Measurement of VOC emission from stacks of installations – Part 2 Measurement of Total Carbon and Individual Organic Substances

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IED Art. 61 and Annex VII Part 8 No 3 and 4: Compliance with emission limit values:

- **For all other cases:**

  compliance shall be verified on the basis of the **total mass of organic carbon** emitted unless otherwise specified in Part 2. 4.
- Gas volumes may be added to the waste gas for cooling or dilution purposes where technically justified but shall not be considered when determining the mass concentration of the pollutant in the waste gas

Need for measurement total organic carbon

Chapter V IED Annex VII Part 2:

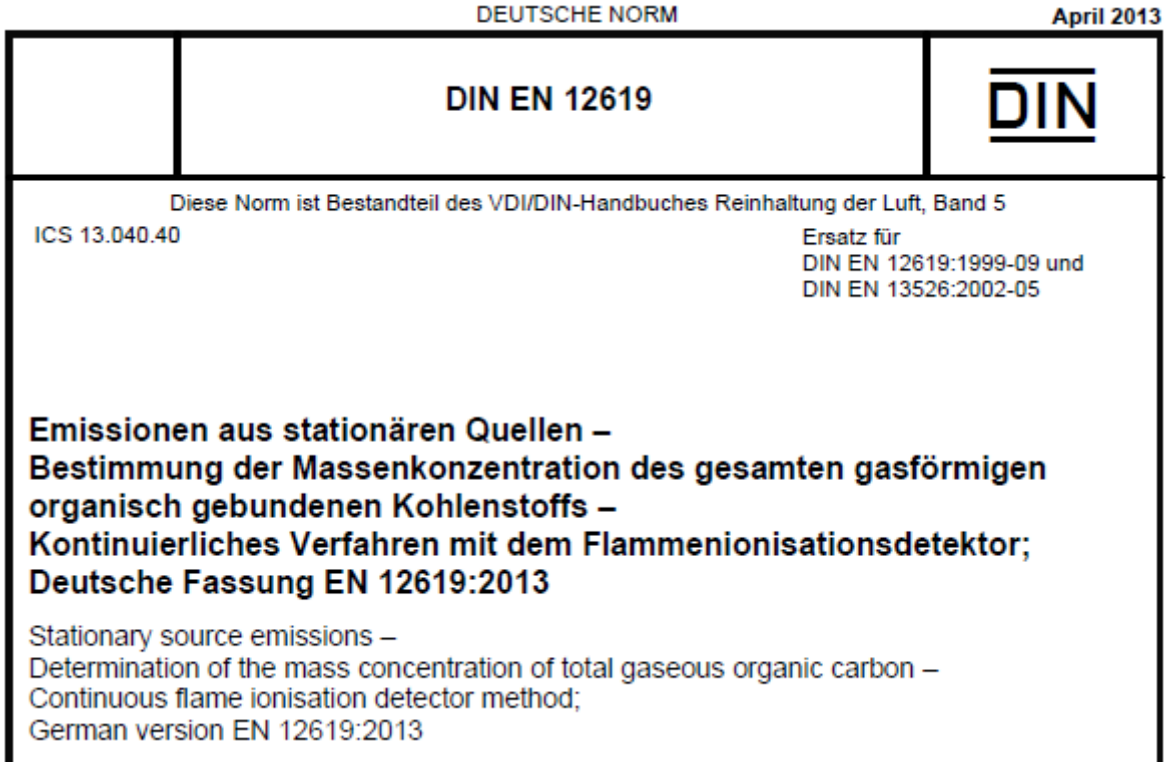
Emission limit values of stack outlets referred as “total carbon” mass concentrations

Petrol Stage I Directive: Annex II:

The mean concentration of vapours in the exhaust from the vapour recovery — unit corrected for dilution during treatment — must not exceed 35 g/normal cubic metre (Nm^3) for any one hour

-> ELV for “vapours” = complex mixture of hydrocarbons -> total emission limit values over all organic vapours

Monitoring: Measurement of volatile organic compounds with a flame ionization detector (FID) – DIN EN12619



DEUTSCHE NORM April 2013

DIN EN 12619

DIN

Diese Norm ist Bestandteil des VDI/DIN-Handbuches Reinhaltung der Luft, Band 5

ICS 13.040.40

Ersatz für
DIN EN 12619:1999-09 und
DIN EN 13526:2002-05

**Emissionen aus stationären Quellen –
Bestimmung der Massenkonzentration des gesamten gasförmigen organisch gebundenen Kohlenstoffs –
Kontinuierliches Verfahren mit dem Flammenionisationsdetektor;
Deutsche Fassung EN 12619:2013**

Stationary source emissions –
Determination of the mass concentration of total gaseous organic carbon –
Continuous flame ionisation detector method;
German version EN 12619:2013

Monitoring: Measurement of volatile organic compounds with a flame ionization detector (FID) – DIN EN12619

Measuring principle: Chemi-

Ionization of organic

compounds in a H_2 flame

Measured signal is approximately proportional to the number of bounded Carbon atoms in sample gas

Signal = r * C_c

Application only of **authorized approved measuring instruments** for emission measurements!

Proportionality factor **r = Response factor** depending from

- Type of chemical bond and bonding partners of Carbon atoms

- Type of instrument and operating conditions

Organic compounds with hetero atoms e.g. N, O, S, Cl, response generally with a lower sensitivity.

Carbon monoxide and Carbon dioxide are not measured

Mass concentration as an **equivalent of Propane:**

$$\mathbf{C_{cp}\ [mg\ C/Nm^3] = 1{,}608 * C_{VP}[ppm]}$$

Mass concentration as **total Carbon**:

$$\mathbf{C_{CS}\ [mg\ C/Nm^3] = C_{cp}\ [mg\ C/Nm^3]/r_s = 1{,}608 * C_{VP}\ [ppm]/r_s}$$

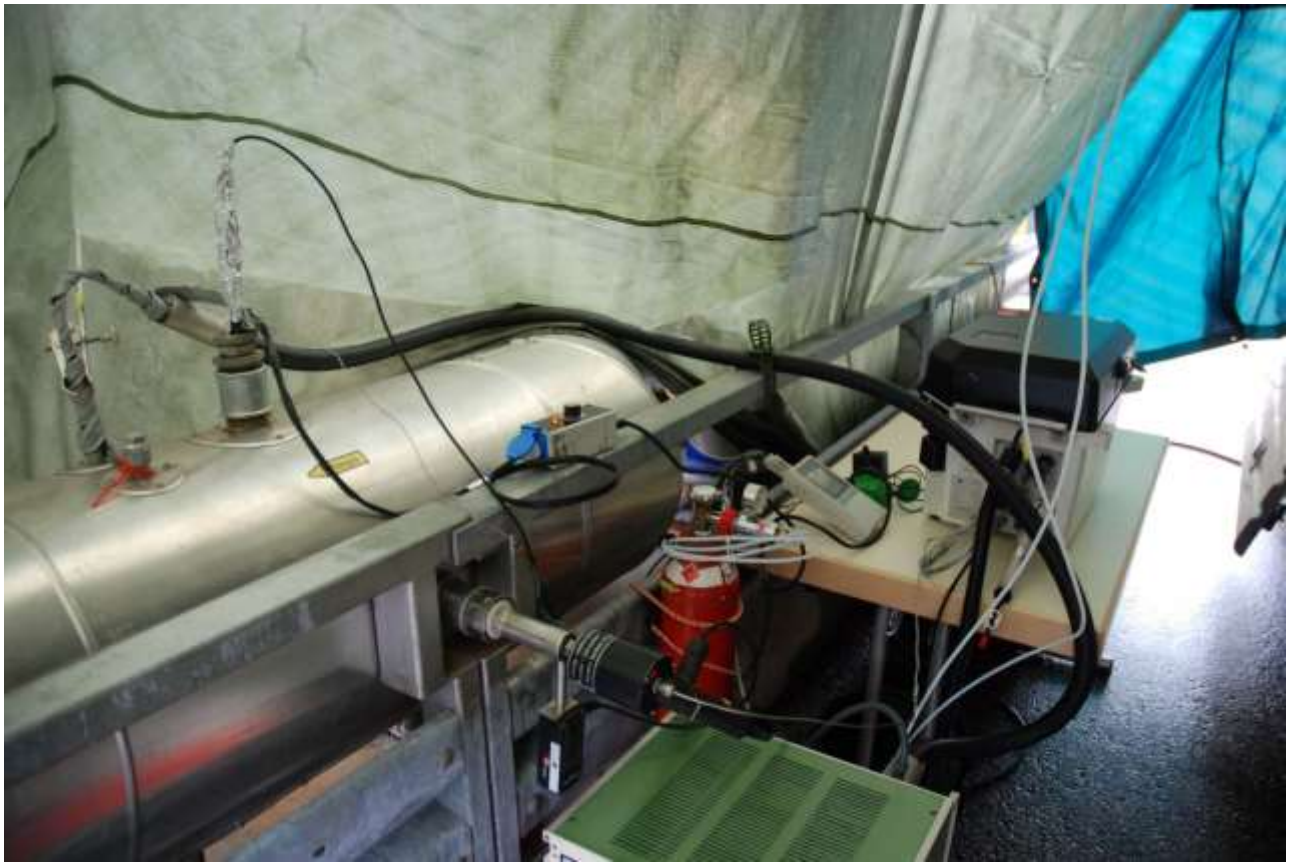
Measurements with FID

- Equipment with a filter for separation of particles: -> protection against occlusion of burner

Measurements with FID

- Condensations after filter have to be avoided alternatively by:
  - completely heated tube until gas inlet of measurement instrument: for hot gases: Temperatures at coldest site minimum 20 °C > waste gas temperature and < 200 °C
  - appropriate device for dynamic dilution

Heated sampling line
(Suction probe covered by Alu foil)



Heated sampling line to FID and humidity sensor because conversion to dry gas is needed

Measurements with FID

Minimum requirements to a FID (DIN EN12619):

- Lowest measuring range: 0 – 50 mg/m^3, 150 or 500 mg/m^3
- Detection limit: 5% of emission limit value

- Response time (time range between escalating concentration of total C and point of time, where the measurement signal of measurement instrument reaches 90 % of final value): < 1 minute

To check measurement device: control gas from probe is extracted and from this time point the response time (= idle time + rise time) is determined by stop watch

<u>For quality assurance:</u>

- **On measurement day control of tightness: sample inlet is closed for a short time -> control of sample pressure display. Several checks of measurement instrument characteristic curve by addition of zero-gas and control-gas (propane)**
- **Regular check of pressure situation and throughput of sample pump**

Minimum requirements to FID (from **DIN EN12619**):

- Linearity: acceptable deviation: 5% of emission limit value
- Combustion air (air to burn of the fuel gas): TOC content ≤ 1%
- Test gas to control of measured value display:
  propane as calibration substance

Conversion of units (C eq in VOC)

Example:

In exhaust gas as volatile organic compound excluding acetone

Received signal: 54 ppm; Calibration on propane; response factor of acetone: 0,77

C_{Aceton} [mg C/Nm^3] = 1,608 * 54 ppm/0,77 = 112,7 mg C/m^3

Conversion to C_{Aceton} [mg/Nm^3]; molecular weight acetone (C_3H_6O) = 58; ration Carbon/molecular weight f = 3* 12/58 = 0,62

C_{Aceton} [mg/Nm^3] = C_{Aceton} [mg C/Nm^3] / f = 182 mg/Nm^3

Example:

Measurement result of FID**: 15 mg C/m³ (including response factor)**

Pollutant in waste gas: Ethanol

Carbon atoms in C2 H6 O: 2

Molar weight of 2 C atoms: 2x 12.011

Molar weight of 6 H atoms: 6x 1.008

Molar weight of O atom: (1x 15.999)

=> Mass ratio C (24.022) to total weight of molecule VOC (46.069): 1:1.92 (C:VOC)

Result of measurement volume flow: 15.000 m³/h; operation hours: 2100 h/y

=> 15 000 m^3/h x 0.015 g C/m^3 x 2100 h/y = 472 500 g C/y

Conversion g total C in kg VOC in waste gas (O 1)

=> 472 500 g C/y x 1.92 (conversion factor) = 907 200 g VOC/y = 907 kg/y

Example 2 Coating company, a mixture of Toluene, Ethanol und Ethyl acetate is in the waste gas in a temporal constant mixture ratio

Known quantities in waste gas

Substance	Response factor r_i	Molar mass [g/mol]	Ration on total weight x_i	Number of Carbon atoms in molecule k_i
Toluene	1.08	92.14	0.12	7
Ethanol	0.76	46.07	0.19	2
Ethyl acetate	0.75	88.11	0.69	4

Calculation of the Carbon mass weight ratio y_i:

$y_i = (x_i * k_i)/\Sigma(x_i * k_i)$

From this follows for the individual substances:

yToluene	=	0.21 = (0.12*7)/(0.12*7 + 0.19*2 + 0.69*4)
yEthanol	=	0.10
yEthyl acetate	=	0.69

Response factor of solvent mixture:

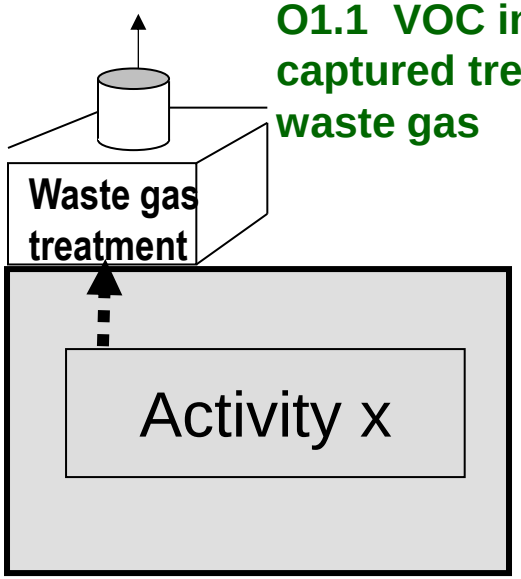
$R_{ges} = \Sigma(y_i\ r_i) = 0.21*1.08 + 0.10*0.76 + 0.69*0.75 = 0.82$

- Therefore a signal of **95.1 ppm** results a **mass concentration of 153 mg C/Nm³** as **Propane equivalent**.
- From this following emission mass concentration of the total of volatile organic substances in waste gas, given as **total carbon C** results:

C_{VOC} [mg C/Nm³] = 1.608 * 95.1 ppm/0.82 = 187 mg C/m³

Solvent in Waste Gas
Output O1.1 and O1.2

- **Clean gas** after an exhaust gas treatment unit
  = Output 1.1 (O1.1) **low relevance of quantity e.g**.:
  - Clean gas of a thermal incineration
  - Clean gas of a catalytic incineration
  - Clean gas of a biofilter
  - Clean gas of a solvent recycling unit



O1.1 = Number of hours of operation (with emissions)/year * emission mass flow [kg/h] * conversion factor x = kg/year

Conversion factor of total C on molecular weight (including response factor of Flame Ionisation Detector): x

$O_{1.1} = c_{Ctot} * 10^{-6} * f_S * V_R * t_R$ in kg/year

where

$O_{1.1}$ VOC mass flow in the clean gas in kg/year

c_{Ctot} total carbon concentration in the clean gas in mg/m^3_N

f_S factor for conversation from c_{Ctot} to VOC (response factor must be taken into account too)

V_R average waste gas flow under normal conditions in m^3_N/h and dry

t_R operation time of the waste gas cleaning unit in hours/year

Determination of single organic compounds

Need for measurement of individual organic pollutants

Chapter V IED:

Total Emission limit over all CMR of 2 mg/m^3 if a mass flow of 10 g/h is exceeded

(Annex VII, Part 4 No 1)

IED Art. 61 and Annex VII Part 8 No 3 and 4

- **CMR and halogenated substances:**

  Compliance shall be verified on the basis of the sum of the mass concentrations of the individual volatile organic compounds concerned.

Need for measurement of individual organic pollutants

Petrol Stage I:

Germany: Benzene – ELV: 1 mg/m^3

Determination of mass concentrations of single gaseous organic substances – DIN EN 13649: Activated carbon and solvent desorption method

Principle:

Adsorption of pollutants on active coal – extraction of pollutants –> Analysis with gas chromatograph

Application range: 0.5 – 2.000 mg/m^3

Organic compounds must be able to be adsorbed on active coal

Particles disturbing measurement must be separated

Condensation of water must be avoided

Determination of mass concentrations of single gaseous organic substances – DIN EN 13649: Activated carbon and solvent desorption method

Gas cooler
before sampling

Condensation of water must be avoided

Temperature of waste gas ≤ 40 °C; use cooler preconditioned there will be no condensation

Sampling with dilution if high content of water or risk of exceedance of capacity of active coal tubes

Determination of mass concentrations of single gaseous organic substances – DIN EN 13649: Activated carbon and solvent desorption method

(1,3-Butadien and Benzene sampling with Chromosorb 106)

- Time period of sampling ≥ 5 Minutes
- Typical time range of periodical individual measurements: 10 – 30 Minutes
- At least 100 mg active coal in main adsorption zone
  Example: Quantity of adsorption material for Screening low boiling substances:
  Zone of sample: about 600 mg // control zone: about 300 mg
- Measurement of volume of gas sample

Determination of mass concentrations of single gaseous organic substances – DIN EN 13649: Activated carbon and solvent desorption method

- Measurement of temperature of sample at volume measurement device as well atmospheric pressure
- Check on tightness
- Analysis on the hand of gas chromatography by use of a FID or mass sensitive detector

Determination of absolute quantities at GC/MS on the hand of a calibration curve created by samples with known concentrations

Concentration Ci [$mg/m^3_{N,dry}$] =
(mass [mg] of component / sample
$volume_{N,dry}$)*1000

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