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# Monitoring of VOC emissions

## EGTEI

### Provisional informal document

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#### **Introduction**

In technical annex VI, there are currently four ways of expressing the ELVs for VOC:

- As total organic carbon (TOC), which is a concentration of carbon in the gas stream, usually expressed in mg C per cubic meter ( $\text{mg C/m}^3$ ), in the standard conditions of temperature and pressure (STP),
- As substance which is a concentration of one or several substances which are assigned to the following risk phrases: 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 mg substances per cubic meter ( $\text{mg/m}^3$ ) in the standard conditions of temperature and pressure,
- As a total emission of VOC, expressed in % of solvent input, or g VOC/unit of activity (g  $\text{VOC/m}^2$ , g  $\text{VOC/kg}$  high solid, ...) for some activities using solvents or % of petrol throughput for activities related to storage and handling of petrol,
- As a fugitive emission of VOC expressed in % of solvent input.

Per activity of annex VI, the situation is as follows (the number of the table in annex VI is provided):

Activity of annex VI	ELVc expressed in $\text{mg VOC / m}^3$	ELVt expressed in % of solvent input	ELVc expressed in $\text{mg C / m}^3$	ELVf expressed in % of solvent input
Loading and unloading of mobiles container at terminals – Table 1	X			
Storage installation at terminals – Table 1		% of throughput		
Service stations Storage – Table 1		% of throughput		
Service stations Car refueling Table 1bis		% of throughput		
Shoe industry – Table 2		g/pair of shoes		
Other adhesive coating Table 2		Or kg VOC/kg solid input	Or ELVc + ELVf	
Wood and plastic lamination – Table 3		g $\text{VOC/m}^2$		
Car manufacturing Table 4		g $\text{VOC/m}^2$ or g/body + g $\text{VOC/m}^2$		
Truck, truck cabin and bus manufacturing Table 4		g $\text{VOC/m}^2$		

Activity of annex VI	ELVc expressed in mg VOC / m <sup>3</sup>	ELVt expressed in % of solvent input	ELVc expressed in mg C / m <sup>3</sup>	ELVf expressed in % of solvent input
Wood coating Table 5		Or kg VOC/kg solid input	Or ELVc + ELVf	
Coating of metals and plastics - Table 5		Or kg VOC/kg solid input	Or ELVc + ELVf	
Textile, fabric foil, and paper coating Table 5		Or kg VOC/kg solid input	Or ELVc + ELVf	
Coating of plastic work pieces Table 5		Or kg VOC/kg solid input	Or ELVc + ELVf	
Leather coating Table 6		g VOC/m <sup>2</sup>		
Winding wire coating Table 6		g VOC/ kg wire		
Coil coating Table 7		Or kg VOC/kg solid input	Or ELVc + ELVf	
Dry cleaning Table 8		g VOC/kg of cleaned and dried product		
Manufacture of paints, varnishes, inks and adhesives - Table 9		Or kg VOC/kg solid input	Or ELVc + ELVf	
Heat set offset Table 10		Or % of the ink consumption	Or ELVc + ELVf	
Publication gravure Table 10		Or % of the ink consumption	Or ELVc + ELVf	
Packaging rotogravure and flexography Table 10		Or % of the reference emission	Or ELVc + ELVf	
Manufacture of pharmaceutical products -Table 11		Or % of solvent input	Or ELVc + ELVf	
Conversion of rubber Table 12		% of solvent input	Or ELVc + ELVf	
Surface cleaning with chlorinated solvents Table 13	X			X
Surface cleaning with non chlorinated solvents - Table 13			X	X
Oil extraction Table 14		kg VOC / t product		
Wood preservation Table 15		Or kg VOC / m <sup>3</sup> of wood	Or ELVc + ELVf	

ELVc expressed as total organic carbon or substance / m<sup>3</sup> can only be controlled by the use of **specific monitoring equipment**, described here after.

ELVt for solvent uses, expressed as % of solvent input or as g/unit of activity can be controlled by a **solvent management plan**.

ELVf can be controlled by a **solvent management plan and determination of stack emissions** with a monitoring equipment.

Total emissions from petrol storages and service stations can be estimated by calculation programmes such as TANKS and compared to ELVt. Other sources of estimations are provided here after.

## ***Monitoring techniques of VOC emissions as total organic carbon***

### Flame ionisation detector

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

The measurement cell contains a pair of electrodes and a current is applied between them. If there are ions present in the cell, a 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. As the abundance of ions within the cell depends on the concentration of the gas, FID provides an effective means of measuring the concentrations of VOC.

The absolute measuring sensitivity depends on the material of the combustion nozzle and the detector geometry.

FID does not differentiate between different compounds since it responds to carbon bonds rather than to specific compounds. Thus the result is given as total organic carbon. The response, however, depends on the type of binding 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.

The method involves extraction of a gas sample through a heated line to avoid condensation losses into the FID detector. The FID is calibrated with propane and give a direct reading as part per million per volume propane equivalent VOC which can be converted at standard temperature and pressure (STP) using the mass of carbon in the calibration gas and the molar volume of 22,4 liters at STP.

The FID technique is used in two European standards for VOC monitoring:

- 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.
- 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.

These two standards are being revised and a new standard is planned for release in 2012. They are widely used in Europe.

### Other techniques

Other techniques are Electron Capture detection, catalytic oxidation.

## ***Monitoring techniques of individual VOC substances***

### Sampling and gas chromatography (GC)

The different VOC can be adsorbed on solid adsorbents.

There is no universal sampling sorbent. It must be selected according to the VOCs to be monitored.

Organic polymeric sorbents can be used. They are hydrophobic. This property enables the adsorption of very small concentrations of VOC. Highly volatile compound are hardly adsorbed on this type of resins as well as polar molecules such as ketones and alcohols.

Inorganic sorbent can adsorb polar molecules but also water which is an inconvenient.

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

Thermal desorption or solvent extraction is then used. The VOC concentration is determined by GC and FID analysis or mass spectroscopy.

VOCs can also be absorbed in a liquid media. They can be analysed after separation by GC.

The method for monitoring individual VOC is described in the following European standard:

- EN 13649 of 2002 : Stationary source emissions — Determination of the mass concentration of individual gaseous organic compounds: activated carbon and solvent desorption method

The standard is based on the principle of sampling onto adsorption media followed by desorption and analysis by GC. Several analytical methods can be used. Sampling is a crucial part of the methodology.

NIOSH and OSHA analytical methods are also widely in use in Europe. NIOSH Manual of Analytical Methods is available at <http://www.cdc.gov/niosh/az/a.html>.

### Non dispersive Infrared spectrometry (NDIR)

VOC can absorb Infra red radiation. Each VOC has an electronic finger print or spectrum. This property is used 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.

### Other techniques :

Other techniques which can be used are Fourier Transform Infrared absorption (FTIR), differential optical absorption spectrometry (DOAS), mass spectroscopy.

## Solvent management plan

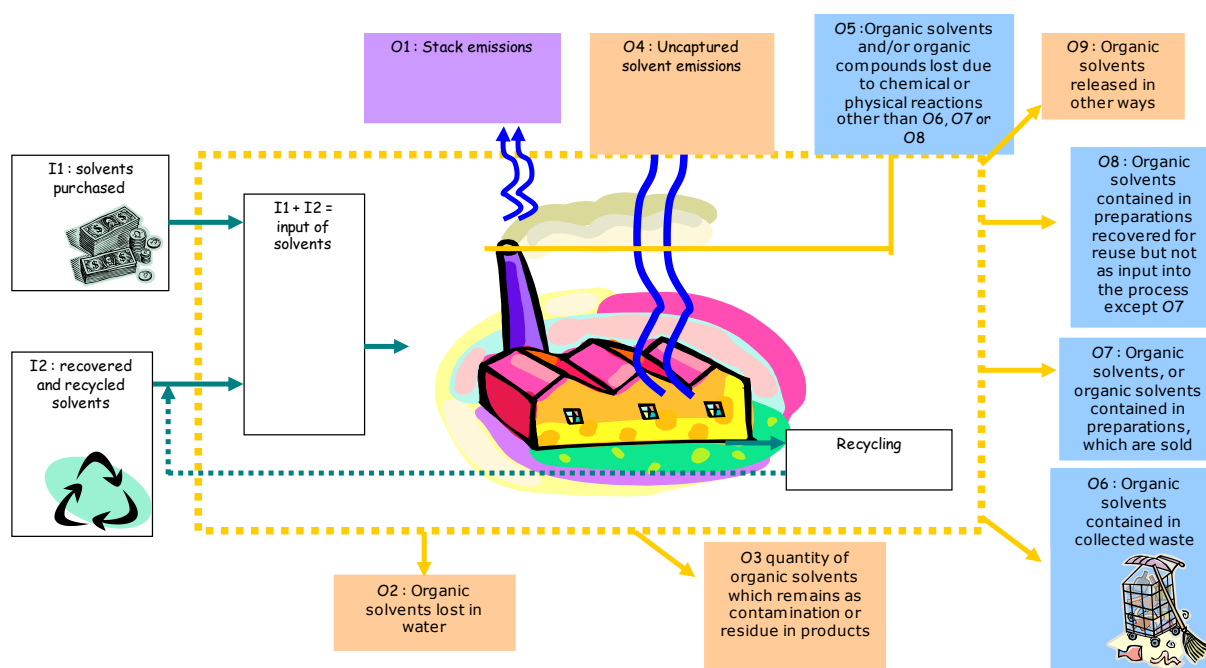
A solvent management plan is a key estimation system to determine the consumptions, uses and emissions of solvents, especially fugitive VOC emissions. It is used to check the compliance of an installation using solvents for which the total VOC ELV applied is expressed in % of solvent input, in a total VOC mass / unit of activity, or for which the fugitive VOC ELV is expressed in % of solvent input.

The solvent management plan consists in estimating solvent inputs and solvent outputs.

Inputs are often easily known.

On contrary, only some outputs can be estimated easily. The solvent mass balance is a tool for estimating VOC emissions based on the following principles.

In order to be equilibrated, the same units have to be used to characterise inputs and outputs. The balance is carried out in mass of solvent or VOC.



Definitions of inputs and outputs to be considered are as follows:

Inputs of organic solvents (I):

I1 The quantity of organic solvents or their quantity in preparations purchased which are used as input into the process in the time frame over which the mass balance is being calculated.

I2 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.)

Outputs of organic solvents (O):

O1 Emissions in waste gases.

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

O3 The quantity of organic solvents which remains as contamination or residue in products output from the process.

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.

O5 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).

O6 Organic solvents contained in collected waste.

O7 Organic solvents, or organic solvents contained in preparations, which are sold or are intended to be sold as a commercially valuable product.

O8 Organic solvents contained in preparations recovered for reuse but not as input into the process, as long as not counted under O7.

O9 Organic solvents released in other ways.

The determination of the solvent consumption and VOC emissions can be done according to equations presented here after:

The consumption of solvent is calculated according to the following equation:

$$C = I1 - O8$$

In annex VI, the thresholds for application of the ELV are based on the consumption of solvents.

Total VOC emissions are defined as follows:

$$E = F + O1$$

Or

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

Total VOC emissions are expressed in mass of VOC.

If O1 has been determined by a monitoring device providing an emission expressed in carbon equivalent, this mass of carbon equivalent must be transformed in mass of VOC taking into account the composition of the waste gas in VOC and the response factors of the monitoring device to the different VOC.

F is the fugitive emission as defined below:

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

or

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

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

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

$$I = I1 + I2$$

The solvent management plan can be done on a regular basis such as an annual basis, 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.

## ***Calculation programmes for estimating NMVOC from petrol storage and service stations***

Emission calculation software is provided by the US EPA. It is available on the following web site <http://www.epa.gov/ttnchie1/ap42/ch07/index.html>

The algorithms developed take into account the different types of storage and their characteristics (tightness of floating roof seals, colour...).

For service stations, the EMEP EEA guidebook<sup>1</sup> or report 1/09 from CONCAWE<sup>2</sup> provides algorithms to estimate VOC emissions according to different situations.

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<sup>1</sup> EMEP EEA Emission Inventory Guidebook – TFEIP – March 2009 – Part b chapter “NFR 1.B.2.a.v - distribution of oil products”

<sup>2</sup> CONCAWE : Air pollutant emission estimation methods for E-PRTR reporting by refineries – 2009