>

(b) **Emission limit values for waste gases** are indicated as **ELVc**;

(c) **Emission limit values for fugitive emissions** are indicated as **ELVf**;

(d) Total emission limit value is simply indicated as **total ELV**. Total ELV include fugitive emissions and stack emissions.

9. Several ways of reporting VOCs and expressing the ELVs are currently in place:

(a) As total organic carbon (TOC), which is a concentration of carbon in the gas stream, usually expressed in  $\text{mg C}/\text{cubic metre}$  ( $\text{m}^3$ ), in the standard conditions of temperature and pressure (STP) (methane is usually excluded unless specified otherwise). Total VOCs emissions may be expressed in percentage (%) of solvent input, or grams (g) VOCs per unit of activity ( $\text{g VOCs per square meter}$  ( $\text{m}^2$ ),  $\text{g VOC per kilogramme}$  (kg) of solid input, etc.) for some activities using solvents or % of petrol throughput for activities related to storage and handling of petrol;

(b) As an individual substance or a sum of individual substances. In annex VI this approach is used for ELVs related to one or several substances, which are assigned to the following risk definitions: suspected of causing cancer and/or suspected of causing genetic defects, may cause cancer, may cause genetic defects, may cause cancer by inhalation, may damage fertility, may damage the unborn child, expressed in  $\text{mg substances per cubic meter}$  ( $\text{mg VOCs}/\text{m}^3$ ) in STP (see annex VI, paragraphs 3(z) and 5);

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<sup>3</sup> In accordance with annex VI, article 3 (l) of the Gothenburg Protocol, as amended, standard conditions means a temperature of 273.15 K and a pressure of 101.3 kPa.

<sup>4</sup> This is the definition used in the Gothenburg Protocol, Annex VI, paragraph 3 (x). Ad hoc measurement techniques exist (see chapter III below).

<sup>5</sup> See chapter III, section D for more information on dilution.

- (c) As a fugitive emission of VOCs, expressed in % of solvent input as example;
- (d) In some cases, emission reduction efficiency is required.

10. Table 1 summarizes the different types of activities outlined in annex VI of the Gothenburg Protocol, as amended. Reference is made to the related tables of that annex.

Table 1

**Summary of units and definitions for VOCs per type of activity in annex VI**

<i>Activity listed in annex VI and related table of Gothenburg Protocol, as amended</i>	<i>ELVc expressed in mg VOCs/m<sup>3</sup></i>	<i>Total ELV expressed in % of solvent input or of throughput</i>	<i>ELVc expressed in mg C/m<sup>3</sup></i>	<i>ELVf expressed in % of solvent input</i>	<i>Total ELV expressed in mass of VOCs per unit if activity</i>	<i>Efficiency</i>
Loading and unloading of mobile containers at terminals — Table 1			ELVc (Including methane)			
Storage installation at terminals — Table 1						%
Service stations Storage — Table 1		% of throughput				
Service stations Car refuelling — Table 2						%
Shoe industry — Table 3					g/pair of shoes	
Other adhesive coating — Table 3		Or kg VOC/kg solid input		Or ELVc + ELVf		
Wood and plastic lamination — Table 4					g VOC/m <sup>2</sup> of finished product	
Car manufacturing — Table 5					g VOC/m <sup>2</sup> or g/body + g VOC/m <sup>2</sup> (electrophoretic area)	
Truck, truck cabin and bus manufacturing — Table 5					g VOC/m <sup>2</sup> (electrophoretic area)	
Wood coating — Table 6		Or kg VOC/kg solid input		Or ELVc + ELVf		
Coating of metals and Plastics — Table 6		Or kg VOC/kg solid input		Or ELVc + ELVf		
Textile, fabric foil, and paper coating — Table 6		Or kg VOC/kg solid input		Or ELVc + ELVf		
Coating of plastic work pieces — Table 6		Or kg VOC/kg solid input		Or ELVc + ELVf		
Coating of metal surfaces — Table 6		Or kg VOC/kg solid input		Or ELVc + ELVf		
Leather coating — Table 7					g VOC/m <sup>2</sup>	
Winding wire coating — Table 7					g VOC/kg wire	
Coil coating — Table 8		kg VOC/kg solid input		Or ELVc + ELVf		
Dry cleaning — Table 9					g VOC/kg of cleaned and dried product	

<i>Activity listed in annex VI and related table of Gothenburg Protocol, as amended</i>	<i>ELVc expressed in mg VOCs/m<sup>3</sup></i>	<i>Total ELV expressed in % of solvent input or of throughput</i>	<i>ELVc expressed in mg C/m<sup>3</sup></i>	<i>ELVf expressed in % of solvent input</i>	<i>Total ELV expressed in mass of VOCs per unit if activity</i>	<i>Efficiency</i>
Manufacture of paints, varnishes, inks and adhesives — Table 10		% of solvent input		Or ELVc + ELVf		
Heat set offset — Table 11		% of solvent input or % of the ink consumption		Or ELVc + ELVf		
Publication gravure — Table 11		Or % of the solid input		Or ELVc + ELVf		
Packaging rotogravure and flexography — Table 11		Or % of the solid input		Or ELVc + ELVf		
Manufacture of pharmaceutical products — Table 12		Or % of solvent input		Or ELVc + ELVf		
Conversion of rubber — Table 13		Or % of solvent input		Or ELVc + ELVf		
Surface cleaning with non-chlorinated solvents — Table 14				ELVc + ELVf		
Surface cleaning with chlorinated solvents — Table 14	+ELVc as the mass of the sum of individual compounds			+ ELVf		
Oil extraction — Table 15					kg VOC / t product	
Wood preservation — Table 16				Or ELVc + ELVf	Or kg VOC / m <sup>3</sup> wood	

11. Compliance with ELVs for waste gases or ELVc, expressed as a mass of **total organic carbon**/m<sup>3</sup> or a mass of a **substance or group of substances**/m<sup>3</sup> can only be verified by the use of **specific measurement equipment**.<sup>6</sup> The type of measuring equipment and methodology used depends on the expression of VOCs concentrations (mass of VOCs expressed in C for VOCs not considered under paragraph 5 of annex VI; or mass of VOCs expressed in mass of substances for those VOCs considered harmful for human health and covered by paragraph 5 of annex VI).<sup>7</sup>

12. Compliance with fugitive ELVs (ELVf), or with total ELVs, can be verified by a **solvent management plan** (mainly calculations) **and/or** by the **determination of stack emissions**<sup>8</sup> (with measurement equipment) for activities using solvents.

### III. Volatile organic compounds measurement techniques

#### A. Total volatile organic compounds concentration measurement techniques

##### Flame ionization detector

13. Organic carbon compounds are relatively easily ionizable in a hydrogen flame. Flame ionization detector (FID) techniques work consequently by a gas being passed into a measurement chamber, which uses a flame to create ions from the VOCs. More specifically, FID analysers make use of the chemi-ionization of organically bound carbon atoms in a hydrogen flame to provide measurements.

14. The measurement cell contains a pair of electrodes; a current is applied between them. If ions are present in the cell, the current can pass between the electrodes. The ionization current measured by the FID depends upon the number of carbon-hydrogen bonds of the organic compounds burning in the fuel gas flame and the ability with which these compounds ionize. The more ions are present in the cell, the greater the current is. As the abundance of ions within the cell depends on the concentration of the gas, FID provides a means of measuring the concentrations of VOCs. The absolute measuring sensitivity depends on the material of the combustion nozzle and the detector geometry.

15. FID does not differentiate between different compounds since it responds to carbon bonds rather than to specific compounds. Thus, the result is given as TOC. The response, however, depends on the bond type of the respective carbon atom. This means that high amounts of compounds with low FID response will lead to underestimated measurement results, if they cannot be corrected with corresponding response factors. The response factors for individual compounds have to be determined experimentally; default values are also available. In the absence of a response factor provided by the manufacturer or determined experimentally, the default values are as indicated in table 2 [1].

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<sup>6</sup> In other words, calculations are not possible.

<sup>7</sup> The definition of harmful VOCs is provided in paragraph 9 (b) of this document.

<sup>8</sup> The solvent management plan alone may be used when no reduction device is in use.

Table 2

**Default response factors for individual compounds in FID method**

	Response factor
C-C (aliphatic)	1
C=C aromatic	0.95
C=O ketone	0
C-OH alcohol	0.3
C-O ether	0.5
C-Cl	1.05

16. The method involves extraction of a gas sample through a heated line to avoid condensation losses into the FID detector and other problems. The FID is calibrated with propane and gives a direct reading as parts per million per volume (ppm) propane equivalent of VOCs, which can be converted to a mass concentration at STP, using the mass of carbon in the calibration gas and the molar volume of 22.4 litres at STP.

**Catalytic oxidation and non-dispersive infrared absorption**

17. A combustion chamber with a catalyst is being used. Carbon from VOCs is oxidized to carbon dioxide (CO<sub>2</sub>). Concentrations of CO<sub>2</sub> are measured by infrared absorption detection. The catalyst may be poisoned by the presence of some components in waste gases; the conversion to CO<sub>2</sub> is not completely efficient [2]. The gas analysers use, as a measurement principle, the absorption of infrared radiation (IR). The total volatile organic compounds (TVOCs) mass concentration at standard conditions is the quotient of the mass of TVOCs to the volume of the dry gas under STP. The analysers operate according to the non-dispersive infrared (NDIR) method, while the selectivity of measurement is achieved by the radiation detector which is filled with the component to be measured. A dust-free sample is essential; moisture in the sample gas tends to cause interference [2]. Problems with complex gas mixtures can occur.

**Photo ionization detection (PID)**

18. Organic carbon compounds are ionized with a source of ionization which is not a flame as in FIDs but an intense ultraviolet (UV) light. They are less suitable than FID due to the response factors being much more variable than in FID. Sample conditioning may also be limiting its use [2].

**CEN standard reference methods for total VOC measurement**

19. The FID technique is considered in two CEN standards for VOCs measurement:

(a) EN 12619 of June 1999: Stationary source emissions — Determination of the mass concentration of total gaseous organic carbon at low concentrations in flue gases — Continuous flame ionization detector method. The standard has been validated for measuring concentrations over a range of 0–20 mg/Nm<sup>3</sup>. The method measures VOCs including methane;

(b) EN 13526 of November 2001: Stationary source emissions — Determination of the mass concentration of total gaseous organic carbon in flue gases from solvent using processes — continuous flame ionization detector method. The standard has been validated as suitable for measuring emissions up to 500 mg/Nm<sup>3</sup> although FIDs can be used to measure higher concentrations. That method measures VOCs including methane [2].

20. Another standard is ISO 13199:2012: Stationary source emissions — Determination of TVOCs in waste gases from non-combustion processes — Non-dispersive infrared analyser equipped with catalytic converter. This standard specifies the principle, the essential performance criteria and quality assurance/quality control (QA/QC) procedures of an automatic method for measuring total TVOCs content in waste gases of stationary sources, using a NDIR analyser equipped with a catalytic converter which oxidizes VOCs to carbon dioxide. This method is suitable for the measurement of TVOCs emissions from non-combustion processes. It allows for continuous monitoring with permanently installed measurement systems, as well as intermittent measurements of TVOCs emissions. That method has been tested in the field operation for painting and printing processes, where TVOCs concentrations in the waste gases ranged from about 70 mg/m<sup>3</sup> to 600 mg/m<sup>3</sup> [3].

## **B. Measurement techniques of individual volatile organic compounds substances**

21. Several existing methods are described below, whereas the list is not exhaustive.

### **Sampling and gas chromatography**

22. VOCs can be adsorbed on solid adsorbents. There is no universal sampling sorbent. It must be selected according to the VOCs to be monitored:

(a) Organic polymeric sorbents can be used. They are hydrophobic. This property enables the adsorption of very small concentrations of VOCs. Highly volatile compounds are hardly adsorbed on this type of resins as well as polar molecules, such as ketones and alcohols;

(b) Inorganic sorbent can adsorb polar molecules but also water, which may cause problems;

(c) Activated carbon based sorbents are also used as they can adsorb a large variety of VOCs.

23. Thermal desorption or solvent extraction is also used. The VOCs concentration is determined by gas chromatography and FID analysis or mass spectroscopy. VOCs can also be absorbed in a liquid media. They can be analysed after separation by gas chromatography.

### **Non Dispersive Infrared Spectrometry**

24. VOCs can absorb infrared radiations. Each VOC has an electronic finger print or spectrum. This property is used in NDIR spectrometry. The wavelength is selected to coincide with the absorption peak of the VOC to be monitored. In case of a mixture, different spectra can overlap. That method is well suited for the monitoring of one single compound.

### Fourier Transform Infrared absorption

25. In FTIR, the overlap of spectra is avoided by splitting the beam into two. One beam is bounded off a fixed mirror while the other is bounded off in a moving mirror. Following a specific arrangement, a new spectrum is created. Specific software is utilized to identify a specific compound by using the Fourier calculation.

26. Most VOCs absorb IR and can be detected by FTIR. This technique can be used to detect and monitor several compounds in a waste gas. It can give a direct indication of total VOCs and individual compounds.

### European standard reference methods for individual VOC measurement and other standards

27. The methods for measuring an individual VOC are described in the following CEN or the standards of the United States of America:

(a) EN 13649 of 2014 (replacing the 2002 version): Stationary source emissions — Determination of the mass concentration of individual gaseous organic compounds: activated carbon and solvent desorption method. This technical specification describes procedures for the sampling, preparation and analysis of individual VOCs in waste gas, such as those arising from solvent using processes. Sampling occurs by adsorption on sorbents, preparation by solvent extraction or thermo desorption and analysis by gas chromatography. Examples of individual VOCs are given in relevant industry sector best available techniques (BAT) reference documents (BREFs). The results obtained are expressed as the mass concentration ( $\text{mg}/\text{m}^3$ ) of individual gaseous organic compounds. This document is suitable for measuring individual VOCs according to different compounds and test methods. This technical specification may be used to meet the monitoring requirements of the European Union Industrial Emissions Directive<sup>9</sup> and associated supporting documents. It is not suitable for measuring TOC. Sampling is a crucial part of the methodology;

(b) NIOSH and OSHA analytical methods are also widely in use in Europe.

### C. Translation of concentrations of single volatile organic compounds expressed in mass of volatile organic compounds to total volatile organic compounds concentrations expressed in mass of carbon

28. To translate a concentration value expressed in mass of VOCs to mass of carbon, the molar mass and the chemical nature of the VOCs has to be known:

The formula (1) is expressed as follows, for one organic compound i:

$$(1) \text{CONC}_i(\text{mass of C eq}) = \text{CONC}_i(\text{mass of VOC}_i) \times \frac{m_{\text{C}_i}}{M_i}$$

$\text{CONC}_i(\text{mass of C eq})$ : concentration of organic compound i expressed in mass of carbon.

$\text{CONC}_i(\text{mass of VOC})$ : concentration of organic compound i expressed in mass of the chemical substance.

<sup>9</sup> Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control).

$mc_i$ : mass of carbon in the organic compound  $i$  (12 x number of carbon).

$M_i$ : molar mass of organic compound  $i$ .

The formula (2) is expressed as follows, if there are several organic compounds in a mixture and if their respective proportions are known:

$$(2) \text{CONC}_{\text{VOC}}(\text{mass of C eq}) = \text{CONC}_{\text{VOC}}(\text{mass of VOC}) \times \sum_i \frac{mc_i}{M_i} \times P_i$$

$\text{CONC}_{\text{VOC}}(\text{mass of C eq})$ : concentration of the mixture of VOC, expressed in mass of carbon.

$\text{CONC}_i(\text{mass of VOC})$ : concentration of organic compound  $i$  expressed in mass of the chemical substance.

$P_i$ : proportion of organic compound  $i$  in the mixture — expressed in weight per weight.

29. If the composition of the mixture of compounds is not exactly known, the previous formula is not applicable. The total concentration of organic compounds cannot be estimated, nor the concentration expressed in carbon.

30. For example: The concentration of a mixture of organic compounds formed by ethanol for 35% weight per weight (w/w) and ethyl acetate for 65% w/w<sup>10</sup> is 300 mg VOC/m<sup>3</sup>. The VOCs concentration expressed in Carbon or C eq is as follows:

Ethanol: CH<sub>3</sub>-CH<sub>2</sub>OH or 2 C, 6 hydrogen (H) and 1 oxygen (O) atoms; molar mass  $M_{\text{Ethanol}}$ : 46 (2x12 + 6x1 + 16) g/mole;  $mc_{\text{Ethanol}}=24$  (2x12) g;  $P_{\text{Ethanol}}=35\%$ ;

Ethyl acetate: CH<sub>3</sub>-CH<sub>2</sub>-CO-O-CH<sub>3</sub> or 4 C, 8 H and 2 O; molar mass  $M_{\text{Ethyl acetate}}$ : 88 (4x12 + 8x1 + 2x16) g/mole;  $mc_{\text{Ethyl acetate}}=48$  (4x12) g;  $P_{\text{Ethyl acetate}}=65\%$ ;

$$\text{CONC}_{\text{VOC}}(\text{mass of C eq}) = \left( 0.35 \times \frac{24}{46} + 0.65 \times \frac{48}{88} \right) \times 300 = 161.1 \text{ mg C eq.}$$

## D. Other useful recommendations

### Exclusion of dilution air for the determination of concentrations of volatile organic compounds

31. According to annex VI, paragraph 3(x) of the Gothenburg Protocol, gas volumes that are added to the waste gas for cooling or dilution purposes shall not be considered when determining the mass concentration of the pollutant in the waste gases. In order to exclude dilution or cooling air, the determination of the dilution air flow rate is required. The following equation can be used if the measurement of the concentrations cannot be made before the entrance of dilution air:

$$C_{\text{real}} \times D_{\text{process}} = C_{\text{measured}} \times D_{\text{stack}};$$

$C_{\text{real}}$  = concentration to be known;

<sup>10</sup> This information can be provided by preparation manufacturers. In case the information is not provided, the determination of concentrations can be made by gas chromatography in combination with techniques described in chapter III, section B.

D: Waste gas flow rate;

$$D_{\text{stack}} = D_{\text{process}} + D_{\text{dilution}};$$

$D_{\text{stack}}$  = Waste gas flow rate measured in the stack including process and dilution air;

$D_{\text{process}}$  : Waste gas flow rate of the process itself;

$D_{\text{dilution}}$  : Dilution air flow rate;

$C_{\text{measured}}$  = concentration measured in the stack waste gases including dilution air;  $C_{\text{real}} = C_{\text{measured}} \times D_{\text{stack}} / D_{\text{process}}$ ;

$$C_{\text{real}} = C_{\text{measured}} \times D_{\text{stack}} / (D_{\text{stack}} - D_{\text{dilution}}).$$

#### **Exclusion of methane in the determination of concentrations of VOCs**

32. The concentrations of CH<sub>4</sub> in the activities using solvents covered by annex VI of the Gothenburg Protocol are very low. CH<sub>4</sub> can evaporate when an oxidator or a drying device are being used. For example, if a FID is being used, the total VOC/VOC excluding methane separation can be achieved by means of a device that eliminates all VOC except CH<sub>4</sub>. When using a catalytic filter, usually CH<sub>4</sub> is more stable thermally.

## **IV. Solvent management plan**

### **A. Aim of the solvent management plan**

33. A solvent management plan (SMP) is an adequate tool to determine the solvent consumptions and emissions, especially fugitive VOCs emissions. A SMP is used to check the compliance of an installation using solvents, for which the total VOCs ELV applied is expressed in % of solvent input, in % of solid input, in a total VOC mass/unit of activity, or for which the fugitive VOCs ELV is expressed in % of solvent input.

34. The SMP is a tool for estimating VOCs emissions based on solvent inputs and outputs, based on the following principle.  $\Sigma$  Solvent inputs =  $\Sigma$  Solvent outputs (including emissions into air):

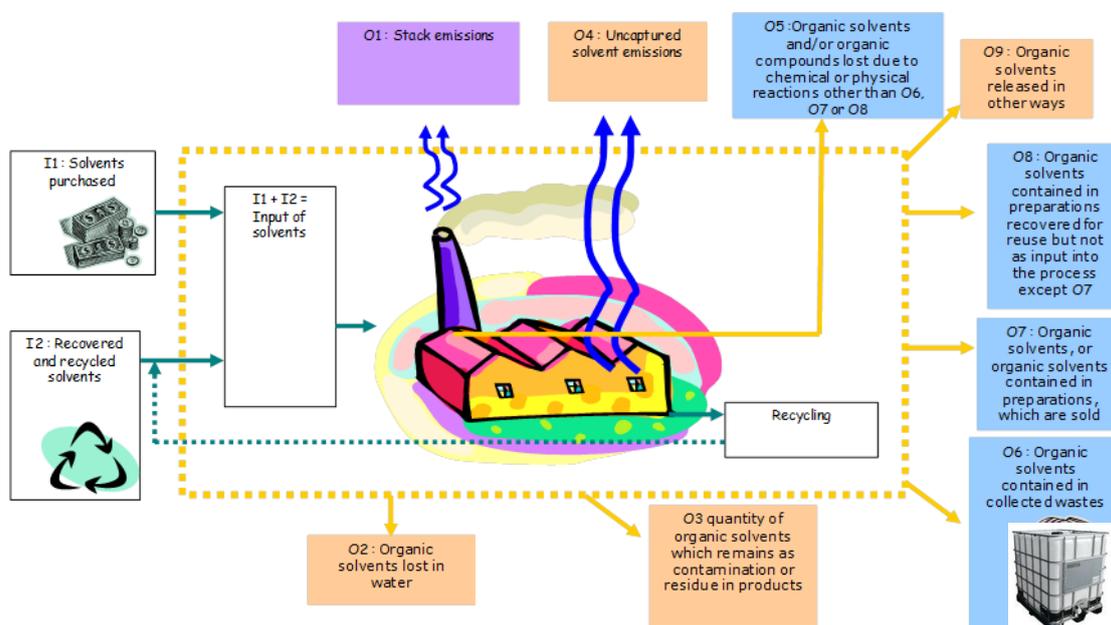
(a) In order to obtain an equilibrated balance, the same units have to be used to characterize inputs and outputs. The balance is carried out in mass of solvent or VOCs;

(b) The balance can be done if the chemical nature of inputs and outputs is the same and if inputs and outputs can be expressed in the same units (mass of solvent). Inputs are often easily known. On the contrary, only some outputs can be estimated easily;

(c) The SMP is generally carried out on an annual basis and is calculated each year to control progress in the VOCs emission reduction.

35. The following figure presents different components of the solvent management plan as defined in the appendix to annex VI to the Gothenburg Protocol, as amended.

Figure 1  
Components of the solvent management plant



## B. How to estimate the different components of the balance

### Inputs of organic solvents

36. I1 in figure 1 represents the quantity of organic solvents or their quantity in the preparations purchased, which are used as inputs into the process in the time frame over which the mass balance is being calculated.

37. An exhaustive inventory of all preparations containing solvents used in the installation covered by the balance has to be carried out. Their respective quantities and mass concentrations of solvents have to be determined. The solvent content of the preparations to be provided in w/w can be obtained from labels and/or safety data sheets of the preparations. Providers of preparations/products may also be a source of information. Attention has to be paid to units used and not mix volume and weight (the density is used to convert volume in mass):

$$\text{Quantity of used solvent} = \text{Quantity bought} - \text{stock of year } n + \text{stock of year } n-1.$$

38. I2 is the quantity of organic solvents or their quantity in preparations recovered and reused as solvent input into the process (the recycled solvent is counted every time it is used to carry out the activity).

39. "Reused" has to be understood as recovered on site after a specific internal regeneration, for example, when solvent input is reused in the process. Recycled solvents in the process require a specific quality. The amount of recycled solvents should be easily determined. A careful follow-up system must be implemented. Cleaning solvents are often recycled solvents. The quantity used shall be registered.

### Outputs of organic solvents

40. O1 represents emissions in waste gases.

41. Only stack emissions have to be considered in this group. Monitoring of VOCs concentrations in waste gases is required provided the necessity of demonstrating compliance. It is recommended to monitor VOCs concentrations during a representative period of work. According to measurement techniques used, the results expressed in C have to be converted into VOCs.

42. O5 are organic solvents and/or organic compounds lost due to chemical or physical reactions (including for example those which are destroyed, e.g. by incineration or other waste gas or waste water treatments, or captured, e.g. by adsorption, as long as they are not counted under O6, O7 or O8).

43. In order to determine the efficiency of the destruction, upstream and downstream concentrations and flow rates have to be monitored. Waste gas monitoring is only valid if the length of the duct is sufficient compared to its diameter. ISO standard 16911-1:2013 and ISO standard 16911-2:2013 describe the measurement of waste gas volume in ducts and the determination of the waste gas speed [5] [6].

44. VOCs may be measured by one of the techniques described in chapter III. In case of use of a technique providing total VOCs concentration expressed in equivalent carbon (eq C), results have to be converted into mass of VOCs. This can be done if the composition in VOCs in waste gases as well as specific FID response factors are known. In most of the cases, it is assumed that this composition does not change from the input flow, as shown in formula (3):

$$CONC_{VOC} = \frac{CONC_{monitored}}{\sum_i \left( P_i \cdot FR_i \frac{mc_i}{M_i} \right)}$$

CONC<sub>monitored</sub>: Concentration of solvent measured (or VOC) in eq C/m<sup>3</sup>;

CONC<sub>VOC</sub>: Real concentration of solvent in waste gases in mass of VOC /m<sup>3</sup>;

i: type of solvent consumed;

P<sub>i</sub>: proportion of a solvent i in waste gases (% mass);

mc<sub>i</sub>: mass of carbon in solvent i (12 x number of carbons);

FR<sub>i</sub>: response factor for solvent I;

M<sub>i</sub> : Molar mass of solvent i.

In order to be accurate, upstream and downstream measurement to determine O5 should be carried out simultaneously.

45. O2 are organic solvents lost in water, if appropriate, taking into account waste water treatment when calculating O5.

46. The determination of the VOCs concentration in waste water is useful if an abatement system exists. The choice of measurement device depends on solvents used and on their ability to be present in waste waters. (O<sub>2</sub> determination requires knowledge of the average concentration of VOCs and of the waste water volume.)

47. In a non-specific monitoring campaign, measurement of total hydrocarbons, or of benzene, toluene, ethylbenzene and xylenes (BTEX) can be used. Parameters, which define abatement efficiency are chemical oxygen demand and total organic carbon. The measurement periodicity depends on the importance of emissions and the variability of the results.

48. O3 is the quantity of organic solvents which remains as contamination or residue in output of products from the process.
49. This is a fugitive output. Some chemical analysis may be required. For example, O<sub>3</sub> can be remaining solvents in printed papers if the drying has been insufficient.
50. O4 are uncaptured emissions of organic solvents to air. This includes the general ventilation of rooms, where air is released to the outside environment via windows, doors, vents and similar openings.
51. This output is determined by the solvent balance by a difference of known inputs and outputs. Various other methods can also be used [7].
52. O6 are organic solvents contained in collected wastes.
53. Solvents in wastes come from mixtures of solvents used, solvents in residues of products, residues of solvents in containers, etc. In order to estimate solvents in wastes, a dedicated management of wastes is necessary. Wastes treated by external companies are well known, as financial transactions are often necessary. In some cases, chemical analyses are necessary. Waste solvents should be stored in closed containers to avoid fugitive emissions.
54. O7 are organic solvents, or organic solvents contained in preparations, which are sold or are intended to be sold as a commercially valuable product.
55. When preparations are sold such as in the production of paints, inks and glues, the solvent contents of products are known as those products that must comply with specific requirement. Depending on the activities, preparations containing solvents are stored in closed containers.
56. O8 are organic solvents contained in preparations recovered for reuse but not as input into the process, as long as not counted under O7.
57. Solvents recovered for recycling after specific treatment or without treatment. The flow rates are known in case of treatment.
58. O9 are organic solvents released in other ways.

### **C. Definitions of the different components of the solvent management plan**

59. With a solvent management plan, the determination of the solvent consumption (C) and VOCs emissions (E) can be done according to equations presented hereafter:

$$C = I1 - O8;$$

C: annual consumption of solvent. Mass of VOCs/year;

I1 and O8 are defined above.

60. In annex VI of the Gothenburg Protocol, as amended, the thresholds for the application of the ELVs are based on the consumption of solvents. Total VOCs emissions (E) are defined as follows:

$$E = F + O1;$$

or

$$E = I1 - O5 - O6 - O7 - O8;$$

E: Total VOC emissions in mass of VOCs/year;

F: VOC fugitive emissions in mass of VOCs/year.

61. If O1 has been determined by a measurement device providing a concentration expressed in carbon equivalent, this mass of carbon equivalent must be transformed into mass of VOCs taking into account the composition of waste gases in VOCs and the response factors of the measurement device to the different VOCs (see chapter III).

62. F is the fugitive emission as defined below:

$$F = I1 - O1 - O5 - O6 - O7 - O8;$$

or

$$F = O2 + O3 + O4 + O9;$$

F: VOC fugitive emissions in mass of VOCs/year.

63. This quantity can be determined by a direct measurement of the different quantities as presented above. Alternatively, an equivalent calculation can be made by other means, for instance by using the capture efficiency of the process.

64. The fugitive emission value as well as the total emission can be expressed as a proportion of the input I, which is calculated according to the following equation:

$$I = I1 + I2;$$

I: input of solvent in mass of VOCs/year.

65. The SMP can be done on a regular basis e.g., annually, in order to control progress carried out, take the necessary measures if deviations are observed and be in position to assess the compliance of the installation with ELVs.

66. A simplified SMP can be prepared when only total ELVs are implemented. If ELVc in waste gases and fugitive ELVf are implemented, a complete management plan is necessary [4]. Generally, annex VI provides flexibility for most activities using solvents in ELVs. In most of the cases, one can choose between a total ELV or an ELVc + ELVf.

67. A simplified SMP requires the determination of C, I and total emissions as follows:

$$C = I1 - O8;$$

$$I = I1 + I2;$$

C: annual consumption of solvent. Mass of VOC/year;

I: input of solvent in mass of VOCs/year.

In case of total emission limit values expressed as emission of solvent per unit of product, the determination of I2 is redundant:

$$E = I1 - O5 - O6 - O7 - O8;$$

E: Total VOC emissions in mass of VOCs/year.

68. A complete SMP requires the determination of C, I and stack and fugitive emissions:

$$C = I1 - O8;$$

$$I = I1 + I2;$$

$$E = I1 - O5 - O6 - O7 - O8 = F + O1;$$

E: Total VOCs emissions in mass of VOCs/year;

F: Fugitive VOCs emissions in mass of VOCs/year;

O1: Stack VOCs emissions in mass of VOCs/year (in waste gases);

Fugitive emissions  $F = I1 - O1 - O5 - O6 - O7 - O8 = O2 + O3 + O4 + O9$ .

In case of total emission limit values expressed as emissions of solvent per unit of product, the determination of I2 is redundant.

69. The complete SMP requires measurement of VOCs concentrations in waste gases and of flow rates (for O1 and O5). Monitoring of O2 may be necessary as well. In case of a simplified SMP, measurement of VOCs is not always necessary except if a reduction device such as an oxidator is used.

## **V. Control of volatile organic compounds for selected activities covered by annex VI**

### **A. Storage of petrol at terminals**

70. There are two components in VOCs emissions from storage tanks: working losses due to vapours displaced during filling; and standing losses due to the impact of temperature and pressure variations on the volume of vapours in the tank. Different types of devices are used to limit VOCs emissions on petrol storage such as external floating roofs and internal floating roofs.

71. The ELV implemented is expressed as an efficiency of the reduction device (a tank fitted with external or internal floating roof) compared to a fixed roof tank.

72. The United States Environmental Protection Agency (USEPA) has developed the TANK software for estimating VOCs emissions from organic liquid storage tanks. It contains detailed descriptions of typical varieties of such tanks, including horizontal, vertical, and underground fixed roof tanks, and internal and external floating roof tanks.

73. The emission estimation equations presented herein have been developed by the American Petroleum Institute (API), which retains the legal right to these equations. The major pollutants of concern are VOCs. The developed algorithms take into account different types of storage and their characteristics (tightness of floating roof seals, colour, etc.).

74. Emission calculation software is provided by the USEPA [10]. A division of the European Petroleum Refiners Association (CONCAWE) has also developed a simple method for estimating VOCs emissions from different types of storages [11].

### **B. Loading/unloading of mobile containers at terminals (excluding load of seagoing ships)**

75. Emissions from loading and unloading of mobile containers at terminals can be estimated through equations developed by API, which have been adopted in several guides such as CONCAWE [11] and USEPA [12].

76. The ELV implemented requires the measurement in the vent of the loading and unloading platform. If equipped with a recovery unit, the measurement devices have to be installed on the vent to the atmosphere of this recovery unit.

### C. Storage of petrol at service-stations (stage I)

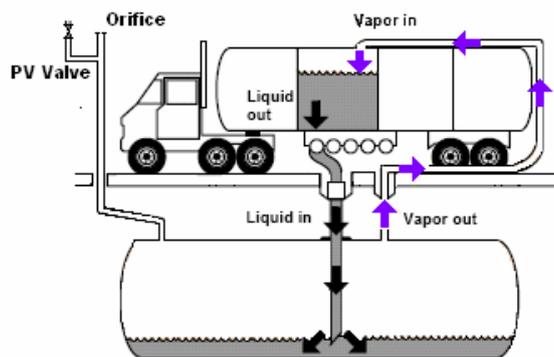
77. During filling of the underground petrol tank, VOCs vapours in the empty portion of the tank above petrol are displaced and emitted in the atmosphere through a vent if a vapour balancing system does not exist. This arrangement is known as “stage 1”. The system is only complete if a vapour recovery unit is present at the terminal, in order to recover VOC emissions.

78. In order to be in compliance with the ELVs stipulated by annex VI of the Gothenburg Protocol, as amended, measurement of emissions is not required if a vapour balancing unit is present. The VOCs vapours exit the tank through a return line to the mobile container.

79. The following figure 2 presents the vapour balancing system [13].

Figure 2

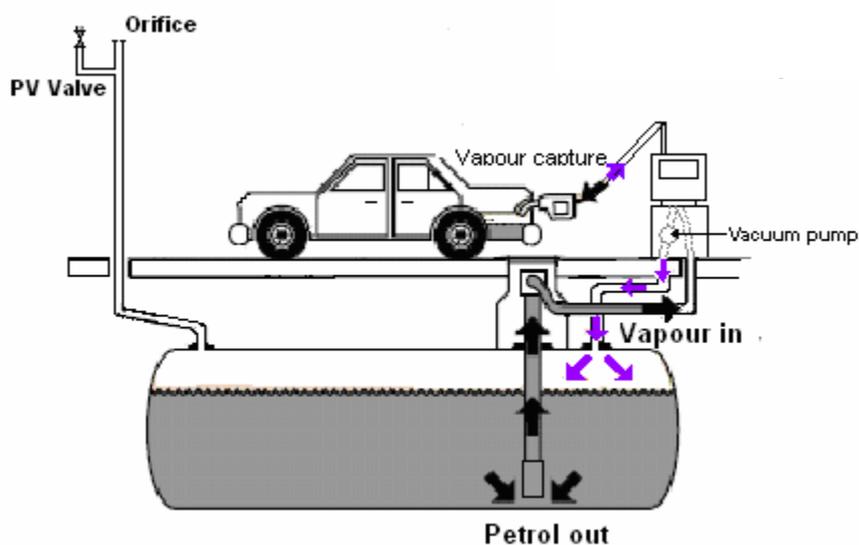
#### Schematic representation of a vapour balancing system



### D. Car refuelling at service stations (stage II)

80. The stage II petrol vapour recovery system is an equipment aimed at recovering the petrol vapour displaced from the fuel tank of a motor vehicle during refuelling at a service station, which transfers that petrol vapour to a storage tank at the service station or back to the petrol dispenser for resale. The following figure presents the arrangement of such a system [13].

Figure 3  
Schematic representation of a vapour recovery system



81. The petrol vapour capture efficiency of the stage II system must be equal to or greater than 85 % (weight %) with a vapour/petrol ratio equal to or greater than 0.95 but less than or equal to 1.05 (volume per volume (v/v)). (The capture efficiency has to be certified by the manufacturer in accordance with relevant European technical standards or type approval procedures referred to in paragraph 8 of annex VI or, if there are no such standards or procedures, with any relevant national standard.)

82. Two CEN standards to establish the petrol vapour recovery efficiency of new stage II petrol vapour recovery equipment and the in-use performance of such equipment, once installed at service stations, are available (M/456 Mandate to CEN) [8] [9]. The first standard specifies the measurement and test methods for the efficiency assessment of petrol vapour recovery systems for service stations (stage I). The second one specifies the test methods for verification of vapour recovery systems at service stations (stage II). This last standard does not specify the test method for the air and vapour tightness testing of the vapour recovery systems at service stations.

## VI. Summary of measurement methods for different activities covered by annex VI

83. The methods which can be used to assess compliance with ELVs are summarized in the table below.

Table 3  
**Methods for assessing compliance with emission limit values**

<i>Activity of annex VI</i>	<i>Type of ELVs</i>	<i>Measurement system</i>
Loading and unloading of mobile containers at terminals — Table 1	ELVc (including methane)	Calculation methods and measurement in vents (see section H)
Storage installation at terminals — Table 1	%	Calculation methods (see section G)
Service-stations Storage — Table 1	% of throughput	No measurement required if a vapour balancing system is present (see section I)
Service-stations Car refuelling — Table 2	%	Measurement methods as described in section J
Shoe industry — Table 3	g/pair of shoes	Solvent management plan with possibly stack concentration measurement in cases of abatement system efficiency determination (see paragraph 40-42, chapters III and IV)
Other adhesive coating — Table 3	Or kg VOC/kg solid input Or ELVc + ELVf	First case: solvent management plan with possibly stack concentration measurement in cases of abatement system efficiency determination (paragraphs see 40–42)  Second case: solvent management plan and stack emission concentration measurement (see chapters III and IV)
Wood and plastic lamination — Table 4	g VOC/m <sup>2</sup> of finished product	Solvent management plan with possibly stack concentration measurement in cases of abatement system efficiency determination (see paragraphs 40–42, chapters III and IV)
Car manufacturing — Table 5	g VOC/m <sup>2</sup> or g/body + g VOC/m <sup>2</sup> (electrophoretic area)	(see paragraphs 40–42, chapters III and IV)
Truck, truck cabin and bus manufacturing — Table 5	g VOC/m <sup>2</sup> (electrophoretic area)	
Wood coating — Table 6	Either kg VOC/kg solid input or ELVc + ELVf	First case: solvent management plan with possibly stack concentration measurement in cases of abatement system efficiency determination (see
Coating of metals and Plastics — Table	Either kg VOC/kg solid input or ELVc + ELVf	paragraphs 40–42, chapters III and IV)

<i>Activity of annex VI</i>	<i>Type of ELVs</i>	<i>Measurement system</i>
6		paragraphs 40–42)
Textile, fabric foil, and paper coating — Table 6	Either kg VOC/kg solid input or ELVc + ELVf	Second case: solvent management plan and stack emission concentration measurement
Coating of plastic work pieces — Table 6	Either kg VOC/kg solid input or ELVc + ELVf	Chapters III and IV
Coating of metal surfaces — Table 6	Either kg VOC/kg solid input or ELVc + ELVf	
Leather coating — Table 7	g VOC/m <sup>2</sup>	Solvent management plan with possibly stack concentration measurement in cases of abatement system efficiency determination (see paragraphs 40–42, chapters III and IV)
Winding wire coating — Table 7	g VOC/kg wire	
Coil coating — Table 8	kg VOC/kg solid input Or ELVc + ELVf	First case: solvent management plan with possibly stack concentration measurement in cases of abatement system efficiency determination (see paragraphs 40-42) Second case: solvent management plan and stack emission concentration measurement (see chapters III and IV)
Dry cleaning — Table 9	g VOC/kg of cleaned and dried product	Solvent management plan with possibly stack concentration measurement in cases of abatement system efficiency determination (see paragraphs 40–42) (see chapters III and IV)
Manufacture of paints, varnishes, inks and adhesives — Table 10	% of solvent input Or ELVc + ELVf	First case: solvent management plan with possibly stack concentration measurement in cases of abatement system efficiency determination (see paragraphs 40–42)
Heat set offset — Table 11	% of solvent input or % of the ink consumption Or ELVc + ELVf	Second case: solvent management plan and stack emission concentration measurement
Publication gravure — Table 11	Either % of the solid input or ELVc + ELVf	(see chapters III and IV)
Packaging rotogravure and flexography — Table 11	Either % of the solid input or ELVc + ELVf	

<i>Activity of annex VI</i>	<i>Type of ELVs</i>	<i>Measurement system</i>
Manufacture of pharmaceutical products — Table 12	Either % of solvent input or ELVc + ELVf	
Conversion of rubber — Table 13	Either % of solvent input or ELVc + ELVf	
Surface cleaning with non-chlorinated solvents — Table 14	ELVc + ELVf	Solvent management plan and stack emission concentration measurement <sup>11</sup> (see chapters III and IV)
Surface cleaning with chlorinated solvents — Table 14	ELVc as the mass of the sum of individual compounds + ELVf	Solvent management plan and stack emission concentration measurement (see chapters III and IV)
Oil extraction — Table 15	kg VOC / t product	Solvent management plan with possibly stack concentration measurement in cases of abatement system efficiency determination (see paragraphs 40-42) (see chapters III and IV)
Wood preservation — Table 16	Either kg VOC / m <sup>3</sup> wood or ELVc + ELVf	First case: solvent management plan with possibly stack concentration measurement in cases of abatement system efficiency determination (see paragraphs 40-42) Second case: solvent management plan and stack emission concentration measurement <sup>12</sup> (see chapters III and IV)

84. Annex VI to the Gothenburg Protocol, as amended, provides flexibility through types of ELVs implemented for some activities using solvent: either a “total ELV” or an “ELVc + ELVf.” In annex VI, for one given activity, it has to be noticed that these two types of ELVs are equivalent in reduction achievement requested. This enables a plant operator to optimize the choice of the reduction programmes to be implemented in order to be in compliance with the ELVs.

85. For solvent uses covered by annex VI, the regulation of fugitive emission is necessary. In some plants, 100% of VOCs emissions may be fugitive emissions. The SMP is the best tool to estimate emissions from such a plant. In most plants, emissions are

<sup>11</sup> There are, however, some exceptions (see annex VI, table 14 of the amended Gothenburg Protocol).

<sup>12</sup> There are, however, some exceptions (see annex VI, table 16 of the amended Gothenburg Protocol).

however captured and the proportion of fugitive emissions may range from 0% to 100% of solvent input.

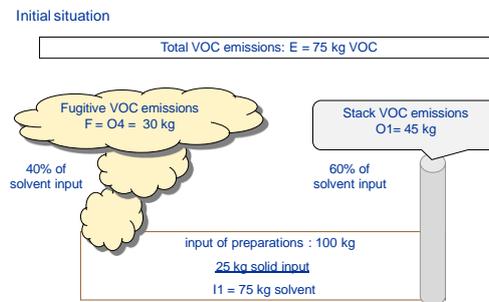
86. The following example is developed to explain the flexibility introduced by the presence of two types of ELVs: Either a “total ELV” or an “ELVc + ELVf.”

**Box 1**

**Example of application of different definitions of ELVs**

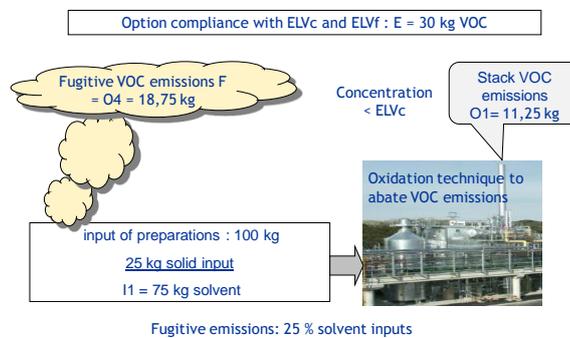
The example developed in the following is based on an installation using solvent contained in a preparation. 25 kg of solid input are needed for the process. This solid input is used with solvent. In the three illustrated cases, the amount of solid input is not changed and always available for the process; however, VOCs emissions change.

Initial situation: In the initial situation presented in the following figure, 25 kg solid input are used with 75 kg of solvent (I1=75 kg VOCs). This solvent input produces 75 kg of VOCs emissions (total VOCs emissions, E) as no VOCs reduction plan is implemented. Fugitive emissions are 30 kg (F or O4) and emissions in waste gases 45 kg (O1). Total VOCs emissions are 3 kg VOC/kg solid input.



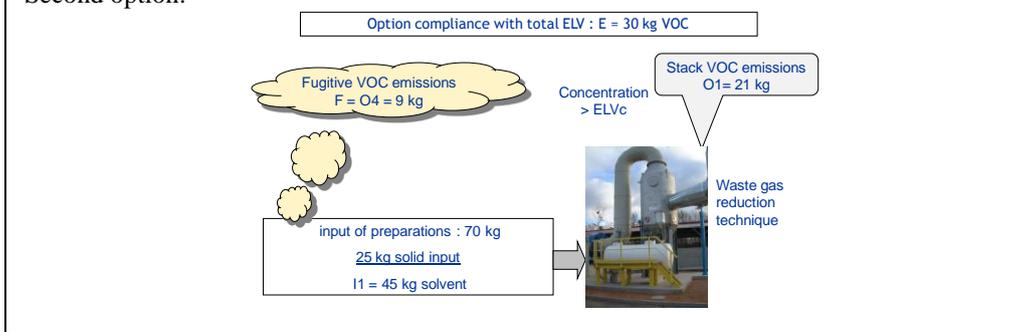
First option to reduce VOCs emissions: The first option is developed in order to be in compliance with ELVc and ELVf. The first option consists in the reduction of fugitive emissions by an improved capture system and a thermal oxidation system to reduce concentrations of VOCs in waste gases to be lower than ELVc. Fugitive emissions are maintained at 25% of the solvent input (75 kg) and concentrations in waste gases are lower than the ELVc. I1 does not change and the solid input is the same as in the initial situation. Total VOC emissions are reduced to 30 kg. Fugitive emissions are 18.75 kg and emissions in waste gases 11.25 kg. Total VOCs emissions are 1.2 kg VOC/kg solid input.

First option:



Second option to reduce VOCs emissions: The second option is developed in order to be in compliance with the total ELVs. The solution consists in reduction of the solvent input, by use of preparations with higher dry extract (lower concentration of VOC) and waste gas treatment by a technique similar to a scrubber. Total VOCs emissions are 30 kg. Fugitive emissions are 9 kg and emissions in waste gases 21 kg. II has been reduced but the solid input is the same as in the initial situation. Total VOCs emissions are 1.2 kg/kg solid input.

Second option:



87. The reduction options in the use of solvents considered by annex VI are different from sector to sector but can be classified as primary measures and secondary measures. Primary measures are measures such as high solid content preparations (lower solvent concentration), water based preparations (water replaces solvents), powder preparations (no solvent), high efficiency application techniques, etc. Secondary measures are waste gas treatment systems (thermal oxidation, activated carbon adsorption, scrubbing, etc.). The goal of the total emission limit value is not to limit the choice of reduction options in contrary to the strict application of ELVc and ELVf. Solutions can be equally efficient or even more efficient, when total VOCs limits are used. The guidance document associated with the Gothenburg Protocol provides information on these primary measures and secondary measures per activity [14]. The SMP associated or not with stack measurements is the best option for checking compliance of installations.

88. The principles of the SMP are applicable to all types of activities using solvents. Measurement of total VOCs by a relatively “simplified” method, such as FID, is adapted to most of cases and enables measurement at reasonable costs compared to specific methods. Except for substances recognized to have harmful effects on human health, the method is adapted to control VOCs emissions in stack.

## VII. Example of development of a solvent management plan

89. An example of SMP is developed for an installation in a printing activity (see box 2).

Box 2

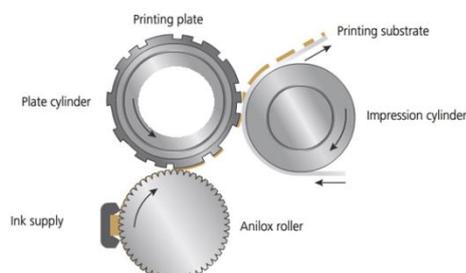
### Example of an SMP development for a printing activity

Plant information and data:

An installation named “SPRINT” has a printing line named “CASSIOPEE”. The printing

technique used is flexography. Plastic surfaces are printed.

Flexography is a printing technique using an image carrier, on which the printing inks are located above the non-printing areas, using liquid inks that dry by evaporation.



The annual quantities of products purchased are as follows:

Printing line	Product	Quantity of product purchased kg / year
CASSIOPEE	<b>Ink</b>	9 850
	Flexo APF Red	
	<b>Dilution and cleaning solvent</b>	19 540
	Ethoxy propanol ( $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}(\text{OH})\text{CH}_3$ )	

The following information is available:

- No variation of stocks has been observed for inks. For ethoxy propanol, a destocking of 500 kg/year is considered.
- 493 kg/year of purchased inks are lost as waste, according to waste disposal records.
- 4 000 kg/year of ethoxy propanol are regenerated externally.
- Proportion of solid content in the ink is 31%.
- VOC contents of inks are provided by the ink manufacturer:

Ink	VOC content (% w/w)	
Flexo APF Red	45%	Ethanol
	24%	Ethyl acetate

The printing line CASSIOPEE is equipped with a stack to capture waste gases and release them into the atmosphere. A measurement of VOCs concentrations is carried out in the stack, one time per year. The results are as follows:

Printing line	VOC concentration $\text{mg C/Nm}^3$	Flow rate $\text{Nm}^3/\text{h}$
CASSIOPEE	74	5 000

During the monitoring exercise, quantities of products used have been recorded in order to be able to use the measurement results in the SMP; the monitoring campaign has been organized accordingly. It is crucial to be able to link the concentration and the VOCs mass flow rate to an activity level which is, generally, variable. The activity level during the monitoring campaign has to be as representative as possible.

The products consumed are as follows:

Product	Quantity of products used during the monitoring exercise kg/h
Flexo APF Red	1.9
Ethoxy propanol (dilution)	1.2

A FID has been used for the VOCs measurement. FID response factors, provided by the FID manufacturer, are as follows:

- (a) 0.82 for ethanol,
- (b) 0.70 for ethyl acetate,
- (c) 0.76 for ethoxy propanol.

Development of the solvent management plan:

The SMP can be developed as explained in the following, to check the compliance of the installation according to ELVs of annex VI of the Gothenburg Protocol, as amended. In a first step, ELVs implemented for the plant are defined.

For flexography printing, ELVs of annex VI are presented in the following table:

Threshold	ELV for VOCs (daily for ELVc and yearly for ELVf and total ELV)
Packaging rotogravure and flexography (solvent consumption 15–25 Mg/year)	ELVc = 100 mg C/m <sup>3</sup> ELVf = 25 wt-% or less of the solvent input Or total ELV of 1.2 kg or less of VOC/kg of solid input
Packaging rotogravure and flexography (solvent consumption 25–200 Mg/year) and rotary screen printing (solvent consumption > 30 Mg/year)	ELVc = 100 mg C/m <sup>3</sup> ELVf = 20 wt-% or less of the solvent input Or total ELV of 1.0 kg or less of VOC/kg of solid input
Packaging rotogravure and flexography (solvent consumption > 200 Mg/year)	For plants with all machines connected to oxidation: Total ELV = 0.5 kg VOC/kg of solid input For plants with all machines connected to carbon adsorption: Total ELV = 0.6 kg VOC/kg of solid input  For existing mixed plants where some existing machines may not be attached to an incinerator or solvent recovery: Emissions from the machines connected to oxidizers or carbon adsorption are below the emission limits of 0.5 or 0.6 kg VOC/kg of solid input respectively. For machines not connected to gas treatment: use of low solvent or solvent free products, connection to waste gas treatment.

There is spare capacity and preferentially a high solvent content work on machines connected to waste gas treatment.  
Total emissions below 1.0 kg VOC/kg of solid input

To determine the ELVs is applicable for the plant, solvent consumption is estimated and compared to the threshold of annex VI.

*Determination of solvent consumption (C)*

The solvent consumption (C) is calculated according to equation:  $C = I1 - O8$ .

I1 is calculated as follows:

Printing line	Product	Quantity of product purchased kg/year	Stock change (stock of year n-1 - stock of year n) kg/year	VOC content %w/w	I1 kg/year	Solid input kg/year
CASSIOPEE	<i>Ink</i>					
	Flexo APF Red	9 850	0	69% (45% + 24%)	6 797	3 054
	<i>Dilution and cleaning solvent</i>					
	Ethoxy propanol	19 540	500	100%	20 040	-
<b>TOTAL</b>					<b>26 837</b>	<b>3 054</b>

**O8** (organic solvents contained in preparations recovered for reuse but not as input into the process, as long as they are not counted under O7):

This output of organic solvents corresponds to the quantity of ethoxy propanol regenerated externally or **4 000 kg/year**.

The annual solvent consumption ( $C=I1-O8$ ) is equal to  $26\ 837 - 4\ 000 = \mathbf{22\ 837\ kg/year}$

*ELVs implemented for SPRINT installation*

According to its solvent consumption, SPRINT is concerned by the first case illustrated in the above table (solvent consumption 15–25 Mg/year) with ELVs as follows:

$$ELVc = 100\ \text{mg C/m}^3$$

$ELVf = 25\ \text{wt-\%}$  or less of the solvent input

or total ELV of 1.2 kg or less of VOC/kg of solid input

ELVc (stack emissions) can only be checked with the use of a measurement device. SPRINT has carried out measurements in the stack. ELVf (fugitive emissions) can be checked by a complete SMP. The total ELV can be checked by a SMP. Due to the fact that no reduction equipment is in place in SPRINT, no monitoring campaign would be necessary to estimate total VOCs emissions.

To check the compliance of SPRINT to ELVc and ELVf, a complete SMP with a monitoring exercise is necessary.

A simplified SMP can be developed to check the compliance with the total ELV.

**Development of a simplified Solvent Management Plan:**

The simplified SMP consists in estimating the different components of the following equation:

$$\text{Total emissions } E = I1 - O5 - O6 - O7 - O8$$

*Inputs of organic solvents*

I1 has been calculated previously:

**26 837 kg/year**

SPRINT is not concerned by I2. There is no internal solvent recovery and reuse.

*Outputs of organic solvents*

SPRINT is not concerned by the following outputs of organic solvents:

- O2 (no organic solvent lost in water);
- O3 (no organic solvent remains as contaminant or residue in output products from the process);
- O5 (no organic solvent lost due to chemical or physical reactions especially due to the presence of an oxidizer);
- O7 (no organic solvent contained in preparations sold);
- O9 (no organic solvent released in other ways).

**O8** (Organic solvents contained in preparations recovered for reuse — however, not as input into the process, as long as they are not counted under O7) has been calculated previously:

**4 000 kg/year**

**O6** (Organic solvents contained in collected waste): 493 kg of the ink purchased are lost as waste.

Ink	Quantity of ink lost as waste kg/year	VOC content %	O6 kg/year
Flexo APF Red	493	69% (45% + 24%)	<b>340</b>

Total emissions  $E = I1 - O5 - O6 - O7 - O8 = 26\,837 - 0 - 340 - 0 - 4\,000 = \mathbf{22\,497}$  kg VOCs/year

Total emissions E are estimated to amount to 22 497 kg VOCs/year.

This is equivalent to 7.4 kg of VOCs/kg of solid input (22 497/3 054). The total emissions of SPRINT being higher than the total ELV (1.2 kg or less of VOC/kg of solid input), the installation would not in compliance with its total ELV.

**Development of a complete SMP**

The complete SMP consists in estimating the different components of the following equations:

$$I = I1 + I2$$

$$\text{Total emissions } E = I1 - O5 - O6 - O7 - O8 = F + O1$$

$$\text{Fugitive emissions } F = I1 - O1 - O5 - O6 - O7 - O8 = O2 + O3 + O4 + O9$$

All components except O1 and O4 have been estimated in the previous paragraphs.

### Output of solvent O1 (VOCs emissions from stack) and fugitive emissions

The determination of stack emissions is based on the annual measurement carried out on the CASSIOPEE printing line.

The results are used as follows:

- Characterization of the mass of solvents used in the printing line during the monitoring campaign.

Products used	Quantity of product used during the measurement kg/h	VOC content %		VOC quantity kg/h
Flexo APF Red	1.9	45%	Ethanol	0.86
		24%	Ethyl acetate	0.46
Ethoxy propanol	1.2	100%	Ethoxy propanol	1.20
<b>TOTAL</b>				<b>2.51</b>

- Determination of the necessary parameters for the conversion of C eq in VOC eq (molar mass, chemical formula, mass of carbon, FID response factors).

VOC	Proportion of VOC in the mixture (Pi)	Chemical formula	Molar mass (Mi) g/mol	Mass of carbon (mci) g/mol	FID response factor	Correction factor (conversion C eq in VOC eq)
Ethanol	34.1% (0.86/2.51)	C <sub>2</sub> H <sub>6</sub> O	46 (2x12+6x1+16)	24 (2x12)	0.82	<b>0.42</b>
Ethyl acetate	18.2% (0.46/2.51)	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	88 (4x12+8x1+2x16)	48 (4x12)	0.70	
Ethoxy propanol	47.8% (1.20/2.51)	C <sub>5</sub> H <sub>12</sub> O <sub>2</sub>	104 (5x12+12x1+2x16)	60 (5x12)	0.76	

- Determination of the hourly flow rate of solvent emitted from the stack.

VOC concentration mg C eq/Nm <sup>3</sup>	Correction factor (conversion C eq in VOC eq)	VOC Concentration mg VOC eq /Nm <sup>3</sup>	Flow rate Nm <sup>3</sup> /h	Hourly flow of solvent kg solvent/h
74	0.42	174.3	5 000	<b>0.87</b> 174.3/1000000 x5000

- Determination of fugitive and stack emission shares compared to the quantity of solvent used on the line during the measurement.
- During the measurement period, inputs of organic solvents on the CASSIOPEE line are 2.51 kg/h. The share of stack emissions represents 0.87/2.51 or **34.7%** of total emissions and therefore the share of fugitive emissions represents **65.3%** of

total emissions.

- Determination of the annual stack and fugitive emissions by applying the stack emissions and fugitive shares to the annual consumption on the printing line.

CASSIOPEE	I1 kg VOC/year	O6 and O8 kg VOC/year	Total emissions kg VOC/year	Stack emissions O1 kg VOC/year	Fugitive emissions O4 kg VOC/year
Flexo APF Red	6 797	340	6 457	<b>7 808</b> (34.7% x 22 947)	<b>14 689</b> (65.3% x 22 947)
Ethoxy propanol	20 040	4 000	16 040		
<b>TOTAL</b>	<b>26 837</b>	<b>4 340</b>	<b>22 497</b>		

**O4** (Uncaptured emissions of organic solvents to air. This includes the general ventilation of rooms, where air is released to the outside environment via windows, doors, vents and similar openings).

O4 is estimated by the calculations to amount to **14 689 kg/year**.

Summary of the SMP:

Inputs and outputs of SMP (kg)	
I1	26 837
I2	<i>not concerned</i>
O1	7 808
O2	<i>not concerned</i>
O3	<i>not concerned</i>
O4	14 689
O5	<i>not concerned</i>
O6	340
O7	<i>not concerned</i>
O8	4 000
O9	<i>not concerned</i>
Solvent consumption (C)	22 837
Solid input	3 054
Total emissions E	22 497
Fugitive emissions F	14 689

Compliance with ELVs:

ELVc can only be checked by the use of a measurement device. SPRINT has carried out measurement in the stack. The measured VOCs concentration (74 mg C/Nm<sup>3</sup>) is lower than the ELVc of 100 mg C/Nm<sup>3</sup>. The installation is in compliance with its ELVc.

Fugitive emissions are estimated to **14 689 kg/year**. They represent **54.7 % of solvent input** (14 689 kg/26 897 kg). Fugitive emissions of SPRINT are higher than the ELVf (25% of solvent input). The installation is not in compliance with its ELVf.

The installation is not in compliance with annex VI ELVs for flexography (both ELVc and ELVf have to be reached).

Remark: The appropriate method to estimate stack emissions depends on the specifics of the installation or activity. It is recommended to organize and schedule the measurement campaign during a representative period of the production. When measurements are carried out, the process parameters such as paint consumption during the period of measurement, the types of paint used and the chemical composition of solvents used should be known and recorded (definition of the input of solvent).

The example presents an ideal situation. The methodology may lead to unreliable emissions in some cases, especially due to the difficulty of quantifying captured emissions (multiplication of the airflow, solvent concentration and time). The airflow and concentration vary over time, and neither can be measured accurately. The resulting error could be greater than 20 per cent [15].

## Annex I

## Carbon content of commonly used solvents

<i>Family</i>	<i>Solvent</i>	<i>CAS Number</i>	<i>Carbon content, %w/w</i>
Alcohols	Methanol	67-56-1	37.5
	Ethanol / Industrial Methylated Spirits (IMS) / Denatured Ethanol	64-17-5	52.1
	n-Propanol	71-23-8	60.0
	Iso-Propanol	67-63-0	60.0
	n-Butanol	71-36-3	64.8
	Sec-Butanol	78-92-2	64.8
	Iso-Butanol	78-83-1	64.8
	Tert-Butanol	75-65-0	64.8
	Amyl Alcohol	71-41-0	68.1
	Iso-Amyl Alcohol	123-51-3	68.1
	Methyl Isobutyl Carbinol	108-11-2	70.5
	Diacetone Alcohol	123-42-2	62.0
	Hexylene Glycol	107-41-5	61.0
	Esters	Methyl Acetate	79-20-9
Ethyl Acetate		141-78-6	54.5
n-Propyl Acetate		109-60-4	58.8
Iso-Propyl Acetate		108-21-4	58.8
n-Butyl Acetate		123-86-4	62.0
Iso-Butyl Acetate		110-19-0	62.0
Amyl Acetate		628-63-7	64.6
n-Butyl Propionate		590-01-2	64.6
Ethylene Glycol Diacetate		111-55-7	49.3
Ethyl 3-Ethoxy Propionate		763-69-9	57.5
Ethers	2,2,4-Trimethyl-1,3-Pentanediol Isobutyrate	25265-77-4	66.6
	Tetrahydrofuran	109-99-9	66.6
	Diethyl Ether	60-29-7	64.8
Glycol Ethers	Diiso-Propyl Ether	108-20-3	70.5
	Ethylene Glycol Mono Isopropyl Ether	109-59-1	57.7
	Ethylene Glycol Mono Butyl Ether	111-76-2	61.0
	Diethylene Glycol Mono Ethyl Ether	111-90-0	53.7
	Diethylene Glycol Mono Butyl Ether	112-34-5	59.2
Propylene Glycol Mono Methyl Ether	107-98-2	53.3	

<i>Family</i>	<i>Solvent</i>	<i>CAS Number</i>	<i>Carbon content, %w/w</i>
	Propylene Glycol Mono Ethyl Ether	1569-02-4	57.7
	Propylene Glycol Mono n-Propyl Ether	30136-13-1	61.0
	Propylene Glycol Mono Butyl Ether	29387-86-8	63.6
	Dipropylene Glycol Mono Methyl Ether	34590-94-8	56.7
	Dipropylene Glycol Mono Ethyl Ether	30025-38-8	59.2
	Dipropylene Glycol Mono Butyl Ether	29911-28-2	63.1
	Propylene Glycol Mono Methyl Ether Acetate	108-65-6	54.5
Glycol Ether Esters	Propylene Glycol Mono Ethyl Ether Acetate	54839-24-6	57.5
	Ethylene Glycol Mono Butyl Ether Acetate	112-07-2	60.0
	Diethylene Glycol Mono Ethyl Ether Acetate	112-15-2	54.5
	Diethylene Glycol Mono Butyl Ether Acetate	124-17-4	58.8
Ketones	Acetone	67-64-1	62.0
	Methyl Ethyl Ketone	78-93-3	66.6
	Methyl n-Propyl Ketone	107-87-9	69.7
	Methyl Iso-Butyl Ketone	108-10-1	72.0
	Methyl Amyl Ketone	110-43-0	73.6
	Methyl Iso-Amyl Ketone	110-12-3	73.6
	Diethyl Ketone	96-22-0	69.7
	Diisobutyl Ketone	108-83-8	76.0
	Cyclohexanone	108-94-1	73.4
	Gamma-Butyrolactone	96-48-0	55.8
	Acetyl Acetone	123-54-6	60.0
	Isophorone	78-59-1	78.2
Cycloparaffins	Cyclopentane	287-92-3	85.6
	Cyclohexane	110-82-7	85.6
	Methylcyclohexane	108-87-2	85.6
Aliphatics	Pentane Blend (n- & iso-pentane mixtures)	109-66-0 / 78-78-4	83.3
	Hexane (technical grade)		84
	Isohexane (technical grade)		84
	Heptane (technical grade, de-aromatized)		84
	Aliphatic de-aromatized solvent 40/65		84
	Aliphatic de-aromatized solvent 60/95		84
	Aliphatic de-aromatized solvent 80/95		85
	Aliphatic de-aromatized solvent 80/110		85
	Aliphatic de-aromatized solvent 100/140		85
	Aliphatic de-aromatized solvent 135/165		85

<i>Family</i>	<i>Solvent</i>	<i>CAS Number</i>	<i>Carbon content, %w/w</i>
	De-aromatized Mineral Spirit 150/200		85
	De-aromatized Mineral Spirit 175/220		85
	De-aromatized Mineral Spirit 200/250		85
	De-aromatized Mineral Spirit 220/280		85
	De-aromatized Mineral Spirit 240/320		86
Mineral Spirits	White Spirit 150/200 (Mineral Spirit)		86
	White Spirit 175/220 (Mineral Spirit)		86
	Heavy Mineral Spirit 200/250		86
	Heavy Mineral Spirit 240/320		86
Aromatics	Toluene	108-88-3	91.3
	Xylene (isomer mix)	1330-20-7	90.5
	Aromatic solvent 160/185		89
	Aromatic solvent 180/215		89
	Aromatic solvent 230/290		88
Isoparaffins	Isoparaffinic solvent 100/150		85
	Isoparaffinic solvent 150/190		85
	Isoparaffinic solvent 180/220		85
	Isoparaffinic solvent 200/300		85

*Source:* European Solvent Industry Group ([www.esig.org](http://www.esig.org)).

## Annex II

### **Volatile organic compounds measurement in countries of Eastern Europe, the Caucasus and Central Asia, and further developments considered necessary**

#### **I. Example of Belarus**

1. Several analytical methods are approved in Belarus. Those methods include [16]:
  - (a) STB EN 12619–2007. Stationary source emissions — Determination of the mass concentration of total organic carbon at low concentrations in flue gases — continuous flame ionization detector method;
  - (b) Method of determination (MVI) of benzene, m-xylene, o-xylene, p-xylene, styrene, toluene, ethylbenzene, saturated (in total), unsaturated (in total) and aromatic hydrocarbons (in total) by gas chromatography (Collection of Methods, 2011). Determination of hydrocarbons based on chromatographic separation of components with their subsequent registration plasma ionization detector;
  - (c) MN 2804–2007. Method for determination of the concentration of organic solvents in gas emissions of the industrial plants (*Collection of Methods, 2011*). The method is based on the quantitative determination of compounds by gas chromatography with plasma ionization detection and pre-concentration of the sample by solid phase extraction. The method determines 35 VOCs;
  - (d) MVI of concentration of amyl acetate, butyl acetate, vinyl acetate, propyl acetate, ethyl acetate (Methods № 1.4.7; 1.4.24.2; 1.4.27; 1.4.86; 1.3.134.3), butadiene (method 1.4.35), styrene (method 1.4.96.3 ) by photometric method (*Collection of Methods ..., 2011*), etc.
2. In Belarus, monitoring of VOCs emissions is accomplished in the framework of the local monitoring of pollutant emissions [16]:
  - (a) Legal entities engaged in economic and other activities that have harmful impact on the environment are obliged to conduct local monitoring in accordance with the regulations on the procedure of local environmental monitoring (2004). Users of natural resources have to carry out local environmental monitoring according to instruction on local monitoring (2007);
  - (b) Local monitoring of emissions into the air is mandatory for operators of stationary sources of emissions from the technological processes and installations listed in annex 9 of the above-mentioned regulations. It includes spray painting chambers, coating lines with a capacity of 15 tons/year and more, process furnaces of chemical and petrochemical plants and other major sources of VOCs emissions. Monitoring is carried out also at other stationary sources identified by the territorial authorities of the Ministry on Natural Resources and Environmental Protection. The list of parameters and frequency of measurement is established by territorial bodies of the Ministry, depending on the emission capacity of a stationary source and the level of its harmful impact on the air, but not less than once a month. Among VOCs, xylene, benzene, toluene, styrene, formaldehyde, acetone, caprolactam, dimethyl and other VOC species are to be controlled using approved analytical methods of determining VOCs emissions;

(c) Operators provide to the territorial authority of the Ministry the results of the monitoring, in accordance with Form 5 of the instructions (2007) within 15 calendar days after the observation. Local monitoring results are presented for each of the compounds controlled in mg/m<sup>3</sup>, g/second(s) and compared to Maximum Permitted Emissions (MPE) (g/s);

(d) Local monitoring of emissions into the air in 2012–2013 was carried out at 155 enterprises of Belarus. In 2012, at the enterprises where local monitoring was carried out 21 thousand measurements were made at 976 stationary sources. The share of emissions of pollutants from emission sources included in the system of local monitoring account for 42% of total stationary sources emissions (National system, 2013, 2014);

(e) Periodic monitoring of pollutants (including VOCs) emissions from different sources is also conducted under the Ministerial authority which controls compliance with emission limits.

## **II. Gaps identified by the Task Force on Techno-economic Issues technical secretariat to implement the requirements of annex VI**

3. The following gaps have been identified by the Task Force secretariat, with the objective of supporting the experts of Belarus in complying with the obligations of the Gothenburg Protocol:

(a) According to information received from Belarus, analytical methods used seem adapted to the implementation of the requirements of annex VI in terms of VOCs measurement. Article 4(a) of the Gothenburg Protocol provides appropriate flexibility to adapt the current practices, if necessary;

(b) Activities covered by the Belarus regulations might be different from activities covered by annex VI. The size of the installations covered might be also different. It is possible that the current Belarussian regulation needs to be adapted in order to take account of the requirements of annex VI (activities covered and size of activities as well as VOCs emission limit values);

(c) VOCs emissions from solvent uses are both fugitive and stack emissions. The control of stack emissions is not sufficient to abate VOCs emissions. The control of fugitive emissions is also required by annex VI. The solvent management plan (SMP) is an adapted calculation tool for that purpose. For the operator, the SMP is a tool to define the reference emissions and implement an improvement plan to reduce VOCs emissions. For the local authorities, the SMP can be used to control compliance of an installation with ELVs, both fugitive and total emissions. A simple calculation method has to be associated (the SMP as described above) with measurement in stacks, in some cases. According to information received, SMPs do not yet exist in Belarus. They should be developed as they are rather simple methods to estimate total emissions and fugitive emissions for activities using solvents covered by annex VI.

## Annex III

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