PRINCIPLES OF THE SOLVENT MANAGEMENT PLAN (SMP)

PRACTICAL STUDIES: PRINTING AND PHARMACEUTICAL ACTIVITIES

Nadine Allemand

(CITEPA/TFTEI technical secretariat)

Prepared by: Valérie IMAD and Nadia TAIEB

Assessment and measurement of emissions of volatile organic compounds:
Requirements, monitoring, best available techniques
Integrated environmental permits:
Improvement of permitting procedures in Belarus
International Workshop – Minsk, October 11th and 12th 2019

Solvent management plan (SMP)

I. Definitions

II. How to estimate the different components of the balance

1. Inputs of organic solvents
2. Outputs of organic solvents

III. Examples of a development of a solvent management plan

1. Plant A (printing)
2. Plant B (chemical processes)

Principles of the solvent management plan (SMP)

I. Definitions

Definition of VOC and organic solvent in Directive (2010/75/UE) and Annex VI of the Gothenburg Protocol are the same (dir. 2010/75, chapter I – Article 3. 45 and 3.46; Protocol annex VI, art. 3n and 3o):

1. Volatile organic compounds (VOC)

means any organic compound as well as the fraction of creosote, having at 293,15 K a vapour pressure of 0,01 kPa or more, or having a corresponding volatility under the particular conditions of use.

2. Organic solvent

means any volatile organic compound which is used for any of the following

a) alone or in combination with other agents, and without undergoing a chemical change, to dissolve raw materials, products or waste materials,

b) as a cleaning agent to dissolve contaminants,

c) as a dissolver,

d) as a dispersion medium,

e) as a viscosity adjuster,

f) as a surface tension adjuster,

g) as a plasticiser,

h) as a preservative.

I. Definitions

According to Gothenburg Protocol – Article 1.(11):

3. Volatile organic compounds (VOC)

means, unless otherwise specified, all organic compounds of an anthropogenic nature, other than methane, that are capable of producing photochemical oxidants by reaction with nitrogen oxides in the presence of sunlight

I. Definitions

1. Aim of a solvent management plan

A solvent management plan (SMP) is an adequate tool to determine the solvent consumptions and emissions, especially fugitive VOCs emissions.

In an installation using solvents, the objectives of a SMP are to:

- Verify the compliance of the installation, regarding to VOCs emission limit value (ELV) implemented
- Identify reduction options

If the installation is not in compliance with ELVs (or ELVc and ELVf), an emission reduction plan has to be implemented

I. Definitions

2. Mass balance

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

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

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.

The balance can only 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 estimated. On the contrary, only some outputs can be estimated easily.

I. Definitions

3. Type of Emission Limit Values implemented

- "Waste gases" means the final gaseous discharge containing volatile organic compounds or other pollutants from a stack or abatement equipment into air.
  - In the Protocol, the ELV in waste gases (or stack emissions) is noted ELVc
- "fugitive emissions" means any emissions not in waste gases of volatile organic compounds into air, soil and water as wellas solvents contained in any products, unless otherwise stated. *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*
  - *In the Protocol fugitive ELV is noted ELVf*
- "total emissions" means the sum of fugitive emissions and emissions in waste gases
  - In the Protocol, total emission ELV is noted "Total ELV"

I. Definitions

3. Complete management plan vs. simplified management plan

Example of ELVs in adhesive coating activities :

16. Manufacturing of coatings, varnishes, inks and adhesives:

Table 10
Limit values form manufacturing of coatings, varnishes, inks and adhesives

Activity and threshold	*ELV for VOC (daily for ELVc and yearly for ELVf and total ELV)*	
New and existing installations with solvent consumption between 100 Mg/year–1,000 Mg/year	ELVc = 150 mg C/m^3 ELVf[a] = 5 wt-% or less of the solvent input	→ Complete SMP
	Or total ELV of 5 wt-% or less of the solvent input	→ Simplified SMP
New and existing installations with solvent consumption > 1,000 Mg/year	ELVc = 150 mg C/m^3 ELVf[a] = 3 wt-% or less of the solvent input *Or* total ELV of 3 wt-% or less of the solvent input	

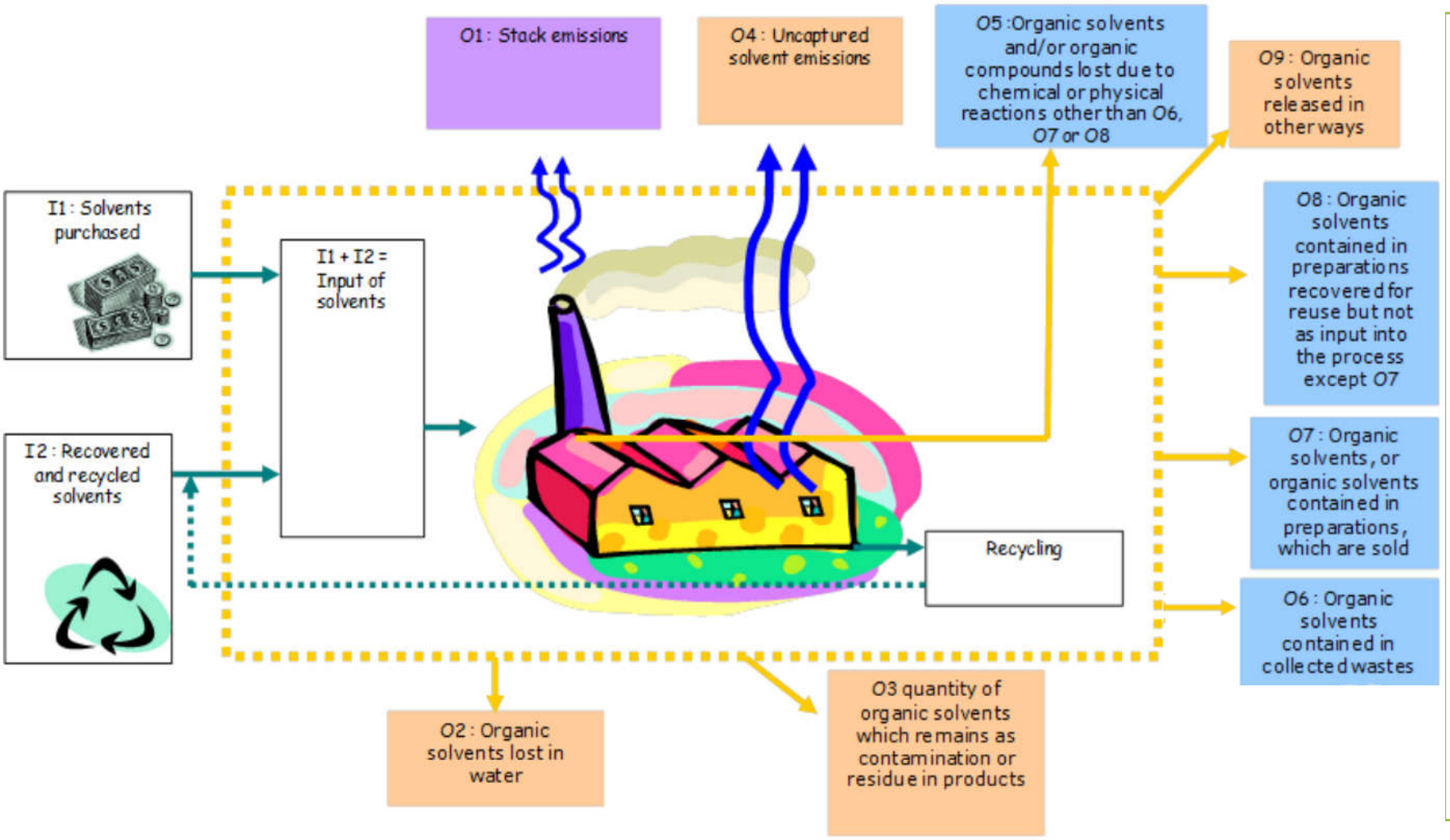
[a] The fugitive limit value does not include solvents sold as part of a preparation in a sealed container.

Extract from Gothenburg Protocol: Annex VI - A - Table 10.

I. Definitions

4. Components of the solvent management plan

Complete management plan



Solvent consumption in mass of VOCs/year
C = I1 - O8

Input of solvents in mass of VOCs/year:
I = I1 + I2

Total VOC emissions in mass of VOCs/year:
E = I1 - O5 - O6 - O7 - O8

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

Extract from "Draft guidelines for estimation and measurement of emissions of volatile organic compounds": Part IV- A - Figure 1.

I. Definitions

4. Components of the solvent management plan

Simplified management plan

Solvent consumption in mass of VOCs/year:

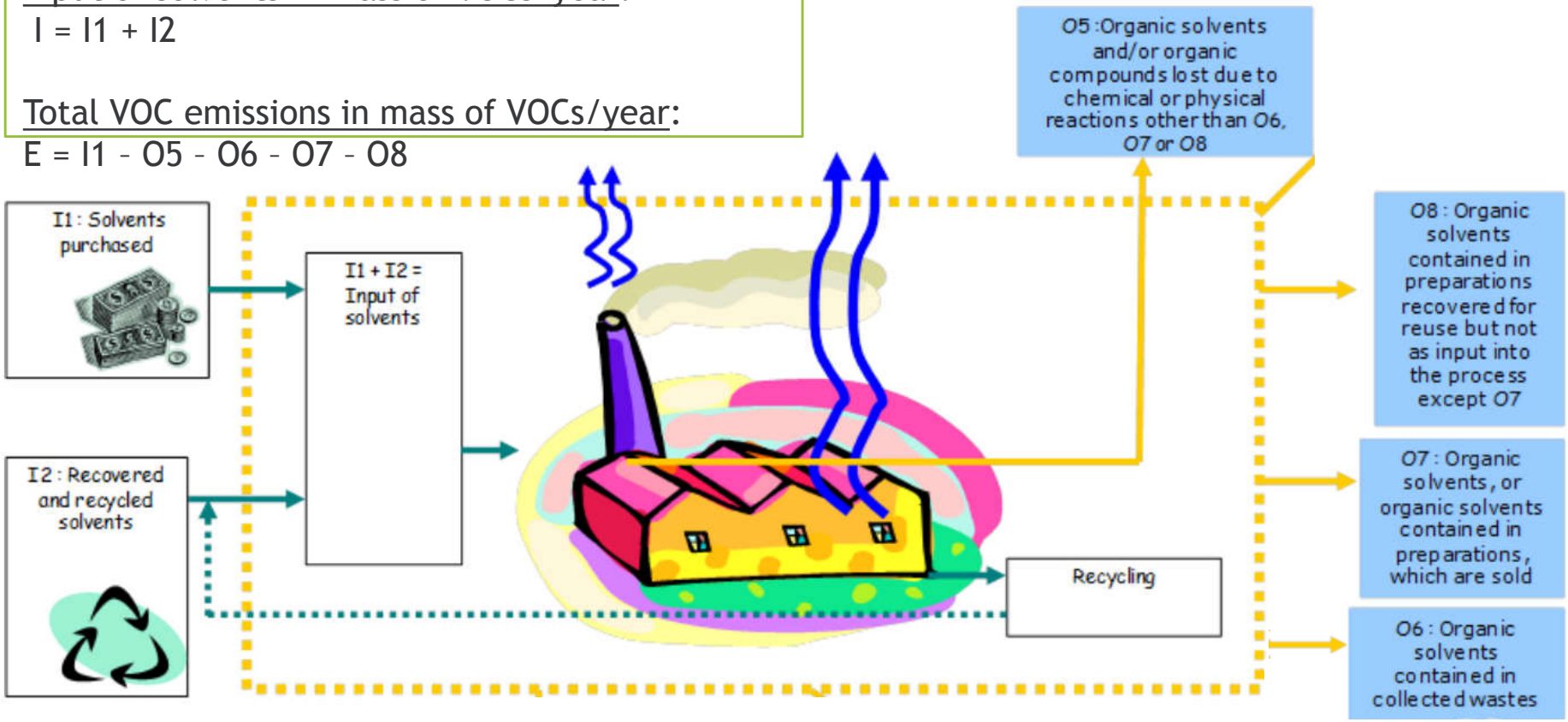
C = I1 – O8

Input of solvents in mass of VOCs/year:

I = I1 + I2

Total VOC emissions in mass of VOCs/year:

E = I1 – O5 – O6 – O7 – O8



II. How to estimate the different components of the balance

1. Inputs of organic solvents

I1: 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.

I1 = Quantity of product used x solvent content

An exhaustive inventory of all preparations containing solvents used in the installation covered by the balance has to be carried out
Quantity used = Quantity bought – stock of year n + stock of year n-1.

Can be obtained from labels and/or safety data sheets of the preparations. Providers of preparations/products may also be a relevant source of information.

Conforme à l'Annexe II du Règlement (CE) No. 1907/2006 (REACH) - France

Security data sheet

SECTION 1: Identification de la substance/du mélange et de la société/ entreprise

1.2 Utilisations pertinentes identifiées de la substance ou du mélange et utilisations non recommandées

Utilisation du produit : Encre d'imprimerie ou Additif
Utilisations déconseillées : Aucune connue.

Historique

Date d'impression : 14.06.2018.
Date d'édition/ Date de révision : 29.03.2018.
Date de publication précédente : Aucune validation antérieure.
Version : 1

SECTION 2: Identification des dangers

2.1 Classement de la substance ou du mélange

Classification selon le règlement 1272/2008/CE [CLP/GHS]

LIQUIDES INFLAMMABLES - Catégorie 3
LÉSIONS OCULAIRES GRAVES/IRRITATION OCULAIRE - Catégorie 2
TOXICITÉ POUR CERTAINS ORGANES CIBLES - EXPOSITION UNIQUE (Effets narcotiques) - Catégorie 3
Consultez la section 11 pour obtenir de l'information plus détaillée sur les effets sur la santé et les symptômes.

2.2 Éléments de l'étiquette

Pictogrammes de danger :

Mention d'avertissement : Attention
Mentions de danger : H226 - Liquide et vapeurs inflammables.
H319 - Provoque une sévère irritation des yeux.
H336 - Peut provoquer somnolence ou des vertiges.

Technical Information Packaging Inks

PROVISOIRE

Version: 03/04/2018

Application	Décolorant pour quadri de la série
Procédé d'impression	• Flexographie
Spécifications	• Extrait Sec: 18,67 +/-2% • Viscosité: 26" DIN4 +/- 5"
Caractéristiques principales	Décolorant à séchage retardé de la série pour les références WB13* contretypes de vos encres WA11*, WA03* et WQ26*
Supports d'impression	• Polyéthylène traité Corona • Polypropylène coextrudé traité Corona
Diluant	Normal: Ethanol 99° Accélérateur: Acétate d'Ethyle Retardateur: Methoxypropanol

Conditions d'emploi

Bien homogénéiser avant emploi.

Stockage

Nous recommandons de stocker les produits à température ambiante et dans l'emballage d'origine non ouvert. Les produits doivent être utilisés dans les 18 mois qui suivent leur date de fabrication à l'exception des encres à base de résine PVB (12 mois), des encres et vernis aqueux, des encres solvant à base de pigments métalliques ou nacrés (6 mois), des encres aqueuses à base de pigment d'aluminium (3 mois) et des encres à base de pigments fluorescents (2 mois).

Les encres diluées doivent être stockées dans des récipients fermés et la viscosité mesurée avant réutilisation. Les produits doivent être correctement homogénéisés avant emploi.

Conditionnement

SECTION 2: Identification des dangers

Conseils de prudence : P403 + P233 - Stocker dans un endroit bien ventilé. Maintenir le récipient fermé de manière étanche.
P280 - Porter des gants protecteurs et une protection oculaire ou faciale.
P305 + P351 - EN CAS DE CONTACT AVEC LES YEUX: Rincer avec précaution à l'eau pendant plusieurs minutes.
P338 - Enlever les lentilles de contact si la victime en porte et si elles peuvent être facilement enlevées. Continuer à rincer.
P210 - Tenir à l'écart des flammes et des surfaces chaudes. Ne pas fumer.
P370 + P378 - En cas d'incendie: Utiliser de la mousse antialcool pour l'extinction.

Éléments d'une étiquette complémentaire : Non applicable.

Ingrédients dangereux : 1-ethoxypropan-2-ol

Annexe XVII - Restrictions applicables à la fabrication, la mise sur le marché et l'utilisation de certaines substances et préparations dangereuses et de certains articles dangereux : Non applicable.

2.3 Autres dangers

PBT : P: Non disponible. B: Non disponible. T: Non disponible.

vPvB : vP: Non disponible. vB: Non disponible.

Autres dangers qui ne donnent pas lieu à une classification

Contient de la nitrocellulose. Les dépôts d'encre nitrocellulosique sèche sont très inflammables.

SECTION 3: Composition/information sur les ingrédients

3.2 Mélanges : Mélange

Nom du produit ou de l'ingrédient	Identificateurs	%	Classification Règlement (CE) no 1272/2008 [CLP]	Type
1-ethoxypropan-2-ol	REACH #: 01-2119462792-32 CAS: 1569-02-4 Indice: 603-177-00-8	≥50 - ≤75	Flam. Liq. 3, H226 Eye Irrit. 2, H319 STOT SE 3, H336	[1]
ethanol	REACH #: 01-2119457610-43 EC: 200-578-6 CAS: 64-17-5 Indice: 603-002-00-5	≥10 - ≤25	Flam. Liq. 2, H225 Eye Irrit. 2, H319	[1]
ethyl acetate	REACH #: 01-2119475103-46 EC: 205-500-4 CAS: 141-78-6 Indice: 607-022-00-5	≤3	Flam. Liq. 2, H225 Eye Irrit. 2, H319 STOT SE 3, H336 EUH066	[1]
titanium chelates	EC: 401-100-0 CAS: 109037-78-7	<2.5	Flam. Liq. 2, H225 Eye Irrit. 2, H319 Aquatic Chronic 2, H411	[1]

Consulter la section 16 pour le texte complet des phrases de danger déclarées ci-dessus.

Aucun autre ingrédient n'est présent qui, à la connaissance actuelle du fournisseur, soit classé et qui contribue à la classification de la substance et qui, par conséquent, exige d'être déclarée dans la présente section.

SECTION 15: Informations sur la réglementation

15.1 Réglementation et législation pour la sécurité, la santé et l'environnement particulières à la substance ou au mélange

UE - Règlement (CE) no 1907/2006 (REACH)

Annexe XIV - Liste des substances soumises à autorisation

Annexe XIV

Aucun des composants n'est répertorié.

Substances extrêmement préoccupantes

Aucun des composants n'est répertorié.

Annexe XVII - Restrictions applicables à la fabrication, la mise sur le marché et l'utilisation de certaines substances et préparations dangereuses et de certains articles dangereux : Non applicable.

VOC content : ~ 81.3 % ~ 713.1 g/L

Inventaire Europe : Tous les composants sont répertoriés ou exclus.

Réglementations nationales

Usage **industriel** : L'information contenue dans cette Fiche de Données de Sécurité ne dégage pas l'utilisateur final de l'évaluation des risques sur le lieu de travail, comme demandée par d'autres législations de santé et de sécurité. Les textes de la réglementation nationale de la santé et sécurité au travail s'adressent à l'utilisation de ce produit au travail.

Code de **la Sécurité Sociale, Art. L 461-1 à L 461-7** : ethyl acetate 84

Surveillance médicale renforcée : Arrêté du 11 Juillet 1977 fixant la liste des travaux nécessitant une surveillance médicale renforcée: non concerné

15.2 Évaluation de la sécurité chimique

Ce produit contient des substances nécessitant encore une évaluation du risque chimique

Application	Décolorant pour quadri de la série
Procédé d'impression	• Flexographie
Spécifications	• Extrait Sec: 18,67 +/-2% • Viscosité: 25" DIN4 +/- 5"
Caractéristiques principales	Décolorant à séchage retardé de la série
Supports d'impression	• Polyéthylène traité Corona • Polypropylène coextrudé traité Corona
Diluant	Normal: Ethanol 99° Accélérateur: Acétate d'Ethyle Retardateur: Methoxypropanol

II. How to estimate the different components of the balance

1. Inputs of organic solvents

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).

“Reused” = recovered on site after a specific internal regeneration

II. How to estimate the different components of the balance

2. Outputs of organic solvents

O1: represents emissions in waste gases.Only stack emissions have to be considered in this group.

Monitoring of VOCs concentrations in waste gases is required to demonstrate compliance with ELVc.

According to measurement technique used (FID), the results expressed in eq. C have to be converted into VOCs.

Correction factor

$$Q_{\text{mesurée}} = Q_{\text{solvant réel}} \times \sum_i \left(P_i \times Mc_i \times \frac{FR_i}{M_i} \right)$$

Qmeasured = amount measured (eq. C).

Qsolvent = amount of solvent.

Pi = proportion of solvent in the effluent (mass %).

Mci = mass of carbon in solvent i (12,01 x number of carbons) (g/mol).

FRi = response factor of solvent i.

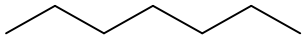
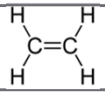
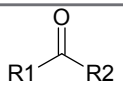
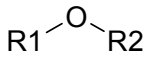
Mi = molar mass of solvent i (g/mol).

II. How to estimate the different components of the balance

2. Outputs of organic solvents

The average response factor of carbon atoms is determined by using a weighted average of the response factors of carbon atoms present in the molecule.

In the absence of response factor transmitted by the provider, it is possible to use standard values:

Type of link	Link scheme	Response factor of one carbon atom
Aliphatic	C-C 	1
Aromatic		1
Alkene	C=C 	0,95
Ketone	C=O 	0
Alcohol	C-OH	0,3
Ether	C-O-C 	0,5
Halogenated (chlorinated)	C-Cl 	1,05
Nitrile	R_2C-NH_2	0,3
Amine	R-NC	0,3

II. How to estimate the different components of the balance

2. Outputs of organic solvents

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 wastewater treatments, or captured, e.g. by adsorption, as long as they are not counted under O6, O7 or O8)

In order to determine the efficiency of the treatment, upstream and downstream concentrations and waste gas flow rates have to be measured

II. How to estimate the different components of the balance

2. Outputs of organic solvents

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

- The determination of the VOCs concentrations in wastewater is useful if an abatement system exists
- The choice of measurement technique depends on solvents used and on their ability to be present in wastewaters (O2 determination requires knowledge of the average concentrations of VOCs and of the wastewater volume)
- 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.

II. How to estimate the different components of the balance

2. Outputs of organic solvents

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.

This output is determined at the end by the solvent balance by a difference between known inputs and outputs.

O6: are organic solvents contained in collected waste.

Solvents in waste come from :

- mixtures of solvents used,
- solvents in residues of products,
- residues of solvents in containers, etc…

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.

II. How to estimate the different components of the balance

2. Outputs of organic solvents

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

This is a fugitive output. Some chemical analysis may be required.

O7: are organic solvents, or organic solvents contained in preparations, which are sold or are intended to be sold as commercially valuable products.

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

Solvents recovered for external regeneration as example

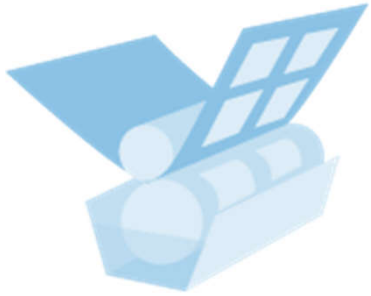
O9: are organic solvents released in other ways.

Practical study: How to develop a SMP

Printing and chemical processes

Example 1

“Plant A”: Printing activity



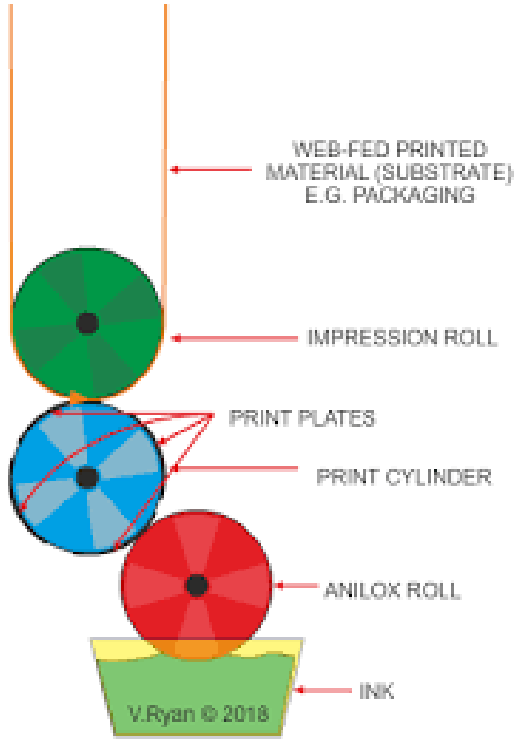
III. Example 1

1. Plant A: plant information and data

The installation named « Plant A » has two printing lines « Line 1 » and « Line 2 ». The printing technique used is flexography. Plastic surfaces are printed.

Reminder:

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



III. Example 1

17. Printing activities (flexography, heat-set web offset, publication rotogravure, etc.):

Table 11
Limit values for printing activities

Activity and threshold	*ELV for VOC (daily for ELVc and yearly for ELVf and total ELV)*
Heat-set offset (solvent consumption 15 Mg/year–25 Mg/year)	ELVc = 100 mg C/m^3 ELVf = 30 wt-% or less of the solvent input[a]
Packaging rotogravure and flexography (solvent consumption 15 Mg/year–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/kg of solid input
Packaging rotogravure and flexography (solvent consumption 25 Mg/year–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/kg of solid input

The installation has to comply with ELVc and ELVf then a complete SMP is necessary.

Extract from Gothenburg Protocol: Annex VI - A - Table 11

III. Example 1

The annual quantities of products purchased are as follows:

Line	Ink	Quantity of product purchased (kg/year)
Line 1	Flexo APF Red	1 380
Line 2	Quadri SP Blue	670

Line	Dilution and cleaning solvents	Quantity of product purchased (kg/year)
Line 1	Ethoxy propanol ($CH_3CH_2OCH_2CH(OH)CH_3$)	4 372
Line 2	Ethanol (CH_3CH_2OH)	4 500

The following information is available:

- No variation of stocks has been observed for inks. For ethanol, a destocking of 500 kg/year occured.
- Inks do not contain aqueous phase.
- 115,7 kg of inks per year are lost as wastes and are recovered by an external company. Analyses done in ink sludges reveal that the dry extract is 39,5 %.
- 421 kg per year of ethanol are regenerated externally. Analyses done reveal that VOC content is 95 % (measure done specifically on ethanol).

III. Example 1

VOC contents of inks are provided by the ink manufacturer:

	VOC content (%m)		
Flexo APF Red	69%	Ethanol (CH_3CH_2OH)	45%
		Ethyl acetate ($C_4H_8O_2$)	24%
Quadri SP Blue	68%	Ethanol (CH_3CH_2OH)	44%
		Ethyl acetate ($C_4H_8O_2$)	24%

III. Example 1

What are the quantity of solvent input and the consumption of solvent?

Inputs of solvents:

Line	Inks	Quantity of product purchased (kg/year)	Stock change (stock of year n - stock of year n-1) in kg	% VOC (manufacturer data)	Solvent in inks purchased (I1)
Line 1	Flexo APF Red	1 380	0	69%	952
Line 2	Quadri SP Blue	670	0	68%	456
	Total	**2 050**			**1 408**

Line	Dilution and cleaning solvents	Quantity of product purchased (kg/year)	Stock change (stock of year n - stock of year n-1) in kg	% VOC (manufacturer data)	Solvent purchased (I1)
Line 1	Ethoxy propanol	4 372	0	100%	4 372
Line 2	Ethanol	4 500	+ 500 kg	100%	5 000
	Total	**8 872**			**9 372**

Difference in stocks must be taken into account to determine the quantity of purchased solvents.

I1 = 1 408 + 9 372 = 10 780 kg of solvents.

I2 = 0 kg.

Input of solvents I = I1 + I2 = 10 780 kg of solvents.

III. Example 1

What are the quantity of solvent input and the consumption of solvent?

O8: 421 kg of ethanol are recovered and regenerated externally. From analyses done, the VOC content is 95 % (measure done specifically on ethanol).

O8 = 421 x 95% = **400 kg.**

Consumption of solvent: I1 - O8 = 10 780 – 400 = **10 380 kg**.

III. Example 1

What is the quantity of solventS in waste ?

O6: 115.7 kg of inks are lost as waste and recovered by an external company.

From analyses done in ink sludges, the dry extract is 39.5 %.

The VOC content is : 100% - 39.5% = **60.5 %** (100% - % dry extract = VOC% (if no aqueous phase).

The amount of solvents lost as waste (O6) is 115.7 x 60.5% = **70 kg**.

III. Example 1

Plant information and data

Each line is equipped with a capture system of waste gases which are released in the atmosphere through a stack. Measurement of VOCs concentrations is carried out in each stack, one time per year.

Line 1	Concentration mg C / Nm^3	Flow rate Nm^3 / h
Mesures	74	5 000

Line 2	Concentration mg C / Nm^3	Flow rate Nm^3 / h
Mesures	187	5 000

Products used	Quantity of product used during the measurement (kg/h)
Flexo APF Red	1.9
Ethoxy propanol (dilution)	1.2

Products used	Quantity of product used during the measurement (kg/h)
Quadri SP Bleu	2.3
Ethanol	1.2

FID (Flame ionization detector) response factor, provided by the manufacturer, is given for Ethanol (0.82), Ethyl acetate (0.70) and Ethoxy propanol (0.76).

Molar mass: M_C = 12 g/mol, M_O = 16 g/mol and M_H = 1 g/mol.

III. Example 1

Determination of O1

Concentrations expressed in eq.C have to be converted in VOCs:

Correction factor

$$Q_{measured} = Q_{solvent} \times \boxed{\sum_i \left(P_i \times Mc_i \times \frac{FR_i}{M_i} \right)}$$

Qmeasured = amount measured (eq. C).

Qsolvent = amount of solvent.

Pi = proportion of solvent in the effluent (mass %).

Mci = mass of carbon in solvent i (12,01 x number of carbons) (g/mol).

FRi = response factor of solvent i.

Mi = molar mass of solvent i (g/mol).

III. Example 1

Determination of O1

Line 1:

Products	Quantity of product used during the measurement (kg/h)	VOC content (%)			VOC quantity (kg)
Flexo APF Red	1.9	69%	45%	Ethanol	0.86
			24%	Ethyl acetate	0.46
Ethoxy propanol	1.2	100%	100%	Ethoxy propanol	1.20
TOTAL					2.51

Ethanol	34.1 %
Ethyl acetate	18.2 %
Ethoxy propanol	47.8 %

III. Example 1

Determination of O1

Line 1:

Line 1	P%	mc	FR	M	Correction factor
Ethanol	34.1 %	24	0.82	46	0.42
Ethyl Acetate	18.2 %	48	0.70	88	
Ethoxy propanol	47.8 %	60	0.76	104	

Qsolvent = Qmeasured (eq. C) / correction factor.

Qsolvent = 74 / 0.42 = 174.3 mg solvents/ Nm^3.

III. Example 1

Determination of O1

Line 2:

Products used	Quantity of product used during the measurement (kg/h)	VOC content (%)			VOC quantity (kg)
Quadri SP Bleu	2.3	68%	44%	Ethanol	1.01
			24%	Ethyl acetate	0.55
Ethanol	1.2	100%	100%	Ethanol	1.20
TOTAL					2.76

Ethanol	80.0 %
Ethyl acetate	20.0 %

III. Example 1

Determination of O1

Line 2:

Line 1	P%	mc	FR	M	Correction factor
Ethanol	80.0 %	24	0.82	46	0.42
Ethyl Acetate	20.0 %	48	0.70	88	

Qsolvent = Qmeasured (eq. C) / correction factor

Qsolvent = 187 / 0.42 = 446.7 mg solvents / Nm^3

III. Example 1

Determination of O1

Line 1	Concentration (mg C/Nm^3)	Corrective ratio	Concentration (mg solvent / Nm^3)	Flow rate (Nm^3/h)	Mass flow (kg solvent/h)
Measures	74	0.42	174.3	5 000	0.87

Flow of solvent used during measures: 2.51 kg/h.

The proportion of stack emissions: 0.87/2.51 = 34.7%.

Line 2	Concentration (mg C/Nm^3)	Corrective ratio	Concentration (mg solvent / Nm^3)	Flow rate (Nm^3/h)	Mass flow (kg solvent/h)
Measures	187	0,42	446.7	5 000	2.23

Flow of solvent used during measures: 2.76 kg/h.

The proportion of stack emissions: 2.23/2.76 = 80.8%.

III. Example 1

Calculation of O1:

Line 1	Solvent purchased I1 (in kg)	Stack emissions O1 (in kg)
INK (solvent from inks)		34.7% x 5 324
Flexo APF Red	952	
SOLVENT		
Ethoxy propanol	4 372	
TOTAL	**5 324**	**1 847**

Line 2	Solvent purchased I1 (in kg)	Stack emissions O1 (in kg)
INK (solvent from inks)		80.8% x 5 456
Quadri SP Blue	456	
SOLVENT		
Ethanol	5 000	
TOTAL	**5 456**	**4 408**

O1 Total: 1847 + 4408 = 6255 kg

III. Example 1

Solvent balance is as follows:

inputs/outputs	Quantities of solvent
I1	10 780 kg
O1	6 255 kg
O6	70 kg
O8	400 kg
Fugitive emissions	I1-O1-O6-O8 = 4 055 kg
% fugitive emissions/solvent input	*37.6%*

III. Example 1

SMP finalisation:

ELVc: 75 mg C/Nm^3 and ELVf: 25% of solvent input.

Fugitive emissions are 37.6% of solvent imput

Fugitive emissions are higher than the ELVf (25% of solvent input)

and

Concentration measured in waste gases of line 2 (187 mg C/Nm^3) is higher than the ELVc.

In conclusion, Plant A is not in compliance with ELVc and ELVf.

The operator has to initiate an emission reduction plan.

Example 2

“Plant B”: pharmaceutical activity

III. Example 2

2. Plant B: plant information and data

Production of active pharmaceutical ingredients.

Use of solvents, source of VOCs emissions.

Products containing VOCs used can be identified with safety data sheets.

There are two types of products:

- Pure solvents,
- Solvent based solutions.

III. Example 2

2. Plant B: Characteristics of the plant

The plant is equipped with an incinerator burning liquid solvent wastes and waste gases containing solvents

- Numerous reactors (Batch process) – All vents are collected to the incinerator
- Storage of used solvents (STOCKS): vents of storages are collected to the incinerator
- Wastewater treatment plant: waste gases are collected to the incinerator

The incinerator is powered by waste gases containing VOCs coming from the VOCs emissions capture system (multiple buildings and evaporation of storages “STOCK”), liquid effluents of storages “STOCK” and waste gases from the wastewater treatment plant installed onsite

III. Example 2

18. Manufacturing of pharmaceutical products:

Table 12
Limit values for manufacturing of pharmaceutical products

Activity and threshold	*ELV for VOC (daily for ELVc and yearly for ELVf and total ELV)*
New installations (solvent consumption > 50 Mg/year)	ELVc = 20 mg C/m^3 [a,b] ELVf = 5 wt-% or less of the solvent input[b]
Existing installations (solvent consumption > 50 Mg/year)	ELVc = 20 mg C/m^3 [a,c] ELVf = 15 wt-% or less of the solvent input[c]

[a] If techniques are used which allow reuse of recovered solvents, the limit value shall be 150 mg C/m^3.
[b] A total limit value of 5% of solvent input may be applied instead of applying ELVc and ELVf.
[c] A total limit value of 15% of solvent input may be applied instead of applying ELVc and ELVf.

The installation has to comply with a total value then a simplified SMP is necessary.

Extract from Gothenburg Protocol: Annex VI - A - Table 12

III. Example 2

I1: quantity of organic solvents, pure solvents or in preparations purchased

The quantity of solvents purchased (I1) has been calculated from quantities of products purchased (71 different solvents used), stocks on 31/12/2017 and 31/12/2018 and VOC content in the solvent based solutions.

Quantity of products purchased (tons) (no solvents)	14 095
Quantity of pure solvents purchased (tons)	9 471
Quantity of solvents in solution (tons)	52
I1 - Quantity of VOCs purchased (tons)	**9 523**

III. Example 2

I2: quantity of organic solvents or their quantity in preparations recovered or reused into the process

Acetone and dichloromethane are distilled and reused on site.

Number of acetone batches	173
Quantity of acetone per batch (tons)	10.67
Quantity of acetone reused per year (tons)	**1 846**
Number of dichloromethane batches	173
Quantity of dichloromethane per batch (tons)	3.75
Quantity of dichloromethane reused per year (tons)	**650**
I2 – Quantity of VOCs reused in the process (tons)	**2 496**

III. Example 2

O5: organic solvents and/or organic compounds lost due to chemical or physical reactions

A measurement campaign has been carried out in order to obtain the incinerator efficiency

The upstream and downstream concentrations of the incinerator, obtained in eq. C have been converted in VOC.

The solvents used during the measurement campaign were not monitored precisely due to the multiple sources of emissions (collection of all emissions of batch reactors)

The correction factor is estimated from the 10 first VOCs associated to the largest amounts of solvents purchased and its value is 0,41

III. Example 2

O5: organic solvents and/or organic compounds lost due to chemical or physical reactions

Correction factor calculation:

		Correction factor	Proportion	Molar mass (g/mol)	Carbon mass (g/mol)	Response factor
VOC	I1					
ACETONE	1 766 058	0,087	21,0%	58	36	0.67
METHANOL	1 668 230	0.023	19.8%	32	12	0.30
TOLUENE	1 106 520	0.119	13.1%	92	84	1.00
PROPANOL	1 096 231	0.060	13.0%	60	36	0.77
METHYLENE CHLORiDE	724 063	0.013	8.6%	85	12	1.05
ETHYL ALCOHOL	665 223	0.027	7.9%	46	24	0.65
ACETONITRILE	487 511	0.013	5.8%	41	12	0.75
TETRAHYDROFURAN	330 968	0.024	3.9%	72	48	0.91
METHYL TERT-BUTYL ETHER	313 851	0.025	3.7%	88	60	0.90
METHYL ETHYL KETONE	266 818	0.015	3.2%	72	48	0.75
SUM OF CORRECTION FACTORS		0.406				

III. Example 2

O5: organic solvents and/or organic compounds lost due to chemical or physical reactions

O5 (VOCs collector) = gas volume sent from the VOCs collected from the reactors and storage vents to the incinerator (m^3) x VOCs concentrations measured upstream (mg/m^3) x incinerator efficiency (%).

O5 (water treatment) = gas volume sent from the water treatment plant to the incinerator (m^3) x VOCs concentrations measured upstream (mg/m^3) x incinerator efficiency (%).

O5 (STOCK) = quantity of liquid wastes sent to incinerator (tons/year) x VOC concentration in liquid wastes (%) x incinerator efficiency (%).

III. Example 2

O5: organic solvents and/or organic compouds lost due to chemical or physical reactions

Results	
VOCs concentration measured upstream (mg eq C/m^3) – VOCs collector	31 603
Corrective factor (eq C/ VOC)	0.41
VOCs concentration measured upstream (mg VOC/m^3) – VOCs collector	77 839
Gas volume sent from the VOCs collector to the incinerator (m^3/year)	3 457 688
Quantity of VOCs sent to the incinerator (tons/year) - VOCs collector	269
VOCs concentration measured upstream (mg eq. C/m^3) – wasre water treatment	497
Corrective factor (eq. C/ VOC)	0.41
VOCs concentration measured upstream (mg VOC/m3) – wasre water treatment	1 224
Gas volume sent from the water treatment to the incinerator (m^3/year)	6 395 561
Quantity of VOCs sent to the incinerator (tons/year) – water treatment	7.8

See end of table on the following slide

III. Example 2

O5: organic solvents and/or organic compounds lost due to chemical or physical reactions

Following data

Quantity of liquid « STOCK » (tons/year)	5 018
VOC content of liquid « STOCK » (%)	91,30%
Amount of VOCs from « STOCK » sent to the incinerator (tons/year)	4 582
Total quantity of VOCs sent to the incinerator (tons/year) (from « STOCK », waste water treatment and VOCs collector)	4 859

III. Example 2

O5: organic solvents and/or organic compouds lost due to chemical or physical reactions

VOCs from collector, wastewater treatment plant and STOCK, upstream the incinerator (kg VOC/h)	42.88
VOCs downstream the incinerator (kg VOC/h)	0.214
Incinerator efficiency (%)	99.5%
Total quantity of VOCs sent to the incinerator (tons/year) (t)	4 859
O5 – Quantity of VOC incinerated by the incinerator (tons)	4 834

III. Example 2

O6: organic solvents contained in collected waste.

Waste quantities come from safety data sheets. VOC contents are estimated using the formula following: VOC content (%) = 100% - sum of contents (water and other components)

	Quantity of waste (tons)	Average water content (%)	Average other components content (%)*	Quantity of VOC (tons)	Average VOC content (%)
Non-halogenated solvents	1 588	11.9%	0.20%	1 396	87.9%
Chlorinated solvents	2 277	11.9%	3.30%	1 932	84.8%
Chlorinated acid solvents	136	13.6%	2.40%	114	84.0%
Chlorinated solvents (>10%)	95	0.0%	-	75	79.1%
Water + acid solvents (ph<8)	270	76.1%	5.52%	50	18.3%
Water + base solvents (ph>8)	1 034	72.0%	1.00%	279	27.0%
Aqueous phase SOTA	148	77.6%	0.50%	32	21.9%
Fluorinated Iodized solvent	62	36.9%	0.00%	39	63.1%

O6 : solvent in wastes: 3918 tons

**Fluor, sodium, bromine, iodine, potassium, phosphorus and soufre content*

III. Example 2

O8: organic solvents contained in preparations recovered for reuse but not as input into the process.

Acetone and isopropyl alcohol are recovered and regenerated externally. A sampling is done at each output of soiled solvent and acetone/isopropyl alcohol content is systematically determined

Quantity of soiled acetone recovered externally (tons)	48.3
Average acetone content (%)	99.8%
Quantity of soiled isopropyl alcohol recovered externally (tons)	538
Average isopropyl alcohol (%)	93.4%
O8 – Quantity of solvents recovered externally (tons)	**551**

III. Example 2

SMP final

Inputs and outputs	Quantity of VOCs (tons)
I1 – Solvents purchased	9 523
I2 – Recovered and recycled solvents	2 496
O5 – Solvents incinerated by the incinerator	4 834
O6 – Solvents contained in waste	3 918
O7 – Solvents which are sold	-
O8 – Solvents regenerated externally	551
Total emissions E total = I1 – O5 – O6 – O7 – O8	220
Solvents consumption C = I1 – O8	8 972
Solvents input I = I1 + I2	12 019
%total emissions compared to the quantity of VOC input	1.83%

Total emissions compared to solvent input are 1.83% (< 5%).

Plant B is in compliance with the ELV.

Thank you very much for your attention! Questions?

Nadine Allemand
TFTEI Technical Secretariat

Definitions

Total emissions: means the sum of fugitive emissions and emissions in waste gases. According to Article 57(3) of Directive 2010/75/EU.

Fugitive emissions: means any emissions not in waste gases of volatile organic compounds into air, soil and water as well as solvents contained in any products, unless otherwise stated in Part 2 of Annex VI. According to Article 57(3) of Directive 2010/75/EU.

Reminder: according to Annex VII (part 7) of Directive 2010/75/EU, fugitive emissions (O4) are defined in the SMP as being « uncaptured emissions of organic solvents to air. This includes the general ventilation of rooms, where air is released to the outside environnement via windows, doors, vents and similar openings ». Emissions from air treatment in offices (Heating, Ventilation and Air-Conditioning (HVAC), air handling unit) are explicitly fugitive emissions, definied in O4.

Definitions

Emission in waste gases: means the final gaseous discharge containing volatile organic compounds or other pollutants from a stack or abatement equipment into air.

The concept of stack has been explained in the AFNOR guide (FD X43-319 novembre 2010): « any emissions released into the atmopshere through any circular pipe or not, the diameter of which is lower then the length. Emissions in waste gases are also emissions whose flow rate is technically and reasonably continuous* measurable ».

There must be a sufficiently stable flow rate, that exclude storage breathing vents or equipements considered as fugitive emissions points.

** The concept of continuous measurement contrats with a ponctual measure for fugitive emissions. It is linked to the fact of having a sufficiently stable flow rate.*

Nature of emissions depending on the emissaries, descending order of importance in terms of VOCs flow

Emissaries	Nature of emissions	Comments
Output of absorption culumn (scrubber) or absorption by carbon, cryocondensation or other techniques.	In waste gases	Output of an abatement reduction equipment
Stack at the incinerator output, incinerator	In waste gases	Output of an impact reduction equipment
Extraction vent of a process equipment as a laminating, granulation, reactors	In waste gases	Measurable and channeled flow rate
Output vent of vacuum pump	In waste gases	Measurable and channeled flow rate
Collective protective equipment receiving VOCs (ponctual extraction, flow cabin, gloves box extraction)	In waste gases	Presence of VOCs, measurable and flow rate

Nature of emissions depending on the emissaries, descending order of importance in terms of VOCs flow

Emissaries	Nature of emissions	Comments
Flange leakage, shaft sealing pump	Fugitive	Continuously non-measurable flow rate
Breathing vent of process equipments as mixer, setup recipe	Fugitive	Continuously non-measurable flow rate
Storage tank breathing or road tanker	Fugitive	Continuously non-measurable flow rate
Heating, Ventilation and Air-Conditioning (HVAC), sanitation ventilation	Fugitive	In O4 definition
Aqueous effluent treatment plant	Fugitive	Exept when overturning and treatments of emissions reservoirs