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Progress in the implementation of the 2014–2015 workplan

Draft guidelines for estimation and measurement of emissions of volatile organic compounds

Summary

The present draft guidelines are submitted by the Task Force on Techno-economic Issues under the Convention on Long-range Transboundary Air Pollution for review by the Working Group on Strategies and Review at its fifty-third session (Geneva, 15–17 December 2015). The aim of the present document is to assist Parties to the Convention in meeting the obligations of annexes VI and XI to the 1999 Protocol to Abate Acidification, Eutrophication and Ground-level Ozone, as amended in 2012.



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List of abbreviations and acronyms

API	American Petroleum Institute
CEN	European Committee for Standardisation
CH ₄	Methane
C ₂ H ₆	Propane
ELV	Emission limit value
ELV _c	Emission limit value in waste gas
ELV _f	Fugitive emission limit value
FID	Flame ionisation detector
FR	Response factor
FTIR	Fourier transform infrared absorption
GC	Gas chromatography
mc	Mass of carbon in a VOC (number of carbon in the molecule x 12)
M	Atomic molar mass in g/mole
NDIR	Non dispersive infrared
QA/QC	Quality assurance/Quality control
STP	Standard temperature and pressure
VOC	Volatile organic compound

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 article 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;

(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 CEN¹ standards. If CEN standards are not available, ISO² 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 and develop solvent management plan or calculate emissions. It answers to the requirement set by annex VI, which stipulated that "...methods of calculation will be reflected in the guidances adopted by the Executive Body...", with the ultimate goal of facilitating the ratification and implementation of the Gothenburg Protocol, as amended.

II. Types of ELVs implemented for VOC 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 considers ELVs for waste gases containing VOCs and for fugitive VOCs emissions but also total ELVs considering both types of the emissions.

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 (m³/h) at standard conditions.

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

¹ European Committee for Standardization

² International Organization for Standardization

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**) 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 (mg C/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.

(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 VOC 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 mg C/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 ($\text{g VOCs per square meter (m}^2\text{)}$, $\text{g VOC per kilogram (kg)}$ 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 $\text{mg substances per cubic meter (mg VOCs/m}^3\text{)}$ in STP (annex VI, articles 3(z) and 5).

(c) As a fugitive emission of VOCs, expressed in % of solvent input as example.

(d) In some cases, emission reduction efficiency is required.

10. For different types of activities outlined in annex VI, the situation can be summarized as in Table 1 (the reference number of the related tables of annex VI is provided):

Table 1

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

Activity of annex VI and related table	<i>ELVc</i>	<i>Total ELV expressed in % of solvent input or of throughput</i>	<i>ELVc expressed in mg C / m³</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>
	<i>expressed in mg VOCs / m³</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 refueling - 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 ² of finished product g VOC/m ² or g/body + g VOC/m ² (electrophoretic area)	
Car manufacturing - Table 5					g VOC/m ² (electrophoretic area)	
Truck, truck cabin and bus manufacturing Table 5					g VOC/m ² (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			

<i>Activity of annex VI and related table</i>	<i>ELVc expressed in mg VOCs / m³</i>	<i>Total ELV expressed in % of solvent input or of throughput</i>	<i>ELVc expressed in mg C / m³</i>	<i>ELVf expressed in % of solvent input</i>	<i>Total ELV expressed in mass of VOCs per unit of activity</i>	<i>Efficiency</i>
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 ²	
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	
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			

Activity of annex VI and related table	<i>ELVc</i>	<i>Total ELV expressed in % of solvent input or of throughput</i>	<i>ELVc expressed in mg C / m³</i>	<i>ELVf expressed in % of solvent input</i>	<i>Total ELV expressed in mass of VOCs per unit of activity</i>	<i>Efficiency</i>
	<i>expressed in mg VOCs / m³</i>					
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 15				Or ELVc + ELVf	Or kg VOC / m ³ wood	

11. Compliance with ELVs for waste gases or ELVc, expressed as a mass of **total organic carbon**/m³ or a mass of a **substance or group of substances**/m³ can only be verified by the use of **specific measurement equipment**³. 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 article 5 of annex VI; or mass of VOCs expressed in mass of VOCs considered harmful for human health and covered by article 5 of annex VI).

12. Compliance with fugitive ELVs or ELVf, or with total ELVs, can be verified by a **solvent management plan** (mainly calculations) **and/or determination of stack emissions**⁴ (with measurement equipment) for activities using solvents.

III. VOCs measurement techniques

A. Total VOCs concentration measurement techniques

Flame ionisation detector

13. Organic carbon compounds are relatively easily ionisable in a hydrogen flame. Flame ionisation 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

³ In other words, calculations are not possible.

⁴ The solvent management plan alone may be used when no reduction device is in use.

specifically, FID analysers make use of the chemi-ionisation of organically bound carbon atoms in a hydrogen flame to provide measurements.

14. The measurement cell contains a pair of electrodes and current is applied between them. If there are ions present in the cell, current can pass between the electrodes. The ionisation 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 ionise. The more ions 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 but default values are also available. In the absence of response factor provided by the manufacturer or determined experimentally, default values are as follows [2]:

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 give 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 liters at STP.

Catalytic oxidation and non-dispersive infrared absorption

17. A combustion chamber with a catalyst is used. Carbon from VOCs is oxidized to carbon dioxide (CO₂). Concentrations of CO₂ are measured by infrared absorption detection. The catalyst may be poisoned by the presence of some components in waste gases and the conversion to CO₂ is not completely efficient [2]. The gas analysers use, as the measurement principle, the absorption of infrared radiation (IR). The TVOC mass concentration at standard conditions is the quotient of the mass of TVOCs to the volume of the dry gas under specified reference conditions of temperature and pressure (273 K, 1 013 hPa), normally. The analyser calculated as carbon component measured in characteristic wavelength ranges. The analysers operate according to the non-dispersive IR (NDIR) method, while the selectivity of measurement is achieved by the radiation detector which is

filled with the component to be measured. According to [12], a dust-free sample is essential and moisture in the sample gas tends to cause interference. They can present problems with complex gas mixtures.

Photo ionisation detection (PID)

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

CEN standard reference methods for total VOC measurement

19. The FID technique is considered in two CEN standards for VOC 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 ionisation detector method. The standard has been validated for measuring concentrations over a range of 0 – 20 mg/Nm³. The method measures VOC 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 ionisation detector method. The standard has been validated as suitable for measuring emissions up to 500 mg/Nm³ although FIDs can be used to measure higher concentrations. The method measures VOC including methane [2].

20. Another standard ISO 13199:2012 - Stationary source emissions — Determination of total volatile organic compounds (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 volatile organic compound (TVOC) content in waste gases of stationary sources, using a non-dispersive infrared absorption (NDIR) analyser equipped with a catalytic converter which oxidizes VOC to carbon dioxide. This method is suitable for the measurement of total VOCs (TVOCs) emissions from non-combustion processes. This method allows continuous monitoring with permanently installed measurement systems, as well as intermittent measurements of TVOCs emissions. The 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/m³ to 600 mg/m³[11].

B. Measurement techniques of individual VOC substances

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

Sampling and gas chromatography (GC)

22. VOCs can be adsorbed on solid adsorbents. There is no universal sampling sorbent. It must be selected according to 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 compound 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 (NDIR)

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, there can be overlapping of spectra. The method is well suited for the monitoring of one single compound.

Fourier Transform Infrared absorption (FTIR)

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. After 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 and this technique can be used to detect and monitor several compounds in a waste gas. They can give direct readings 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 United States of America standards:

(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 specifies 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 thermodesorption and analysis by gas chromatography. Examples of individual VOCs are given in relevant industry sector best available technique (BAT) reference documents (BREFs). The results obtained are expressed as the mass concentration (mg/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 Industrial Emission Directive (IED) of the European Union and associated supporting documents. This Technical Specification 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 [6].

C. Translation of concentrations of single VOC expressed in mass of VOC to total VOC concentrations expressed in mass of carbon

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

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

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

$\text{CONC}_i(\text{mass of C eq})$: 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

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:

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

$\text{CONC}_{\text{VOC}}(\text{mass of C eq})$: 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. 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 is 300 mg VOC/m³. The VOC concentration expressed in Carbon or C eq is as follows:

Ethanol: CH₃-CH₂OH or 2 C, 6 hydrogen (H) and 1 oxygen (O) atoms; molar mass M_{Ethanol} : 46 (2x12 + 6x1 + 16) g/mole; $mc_{\text{Ethanol}}=24$ (2x12) g; $P_{\text{Ethanol}}=35\%$

Ethyl acetate: CH₃-CH₂-CO-O-CH₃ 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; $P_{\text{Ethyl acetate}}=65\%$

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

IV. Solvent management plan

A. Aim of the solvent management plan

31. A solvent management plan (SMP) is an adequate tool to determine the solvent consumptions and emissions, especially fugitive VOCs emissions. An SMP is used to check the compliance of an installation using solvents, for which the total VOC 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 VOC ELV is expressed in % of solvent input.

32. The SMP is a tool for estimating VOCs emissions based on solvent inputs and outputs, based on the following principle:

$$\sum \text{Solvent inputs} = \sum \text{Solvent outputs (including emissions into air)}$$

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

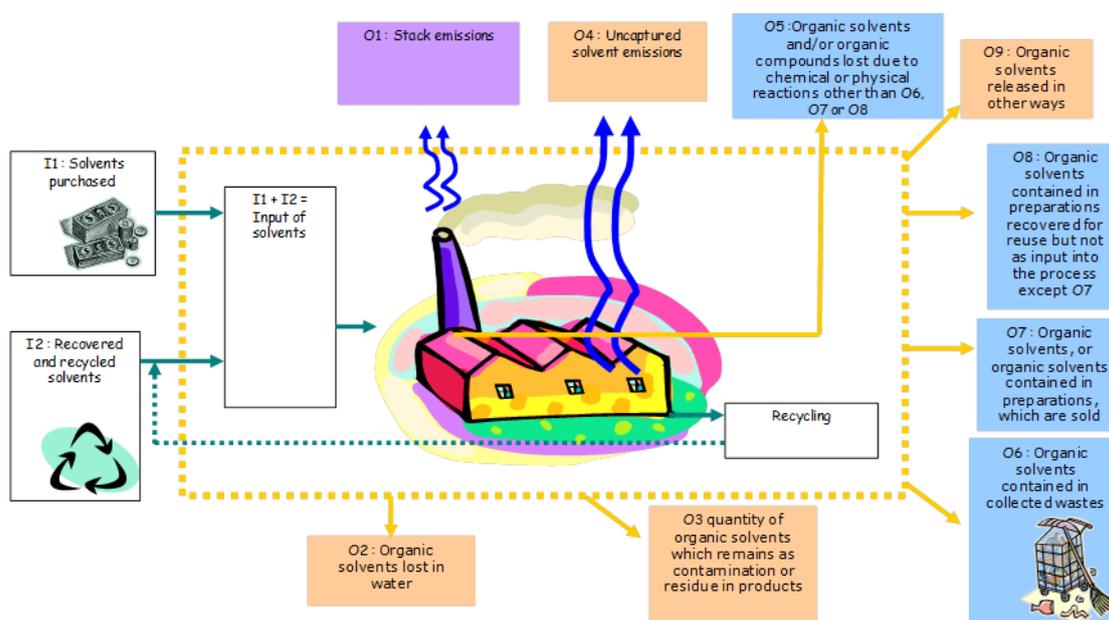
(b) The balance can be done if the chemical nature of inputs and outputs is the same and if inputs and outputs can be expressed in the same units (mass of solvent). Inputs are often easily known. On the contrary, only some outputs can be estimated easily.

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

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

Figure 1

Components of the solvent management plan



B. How to estimate the different components of the balance

Inputs of organic solvents (I):

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

35. An exhaustive inventory of all preparations containing solvent used in the installation covered by the balance has to be carried out. Their respective quantities and mass concentrations of solvent have to be determined. The solvent content of preparations to be provided in w/w, can be obtained from labels and/or factsheets on safety data 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).

Quantity of used solvent = Quantity bought – stock of year n + stock of year n-1

36. *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).*

37. “Reused” has to be understood as recovered on site after specific internal regeneration as example and reused as solvent input in the process. Recycled solvents in the process require specific quality and the amount of recycled solvent 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 (O):

38. *O1 represents emissions in waste gases.*

39. Only stack emissions have to be considered in this group. Monitoring of VOCs concentrations in waste gases is required. 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 in VOCs.

40. *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).*

41. 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 [14] [15].

42. 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 is known as well as specific FID response factors. In most of the cases, it is assumed that this composition does not change from the input flow, as shown in formula (3):

$$(3) \quad \text{CONC}_{\text{VOC}} = \frac{\text{CONC}_{\text{monitored}}}{\sum_i \left(P_i \cdot mc_i \cdot \frac{FR_i}{M_i} \right)}$$

CONC_{monitored}: Mass of solvent measured (or VOC) in eq C

CONC_{VOC}: Real mass of solvent in waste gases in mass of VOC

i: type of solvent consumed

P_i: proportion of a solvent i in waste gases (% mass)

mc_i: mass of carbon in solvent i (12 x number of carbons)

FR_i: response factor for solvent i

M_i: Molar mass of solvent i

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

43. *O2 are organic solvents lost in water, if appropriate, taking into account waste water treatment when calculating O5.*
44. The determination of the VOCs rate 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.
45. 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 variability of results.
46. *O3 is the quantity of organic solvents which remains as contamination or residue in products output from the process.*
47. This is a fugitive output. Some chemical analysis may be required.
48. *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.*
49. This output is determined by the solvent balance by difference of known inputs and outputs. Different other methods can also be used [13].
50. *O6 are organic solvents contained in collected wastes.*
51. Solvents in waste 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.
52. *O7 are organic solvents, or organic solvents contained in preparations, which are sold or are intended to be sold as a commercially valuable product.*
53. When preparations are sold such as in the production of paints, inks and glues, the solvent contents of products are known as those products must comply with specific requirement.
54. *O8 are organic solvents contained in preparations recovered for reuse but not as input into the process, as long as not counted under O7.*
55. Solvents recovered for recycling after specific treatment or without treatment. The flow rates are known in case of treatment.
56. *O9 are organic solvents released in other ways.*

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

57. The determination of the solvent consumption and VOCs emissions can be done according to equations presented hereafter:

$$C = I1 - O8$$

58. In annex VI, the thresholds for application of the ELVs are based on the consumption of solvents. Total VOCs emissions are defined as follows:

$$E = F + O1$$

or

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

Total VOCs emissions are expressed in mass of VOCs.

59. If O1 has been determined by a measurement device providing a concentration is 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.

60. F is the fugitive emission as defined below:

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

or

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

61. This quantity can be determined by 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.

62. 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:

$$I = I1 + I2$$

63. 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.

64. A simplified solvent management plan 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. 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.

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

$$C = I1 - O8$$

$$I = I1 + I2$$

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

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

$$C = I1 - O8$$

$$I = I1 + I2$$

$$\text{Total emissions} = I1 - O5 - O6 - O7 - O8 = Ed + Ec$$

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

$$\text{Emission in waste gases } Ec = O1$$

67. The complete SMP requires measurement of VOCs emissions in waste gases and of flow rates (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 VOCs for selected activities covered by annex VI

A. Storage of petrol at terminals

68. There are two components in VOCs emissions from storage tanks: working losses due to vapors displaced during filling; and standing losses due 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.

69. 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.

70. 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.

71. 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 pollutant of concern is volatile organic compounds. The developed algorithms take into account different types of storage and their characteristics (tightness of floating roof seals, colour, etc).

72. Emission calculation software is provided by the USEPA [3]. A division of the European Petroleum Refiners Association (CONCAWE) has also developed a simple method for estimating VOCs emissions from different types of storages [4].

B. Loading/unloading of mobile containers at terminals (excluding load of sea going ships)

73. Emissions from loading and unloading of mobile containers at terminals can be estimated through equations developed by API and translated in several guides such as CONCAWE [4] and USEPA [5].

74. The ELV implemented requires 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.

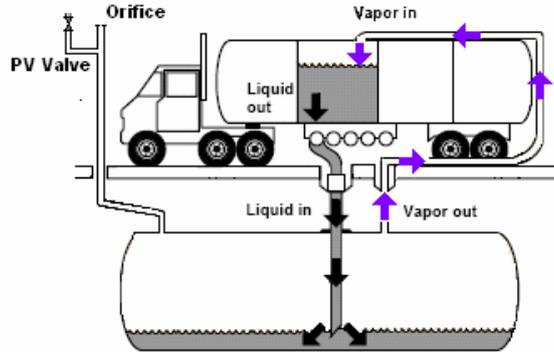
C. Storage of petrol at service-stations (stage I)

75. During filling of the underground petrol tank, VOC 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 under the name stage 1. The system is only complete if a vapour recovery unit is present at the terminal, in order to recover VOC emissions.

76. In order to be in compliance with the ELV implemented by annex VI, 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.

77. The following figure presents the vapour balancing system[7]:
Figure 2

Schematic representation of a vapour balancing system

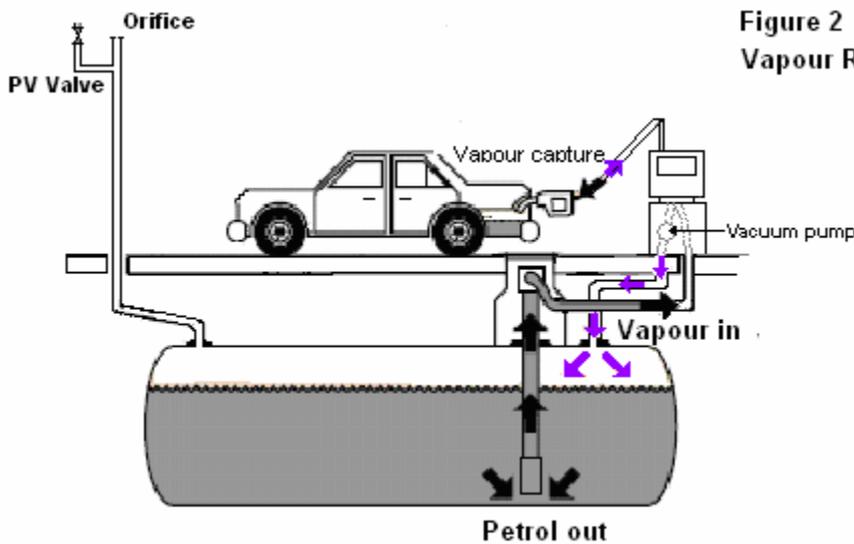


C. Car refueling at service stations (stage II)

78. 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 and 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 [7].

Figure 3

Schematic representation of a vapour recovery system



**Figure 2
Vapour Recovery Stage 2**

79. The petrol vapour capture efficiency of the stage II system must be equal to or greater than 85 % (weight %) (the capture efficiency has to be certified by the manufacturer in accordance with relevant European technical standards or type approval procedures referred to in article 8 of annex VI or, if there are no such standards or procedures, with any

relevant national standard) 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)).

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) [9] [10]. The first standard specifies the measurement and test methods for the efficiency assessment of petrol vapour recovery systems for service stations (Stage II). 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

80. 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 (section H)
Storage installation at terminals - Table 1	%	Calculation methods (section G)
Service-stations Storage - Table 1	% of throughput	No measurement required if a vapour balancing system is present (section I)
Service-stations Car refueling - 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. 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 Second case: solvent management plan and stack emission concentration measurement Chapters III and IV

<i>Activity of annex VI</i>	<i>Type of ELVs</i>	<i>Measurement system</i>
Wood and plastic lamination – Table 4	g VOC/m ² of finished product	Solvent management plan with possibly stack concentration measurement in cases of abatement system
Car manufacturing Table 5	g VOC/m ² or g/body + g VOC/m ² (electrophoretic area)	Chapters III and IV
Truck, truck cabin and bus manufacturing Table 5	g VOC/m ² (electrophoretic area)	
Wood coating Table 6	Or kg VOC/kg solid input Or ELVc + ELVf	First case: solvent management plan with possibly stack concentration measurement in cases of abatement system
Coating of metals and Plastics Table 6	Or kg VOC/kg solid input Or ELVc + ELVf	Second case: solvent management plan and stack emission concentration measurement
Textile, fabric foil, and paper coating Table 6	Or kg VOC/kg solid input Or ELVc + ELVf	Chapters III and IV
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 ²	Solvent management plan with possibly stack concentration measurement in cases of abatement system
Winding wire coating Table 7	g VOC/kg wire	Chapters III and IV
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 Second case: solvent management plan and stack emission concentration measurement 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

<i>Activity of annex VI</i>	<i>Type of ELVs</i>	<i>Measurement system</i>
		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 Second case: solvent management plan and stack emission concentration measurement
Heat set offset Table 11	% of solvent input or % of the ink consumption Or ELVc + ELVf	Chapters III and IV
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	Solvent management plan and stack emission concentration measurement 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 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 Chapters III and IV
Wood preservation Table 15	Or kg VOC / m ³ wood Or ELVc + ELVf	First case: solvent management plan with possibly stack concentration measurement in cases of abatement system Second case: solvent management

Activity of annex VI	Type of ELVs	Measurement system
		plan and stack emission concentration measurement
		Chapters III and IV

81. Annex VI to the Gothenburg Protocol provides flexibility through types of ELVs implemented for some activities using solvent: or 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. For a plant operator, this enables to optimize the choice of reduction programmes to be implemented in order to be in compliance with ELVs.

82. For solvent uses covered by annex VI, 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 however captured and the proportion of fugitive emissions may range from 0% to 100% of solvent input.

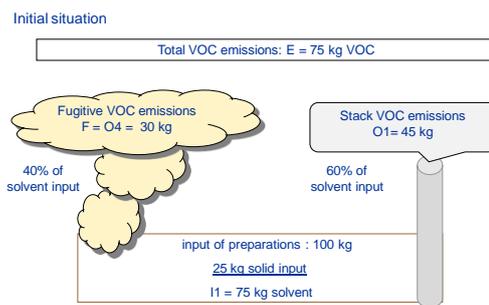
83. The following example is developed to explain the flexibility introduced by the presence of two types of ELVs: Or a “total ELV” or an “ELVc + ELVf”.

Box 1

Example of application of different ELV definitions

The example developed 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 3 cases, this amount of solid input is not changed and always available for the process but VOCs emissions change.

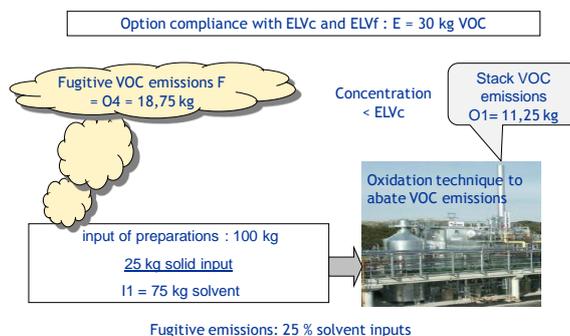
Initial situation : in the initial situation presented in the following figure, 25 kg solid input are used with 75 kg of solvent (I1=75 kg VOC). This solvent input produces 75 kg of VOCs emissions (total VOCs emissions, E) as no VOCs reduction plan is implemented. Fugitive emissions are 30 kg (F or O4)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

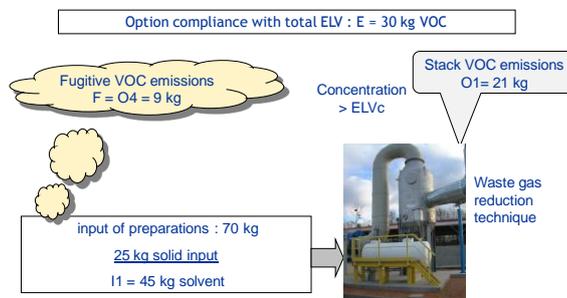
Total VOCs emissions are 1.2 kg VOC/kg solid input.

First option:



Second option to reduce VOCs emissions: the second option is developed in order to be in compliance with the total ELV. 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. I1 has been reduced but the solid input is the same as in the initial situation. Total VOC emissions are 1.2 kg/kg solid input.

Second option:



The reference situation has to be recorded, to demonstrate progress from the initial situation.

84. 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 [16]. The SMP associated or not with stack measurements is the best option for checking compliance of installations.

85. 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 VOC emissions in stack.

VII. Example of development of a solvent management plan

86. An example of SMP is developed for an installation in a printing activity:

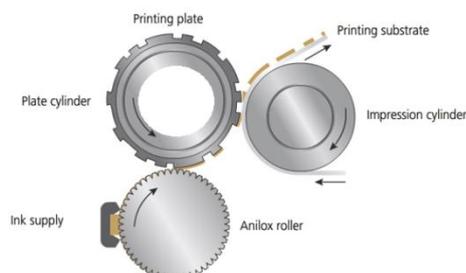
Box 2

Example of a 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.

For information, flexography is a printing technique using an image carrier on which the printing inks are 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	<i>Ink</i>	9 850
	Flexo APF Red	
	<i>Dilution and cleaning solvent</i>	19 540
	Ethoxy propanol ($\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}(\text{OH})\text{C}$ H_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 periodical measurement of VOCs concentrations is carried out in the stack, one time per year.

The results are as follows:

Printing line	VOC concentration mg C/Nm ³	Flow rate Nm ³ /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 indeed organised in such a way. 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 (Flame Ionization Detector) has been used for the VOC measurement. FID response factors, provided by the FID manufacturer, are as follows:

- 0.82 for ethanol,
- 0.70 for ethyl acetate,
- 0.76 for ethoxy propanol.

Development of the solvent management plan:

The SMP can be developed as follows. It enables to check the compliance of the installation according to ELVs of annex VI.

In a first step, ELVs implemented for the plant are defined.

ELVs implemented according to annex VI for flexography printing

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

Threshold	ELV for VOC (daily for ELVc and ELVf and total ELV)
Packaging rotogravure and flexography (solvent consumption 15–25 Mg/year)	ELVc = 100 mg C/m ³ ELVf = 25 wt-% or less of the solvent input Or total ELV of 1.2 kg or less of VOC 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 ³ ELVf = 20 wt-% or less of the solvent input Or total ELV of 1.0 kg or less of VOC input
Packaging rotogravure and flexography	For plants with all machines c

(solvent consumption > 200 Mg/year)	<p>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</p> <p>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 when There is spare capacity and preferentially run high solvent content work on machines connected to waste gas treatment. Total emissions below 1.0 kg VOC/kg of solid input</p>
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To know ELVs applicable for the plant, solvent consumption is estimated to compare it 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	-
TOTAL					26 837	3 054

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 $26\ 837 - 4\ 000 =$ **22 837 kg/year**

ELVs implemented for SPRINT installation

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

follows:

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

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

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

ELV_c (stack emissions) can only be checked by the use of a measurement device. SPRINT has carried out measurement in the stack. ELV_f (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 VOC emissions.

The check the compliance of SPRINT to ELV_c and ELV_f requires a complete SMP with a monitoring exercise. 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:

$$I = I1 + I2$$

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

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 oxidiser), 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 but 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%)	340

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

87. Development of a complete SMP

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

$$I = I1 + I2$$

$$\text{Total emissions} = I1 - O5 - O6 - O7 - O8 = Ed + Ec$$

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

$$\text{Emission in waste gases } Ec = O1$$

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:

- Characterisation 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
TOTAL				2.51

- 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 ₂ H ₆ O	46 (2x12+6x1+16)	24 (2x12)	0.82	0.42
Ethyl acetate	18.2% (0.46/2.51)	C ₄ H ₈ O ₂	88 (4x12+8x1+2x16)	48 (4x12)	0.70	
Ethoxy propanol	47.8% (1.20/2.51)	C ₅ H ₁₂ O ₂	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 ³	Correction factor (conversion C eq in VOC eq)	VOC Concentration mg VOC eq /Nm ³	Flow rate Nm ³ /h	Hourly flow of solvent kg solvent/h
74	0.42	174.3	5 000	0.87 174.3/1000000 *5000

- 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 emissions by applying the stack emissions share to the annual consumption on the printing line.

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

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. O4 corresponds to fugitive emissions calculated previously or **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	22 497
Fugitive emissions	14 689

Compliance with ELVs:

Total emissions are estimated to **22 497 kg/year**. This is equivalent to **7.4 kg of VOCs/kg of solid input**. Total emissions of SPRINT being higher than total ELV (1.2 kg or less of VOC/kg of solid input) the installation is not in compliance with its total ELV.

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/Nm³) is lower than the ELVc of 100 mg C/m³. 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.

VIII. References

- [1] S. Collet. INERIS. Méthode de réalisation d'un PGS. 2003
- [2] Environment Agency. Technical Guidance note. Monitoring volatile organic compounds and methane in stack gas emissions. Version 4 June 2012.
- [3] Tanks. <http://www.epa.gov/ttnchie1/ap42/ch07/index.html>
- [4] D. Withinshaw and alls - Air pollutant emission estimation methods for E-PRTR reporting by refineries - 2009 edition. Prepared by the CONCAWE Air Quality Management Group's Special Task Force on Emission Reporting Methodologies (STF-69) - <https://www.concawe.eu/publications/23/40/Report-No-1-09>
- [5] US EPA – AP42 - 5.2 Transportation And Marketing Of Petroleum Liquids
<http://www.epa.gov/ttnchie1/ap42/ch05/final/c05s02.pdf>
- [6] <http://www.cdc.gov/niosh/az/a.html>.
- [7] NSW Environment Protection Authority (EPA). Guidelines for vapour recovery at petrol service stations. 2009
- [8] Directive 2009/126/EC of the European parliament and of the council of 21 October 2009 on Stage II petrol vapour recovery during refueling of motor vehicles at service stations
- [9] Technical Committee CEN/TC 393. EN 16321-1:2013 - Petrol vapour recovery during refuelling of motor vehicles at service stations - Part 1: Test methods for the type approval efficiency assessment of petrol vapour recovery systems. 2013.
- [10] Technical Committee CEN/TC 393. EN 16321-1:2013 - Petrol vapour recovery during refuelling of motor vehicles at service stations - Part 2: Test methods for verification of vapour recovery systems at service stations. 2013

- [11] <https://www.iso.org/obp/ui/#iso:std:iso:13199:ed-1:v1:en>
- [12] Environmental Technology Best practice programme. CG203 guide. Monitoring VOC emissions, choosing the best option. AEAT 1999
- [13] ESIG/ESVOC - Guidance on the interpretation of the Solvents Emissions Directive – 2007
- [14] EN ISO 16911-1:2013. Stationary source emissions - Manual and automatic determination of velocity and volume flow rate in ducts - Part 1: Manual reference method (ISO 16911-1:2013)
- [15] EN ISO 16911-2:2013. Stationary source emissions - Manual and automatic determination of velocity and volume flow rate in ducts - Part 2: Automated measuring systems (ISO 16911-2:2013)
- [16] Guidance document Guidance document on control techniques for emissions of sulphur, NO_x, VOC, and particulate matter (including PM₁₀, PM_{2.5} and black carbon) from stationary sources.
- <http://www.unece.org/environmental-policy/conventions/envlirtapwelcome/guidance-documents-and-other-methodological-materials/gothenburg-protocol.html>
- [17] Sergei Kakareka. Communication to TFTEI technical secretariat in July 2015.

Annex

VOCs measurement in countries of Eastern Europe, the Caucasus and Central Asia, and further developments considered necessary

A. Example of Belarus

The following information was received from Belarus[17].

Several analytical methods are approved in Belarus. Those methods include [17]:

- STB EN 12619-2007. Stationary source emissions - Determination of the mass concentration of total organic carbon at low concentrations in flue gases - continuous flame ionisation detector method.
- 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.
- Method of determination (MVI). 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.
- 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.

In Belarus, monitoring of VOCs emissions is accomplished in the framework of local monitoring of pollutant emissions [17].

- Legal entities engaged in economic and other activities which 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).
- Local monitoring of emissions into the air is mandatory for operators of stationary sources of emissions from the technological processes and installations listed in the annex 9 of the Regulations. It includes spray painting chambers, coating lines with capacity 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 Ministry on Natural Resources and Environmental Protection territorial authorities. The list of parameters and frequency of measurement is established by territorial bodies of the Ministry, depending on 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 determination of VOCs emissions.
- Operators provide to territorial authority of the Ministry results of monitoring according to the Form 5 of Instructions (2007) within 15 calendar days after the

observation. Local monitoring results are presented for each of the compounds controlled in mg/m^3 , $\text{g}/\text{second}(\text{s})$ and compared to Maximum Permitted Emissions (MPE) (g/s).

- 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).
- Periodic monitoring of pollutants (including VOCs) emissions from different sources also operate under the Ministry authority control of compliance with emission limits.

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

In following gaps have been identified by the Task Force secretariat with regard to facilitating the experts of Belarus to comply with the obligations of the Gothenburg Protocol:

(a) According to information received from Belarus, analytical methods used seem adapted for 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 regulation might be different from activities covered by annex VI. Sizes of installations covered might be also different. It is possible that the current Belarus regulation should 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. For the operator, the SMP is a tool to define the reference emissions and implement an improvement plan to reduce VOC emissions. For 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.