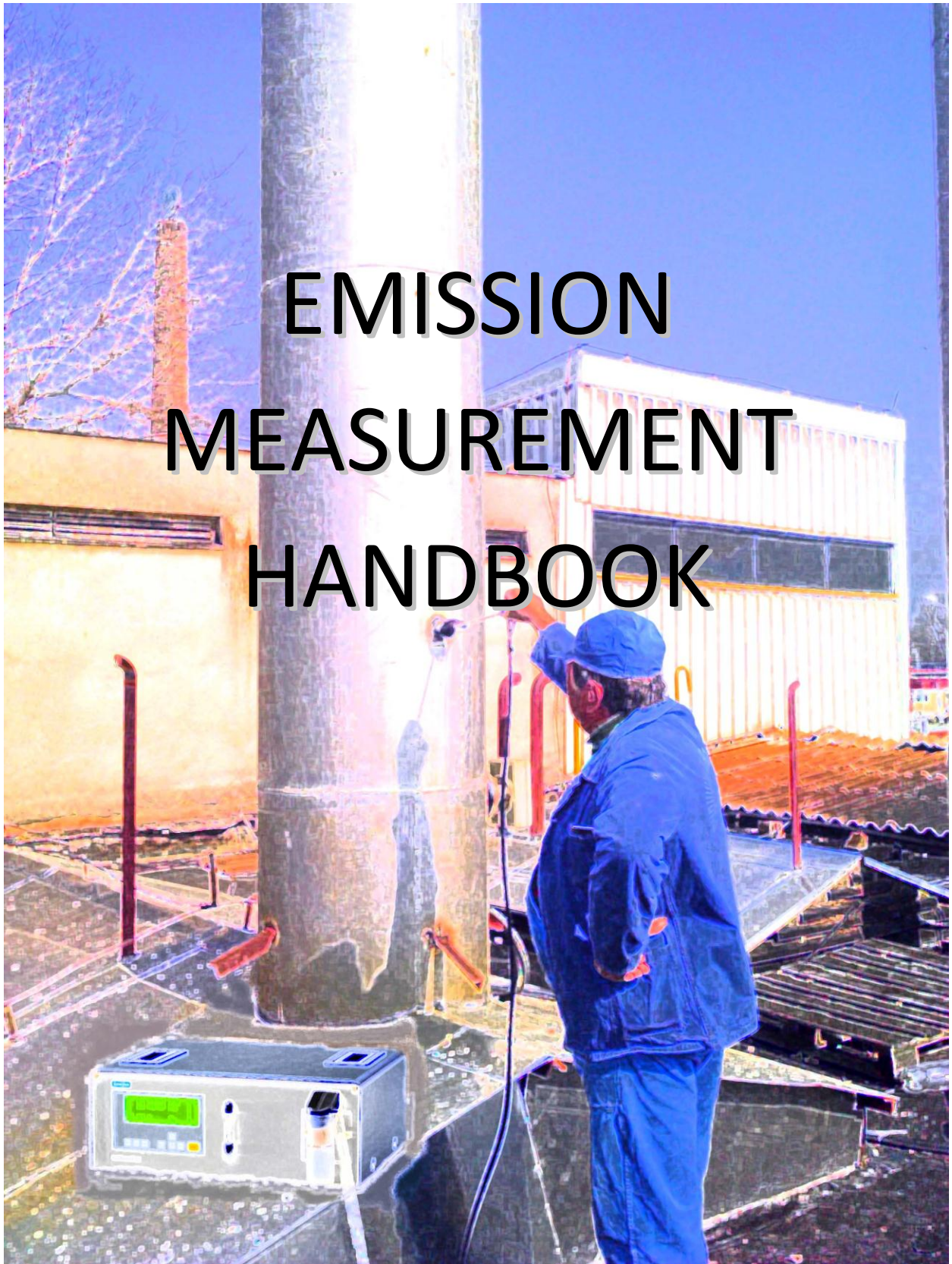


# EMISSION MEASUREMENT HANDBOOK



# Handbook for Emission Measurements for Macedonia

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# 1. Introduction

Air Quality continues to be among the main environmental problems in the Republic of Macedonia. To fulfil the objective of emission reduction, we are using emission monitoring. We are monitoring and measuring in order to fulfil the measures described in the Plans for air quality improvement. This refers especially to the installations having significant share in the total emission in the country, in order to determine whether they abide the prescribed emission limit values.

The implementation of the plans should ensure whether air quality is on a satisfactory level, i.e. whether concentrations of pollutants in the ambient air are according to the limit values.

The aim of this guideline is to assist the owners of the installations and the consultant-analysts in performing emission monitoring and measurement, and in order to abide the Law on Ambient Air Quality article 47 (Official Gazette of RM, No. 67/04, 92/07, 35/10, 47/11, 59/12) and the Rulebook on the methods, means and methodology for measurement of emissions from stationary sources (Official Gazette of RM, No.11/2012).

The guideline describes the general aspects of measurement of emissions from stationary sources and they are further précised with the standards specified in it. The QA/QC procedures of measurement of emissions from stationary sources have been described.

The ten chapters specify directions for performing the measurement process starting from:

- the requirement for measurement, selection and number of measurement points, the size of the measurement ports, working area and measurement place conditions, the measurement place equipment and the work safety;
- determining the velocity of the flue gas, the flow rate, water content in the flue gas and wet gas density;
- particulate measurement, factors influencing the reliability of the measurement, the isokinetic sampling, in-stack and out-stack sampling;
- gas components measurement – continuous methods starting from sampling, , most frequent gas component measurement techniques, other gas component techniques, factors influencing the measurement uncertainty and calibration;
- gas component measurement – discontinuous methods under absorption methods, sampling according to absorption methods, analysis methods adsorption methods;
- emission calculation, flow rate calculation, calculation of particulate and emission calculation, conversion of units of gaseous components from wet into dry concentrations and normalization of the oxygen reference level
- calculation of the measurement uncertainty
- emission measurement reporting, from the emission measurement teams, from installations for the emission data, international reporting from MEPP
- standardization of emission measurement

The directions are also invaluable for any company or agency wanting to get accurate assessment of the environmental impact of their activity.

## 2. Requirements for measurement site

### 2.1 General

For the measurements to be carried out safely and efficiently by the measurement personnel it is needed to have free access to the sampling plane and appropriate measuring ports and working platforms for typical sampling equipment.

Before measurement is being conducted, it is necessary to have a discussion with the persons responsible for environmental issues in the installation for the purpose of sampling/measurement. The nature of the process, continuous or batch process can influence the sampling programme.

Representative of the plant should be present for guidance and information about the plant operating conditions for the measurement objective and further assessment strategy and planning of the measurements.

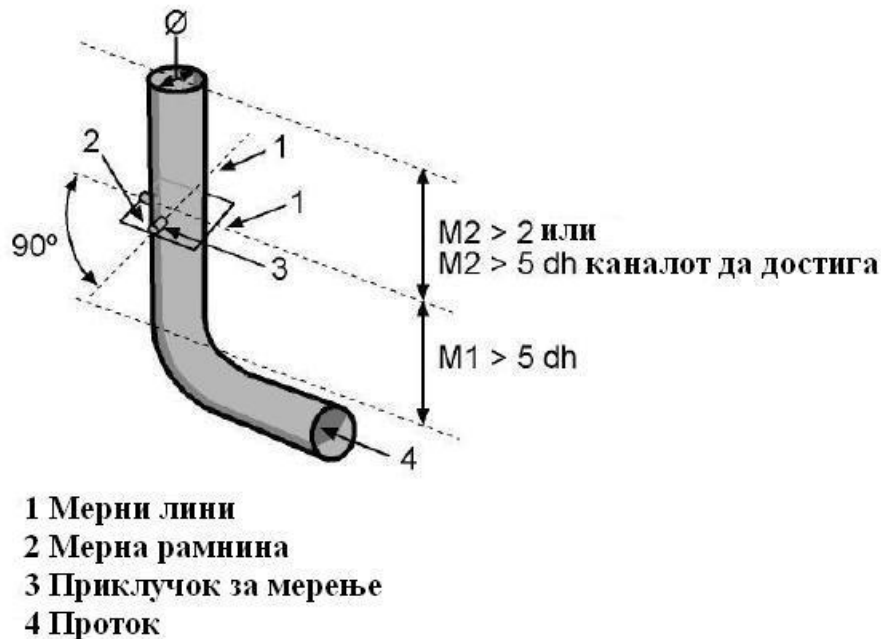
The preliminary review of the factory will enable determination of the best measurement location and determine the number and the scheme of the sampling points.

Working areas should be protected from heat and dust and ensure the necessary environmental working conditions.

The planning of measurement site and inspections during the use will limit personal injuries and unnecessary investments.

The access to the site has to be easy and unlimited, the site must have appropriate facilities and protective equipment in case of emergency and the measurement level must be on the correct part of the stack. The location of the measurement level is the most significant factor in the reliability of the results. The size of the measurement port has to be large enough and be located in a correct place in the canal to ensure good quality results.

The flow of gases has to be stable and homogenic for the measured components, because the measured emission concentration of the component has to be representative of the emission. If this is not the case, the result from an individual monitor is not representative of the emission and the results cannot be used. If the flow conditions of the measurement level are not for all parts according to the standards MKC ISO 10780 and MKC ISO 9096 and the measurements have to be done nevertheless, it should be evaluated in the emission measurement report whether the gas flow conditions have affected the reliability of the measurement results. This impact on the reliability of the measurement results, should be taken into consideration when determining the total measurement uncertainty. The requirements for emission measurements should be taken into account already when planning the structure of a new installation. The changes in the structure of already constructed installation will create additional expenses but are needed for reliable emission measurement results and work safety.



**Figure 1.** Selection of level of measurement place of circular duct

## 2.2 Access to measurement site

Measurement sites shall be installed in such a way as to comply with national safety requirements.

- Important to guarantee ergonomically correct access without too heavy physical load to fixed measurement equipment for maintenance and regular comparison measurements.
- The route should be a fixed part of the structure of the installation taking into account the safety concerns. For example ladders or removable scaffold should not be used in the measurement site or in the measurements.
- To avoid areas of sources that emit unexpectedly such as rupture disks overpressure valves or steam discharges. Any hazard measures by engineering, areas of positive pressure.
- To take into consideration the design of the installation. Many installations were designed before the time of current level emission measurement practices. Since the emission measurements activities were not taken into account in planning, the stack often have only spiral stairs and lifting equipment for maintenance. The emission measurement equipment are lifted up usually with lifting equipment or if not available, carrying or lifting with rope to the measurement site.
- For large combustion plants and waste incinerators the control measurements are done at least once per year for several days. If the measurement technician needs go to the site tens of times per day, which using spiral stairs is very heavy and time consuming, having a mobile platform is preferable, therefore contributing to the increase of safety and effectiveness.



### 2.3 Selection for measurement site and measurement section

The following criteria need to be taken into account when selecting the measurement site and measurement section.

- Selected according to the standard criteria.
- The measurement section should be situated in the vertical part of the canal.
- The measurement section is the surface of the cross-section of the canal, where the samples are taken (AMS and SRM).
- Disturbing factors to the flow (bends on the canal, fans) should be as far as possible from the measurement level. Usually it is enough that the distance is five times the hydraulic diameter before the measurement level and two times the hydraulic diameter after the measurement level. Five times the hydraulic diameter is needed before the end of the stack.
- The gas flow direction deviation can be maximum  $15^\circ$  of the canal axis direction. Determination of the direction deviation can be challenging in practice and can be done with Pitot tube. There should not occur local negative flow and the dynamic pressure of the flow should be more than 5 Pa. The ratio between the lowest and highest velocity of the gas flow should be smaller than 3:1.
- If the sampling (measurement) in the horizontal channels cannot be avoided, the access entries located at the top of the canal can be taken into account as practical advantage. However, the nozzles of probes should not be in contact with the possible bottom dust layer of the canal.

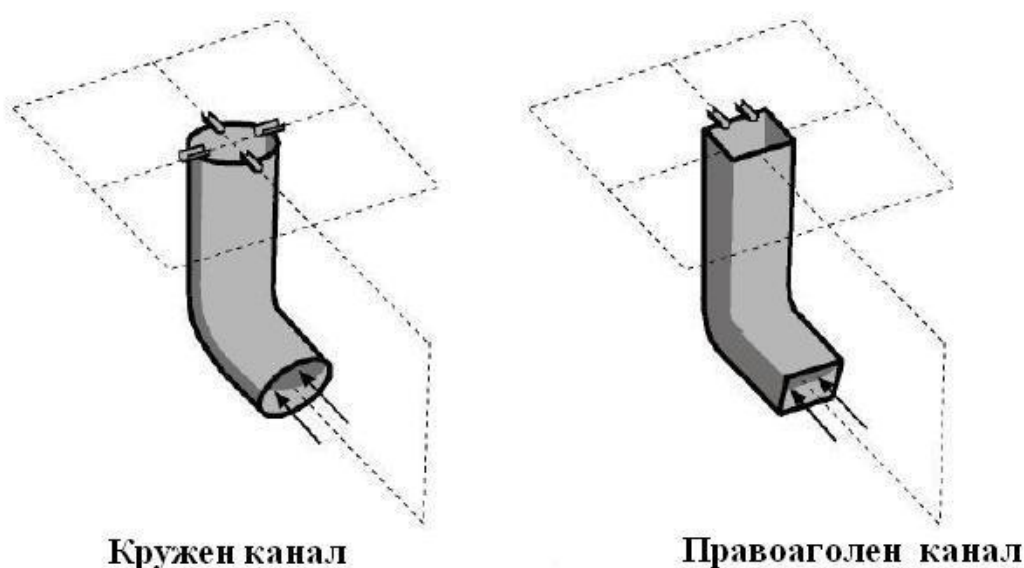


Figure 2. Measurement points after the duct bend (SFS 5625).

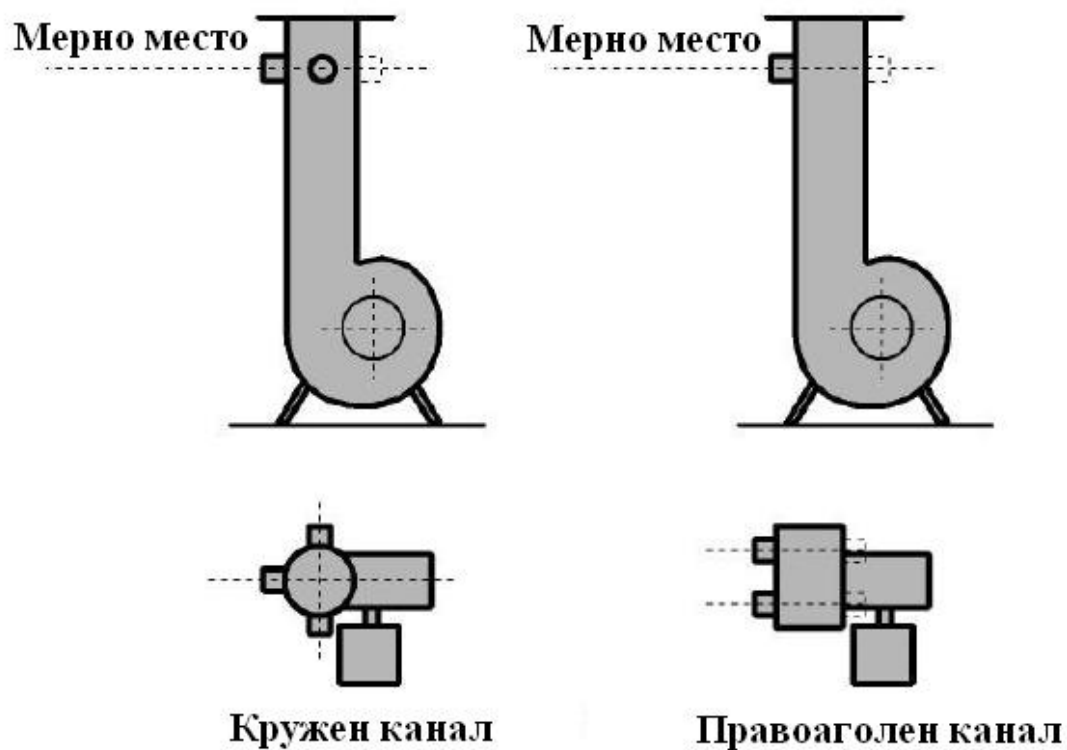


Figure 3. Measurement points after the vent (SFS 5625).

### 2.3.1 Selection of measurement point and number

In case of circular ducts you can have two options how to choose the location of the measurement points. In method A, one measurement point is located at the center of the channel and in method B, there is no measurement point in the center of the channel.





Figure 4. The locations of the measurement points in a circular duct , methods A and B (SFS-EN 13284-1, source Finnish Handbook for Emission Measurements)

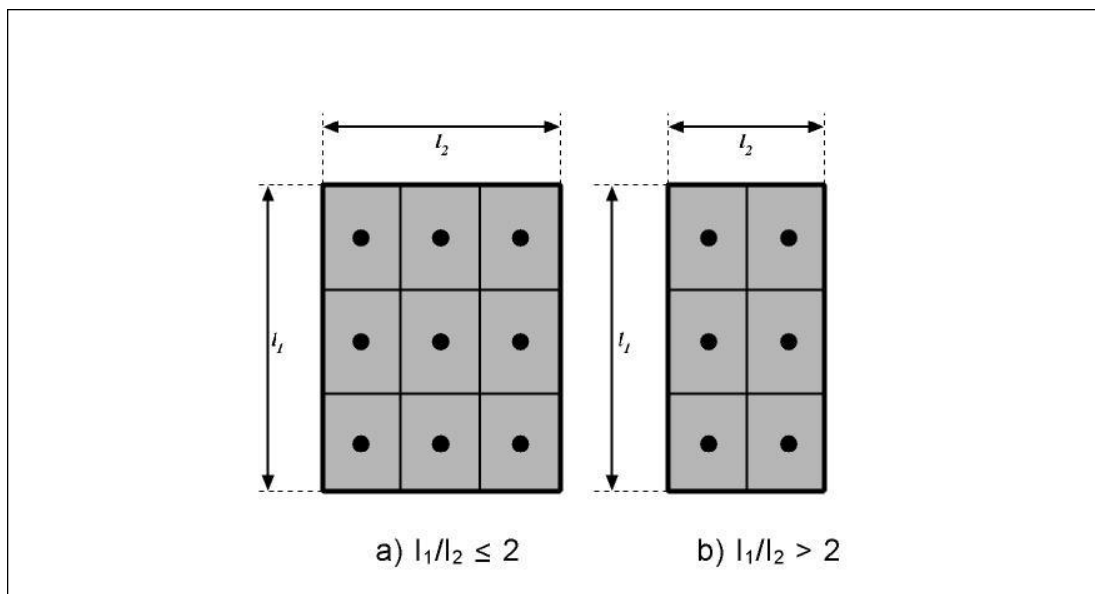


Figure 5. The locations of the measurement points in a rectangular duct (SFS-EN 13284-1, source Finnish Handbook for Emission Measurements)

The minimum number of measurement points is established by the dimensions of the channel. Generally speaking, this number is increasing by increasing the dimensions of the channel. The minimum number of required measurement points is given in the relevant standards EN 13284-1 and ISO 9096. If there is an increase of the turbulence it is recommended that the number of measurement points is increased from the minimum in

order to achieve more reliable results. Sampling points shall be located either more than 3 % of the sampling line length or more than 5 cm whichever is the greater value from the inner duct wall.

### 2.3.2 Fixed measurement equipment of installations

- Requirements from appropriate standards (e.g. EN 15259) should be taken into account in the selection of the location of the measurement equipment and the measurement level.
- The equipment should be located so that the results will be representative.
- Easy and safe access to the equipment should be guaranteed as well as the requirements of the maintenance taken into account.
- Mostly installation of the measurement equipment is suppliers responsibility, but the operator must show a location to the measurement equipment and level which follows the requirements of the standards.
- The supplier and the operator should go through the requirements caused by the specific measurement technique well advance the installation.
- Also safety issues should be taken into account

### 2.4 Size of measurement ports

- The measurement port should primarily be with flange and the recommended nominal size is 125 mm (5 inches). For small canals the port can be smaller but large enough for measurements probes. Selected according to the MKC EN 15259 standard criteria..
- The ports with flanges should reach so far outside the insulation that the placement of fastening bolt is easy.
- The measurement ports should always be covered with insulating gap to prevent condensation.
- The ports can be also equipped with u-shaped iron stand that is welded to the stack below the port to support the probes.

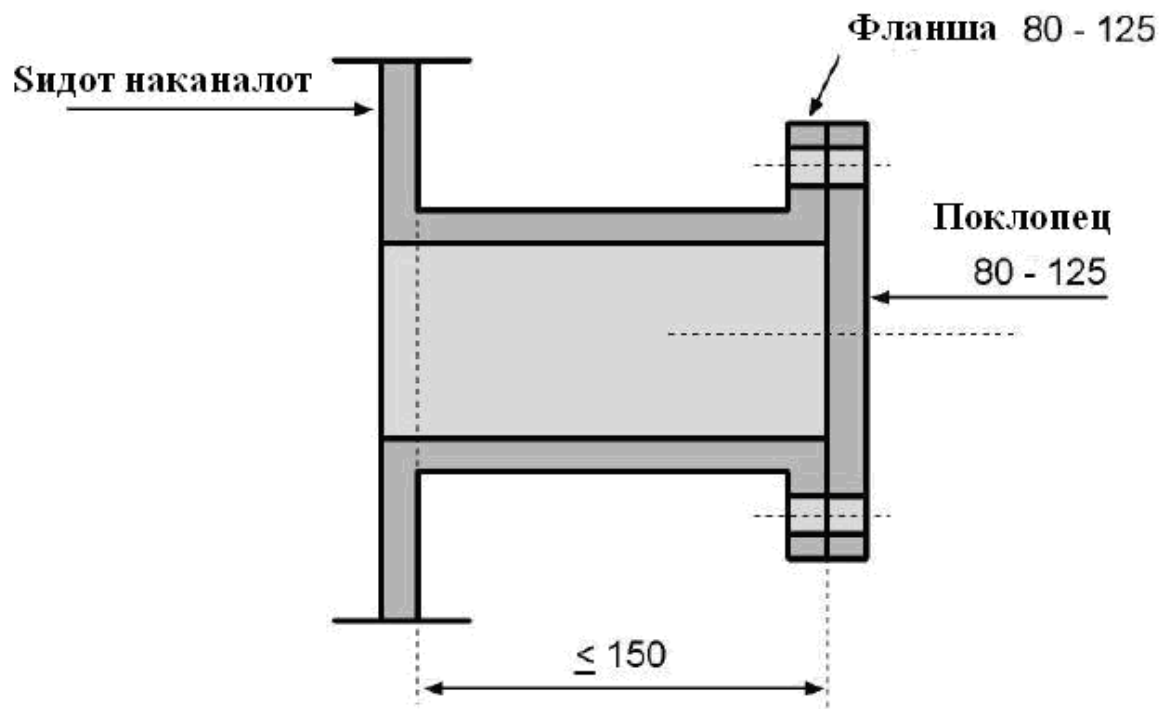


Figure 6. Size of the measurement ports (SFS 5625)

Source Finnish handbook on emission measurement

## 2.5 Working space and conditions of the measurement site

- The basic requirement is that there is a space for measurements where the conditions are controlled.
- The temperature should be such that there will not be disturbances regarding the measurement methods and that the temperature does not cause harm to the health or working capabilities of the measurement technician.
- The dust or vibration shall not affect the measurement method reliability.
- It is recommended to build a shelter for measurements where the conditions are controlled in case of outside stack. Temporary measurement tents or similar do not guarantee adequate protection for example due to changes in weather. This is also valid for inside stack measurement sites, where measurement room is required due to the dust and vibration. (when there are comparison measurements with SRM and AMS), the used analysers have to be able to be situated as close as possible to the AMS.
- For the sampling line there is recommended to make through holes to the walls to avoid the lines being compressed by the doors.(if needed)
- The width of the work plane has to be at least the length of the probe needed in the measurements, when the diameter of the canal is two meters (two particle sampling ports

and gas sampling port). It can be estimated that generally the width of the space needed is at least the diameter of the stack + 1 meter. If the diameter of a round canal is larger than 2 meters when usually four particle sampling ports and equivalent gas sampling ports are needed, should the working base be around the stack and the width be 50 % of the diameter of the stack. The free space in front of the measurement port should be at least the length of the sampling probe needed in the measurements in order to install and remove the probe safely and without problems.

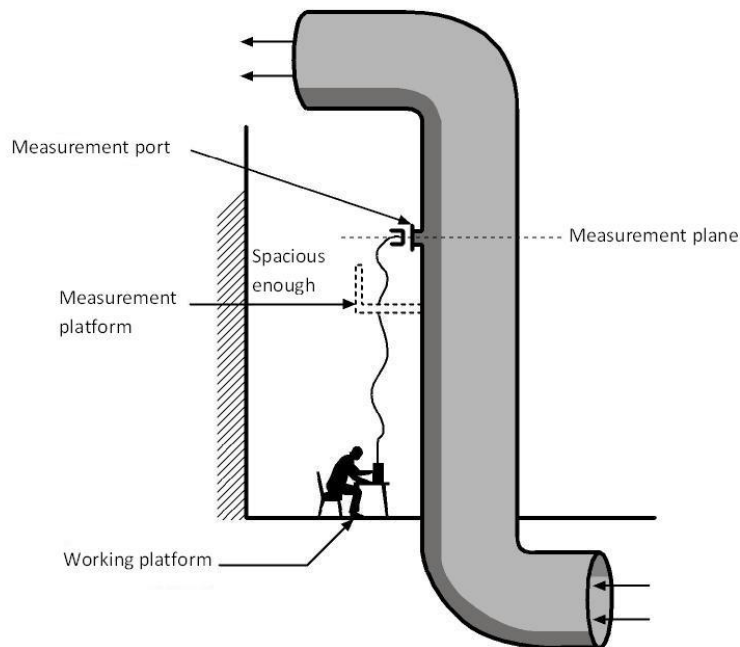


Figure 7. Measurement place (SFS 5625, source Finnish Handbook for Emission Measurements)

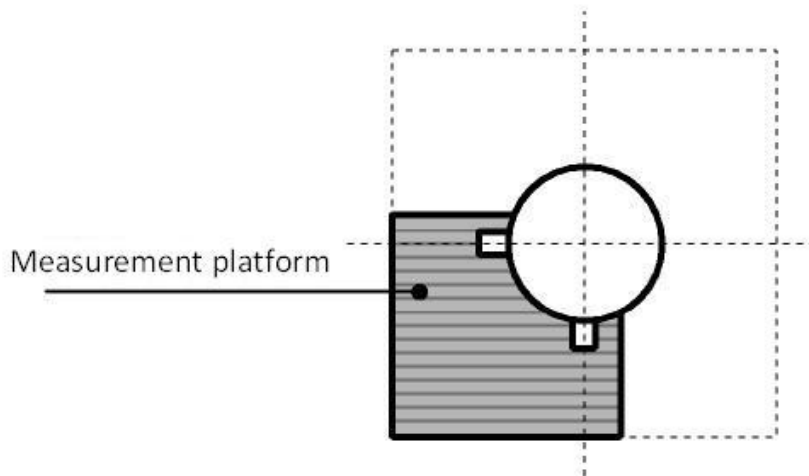


Figure 8. Measurement platform (SFS 5625, source Finnish Handbook for Emission Measurements)

## 2.6 Equipment for the measurement site

- Equipment to the measurement site depends on the measurement techniques and work safety.
- The route and measurement site should have adequate lightning.
- Electricity, compressed air and running water should be available depending of the used measurement equipment and the extent of the measurements.
- The site should have land line phone or other way of communicating if there is a risk than mobile phones cannot be used.
- All stack levels (including the cap between the stack and the level) should be covered to prevent fall of items. Most of the inner stacks of concrete stacks have been built so that they can move sideways and the cap between the inner stack and measurement level can vary due to the conditions. This kind of cap can be covered with special ring built to the stack. Step is built to the measurement level under the ring to prevent items falling.
- Information board about the measurements should be placed on the foot of the stack.
- The by-pass gases from the analysers should be directed outside through outlet tube to prevent intoxication of technicians. For this there should be through holes on the walls of the measurement site.

## 2.7 Work safety

- The safety of the measurement team is provided by wearing safety equipment as follows:
  - helmets
  - shoes
  - personnel alarm systems for example for CO
  - protection for ears, eyes...
- Obtaining Instructions how to escape from the measurement place e.g in case of fire
- Proper stairs to climb to the measurement place

## 3. Determining the flue gas velocity and flow rate

Data about the gas volume flow is needed in order to determine emission. Volume flow can be determined by sampling the velocity of the gas flow.

International standards direct to manual methods to determine the velocity and volume flow of gas streams in ducts, big and small stacks with emissions of pollutants in the atmosphere. The velocity of the gas flow can be determined with measurements with the so called Pitot tube.

Rough calculations can be made using data on the fuel type used and the technological process. To determine the volume flow and emission, the local values of the velocity is also needed to select the input nozzle for isokinetic sampling when measuring dust. The emission mass flow is needed to determine the data of the volume of the leaking gas.

The flow can be determined by measuring the velocity of the gas and the diameter of the measurement plane.

The measurement plane can be determined by determining the inner diameter of the duct, for example by placing a calibrated stick (meter) through the entrance of the measurement port and repeating that at the second measurement port at an  $90^\circ$  angle, therefore determining the diameter of the duct (stack). For rectangular ducts, the plane can be determined by measuring the external dimensions of the duct, taking into account the thickness of the duct wall. When it is not possible to measure the diameter of the duct, the layout of the duct provided by the company can be used.

The bends of the duct, the valves, the compressors as well as changes to the size of the duct can cause interferences of the gas flow and therefore, there should be adequate distance between these disturbing factors and the measurement port. Cyclones can additionally cause turbulences in the flow. These factors have to be taken into consideration when the measurement level and measurement points are being selected.

The variations in the process cause changes in the gas flow during measurement of the gas emissions, which can also cause measurement uncertainty. These variations can be noticed in the industry where continuous measurements are performed when, during the entire process, there are changes in the dynamic pressure at one individual location. In order to

obtain the true velocity during the measurement, if needed, the measurement should be repeated.

### 3.1 Pitot measurements

During sampling (taking samples) with Pitot tube, the velocity of the gas is determined from the dynamic gas flow in the stack and the wet gas density. The dynamic gas pressure is measured with a Pitot tube and micro manometer. Figure? presents the dynamic pressure measurement principle used with Pitot sampling tube. The prevailing pressure in the duct is determined by measuring the difference between the pressure in the duct and the outside pressure.

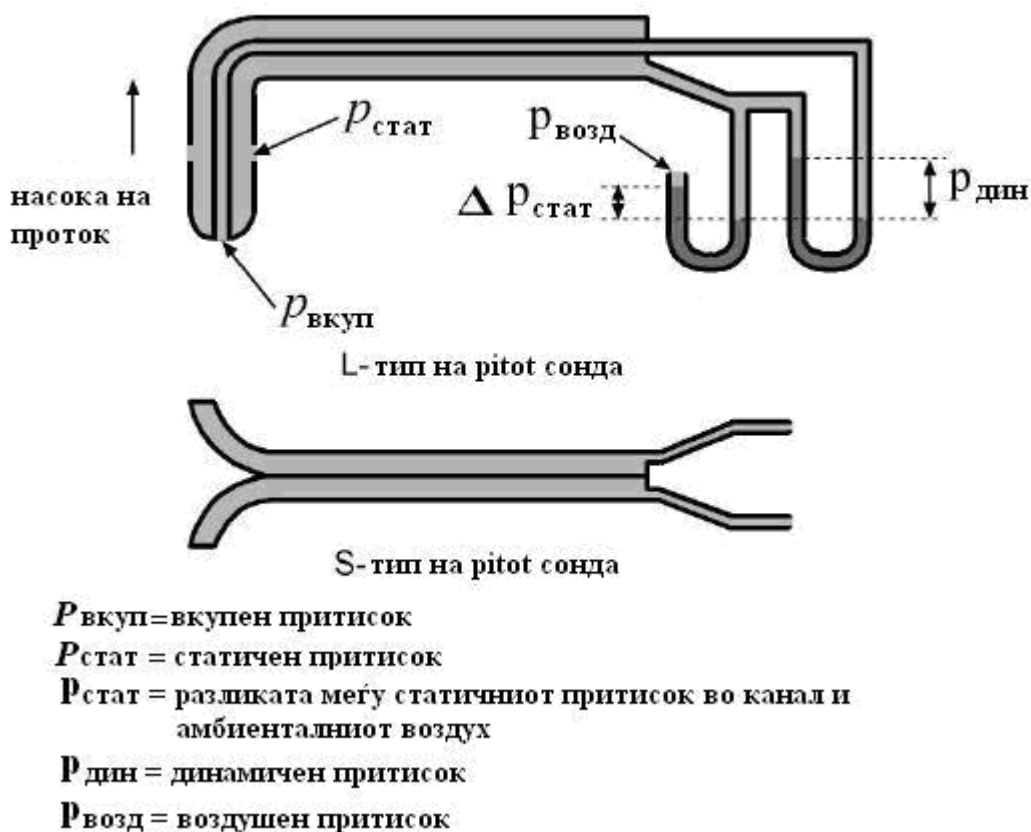


Figure 9. L and S type of Pitot tube

There are two types of Pitot-tubes, L and S type. L type tube is used for relatively dry gases and low concentrations of particles (dust) since the tube could be clogged. S type tubes are used for gases with high concentration of particles and humidity. The velocity correction factor for S Pitot-tube varies between 0,82 and 0,83.

Pitot tubes can be calibrated as described in the international standard (ISO 10780).

The main opening of the Pitot tube is directed downwards opposite to the gas flow direction, as precisely as possible, so that measurement uncertainties do not occur.



The dynamic pressure is a function of the flow according to the following equation:

$$p_{\text{дин}} = \frac{\rho_{\text{вг}} * v_{\text{вг}}^2}{2} \quad (1)$$

каде

$\rho_{\text{вг}}$  = густина на влажният газ во оцак

$v_{\text{вг}}$  = брзина на влажениот газ во оцак

$$\Rightarrow v_{\text{вг}} = \sqrt{\frac{2p_{\text{дин}}}{\rho_{\text{вг}}}} \quad (2)$$

On site, the dynamic pressure values are being measured at several measurement points of the measurement plane. Therefore, the mean gas flow velocity is :

$$v_{\text{вг}}_{\text{прос}} = \sqrt{\frac{2}{\rho_{\text{вг}}}} * \frac{\sum_{i=1}^n \sqrt{p_{\text{дин } i}}}{n} \quad (3)$$

If the dynamic pressure is determined at 4 points, the mean gas flow can be calculated by determining the mean at each point:

$$v_{\text{вг}}_{\text{прос}} = \sqrt{\frac{2}{\rho_{\text{вг}}}} * \frac{\sqrt{p_{\text{дин } 1}} + \sqrt{p_{\text{дин } 2}} + \sqrt{p_{\text{дин } 3}} + \sqrt{p_{\text{дин } 4}}}{4} \quad (4)$$

The example of calculations of the flow rate is displayed in chapter 7.1.

### 3.2 Determining the water content in the wet gas

The water content of flue gas is often determined gravimetric with condensation of the sampled gas. If the determination is done separately, the duration of the sampling should be long enough to enable the condensate water quantity to be measured with appropriate precision.

In order for the condensation to take place, the residual water moisture should be small enough to absorb the silica gel.

The condensate collection container should be kept at sufficiently low temperature (for example acclimatized water bath) so that the condensate would be complete. Before and after the sampling, the sampling line and the gathered condensate water and the silica gel cartridge are weighed.

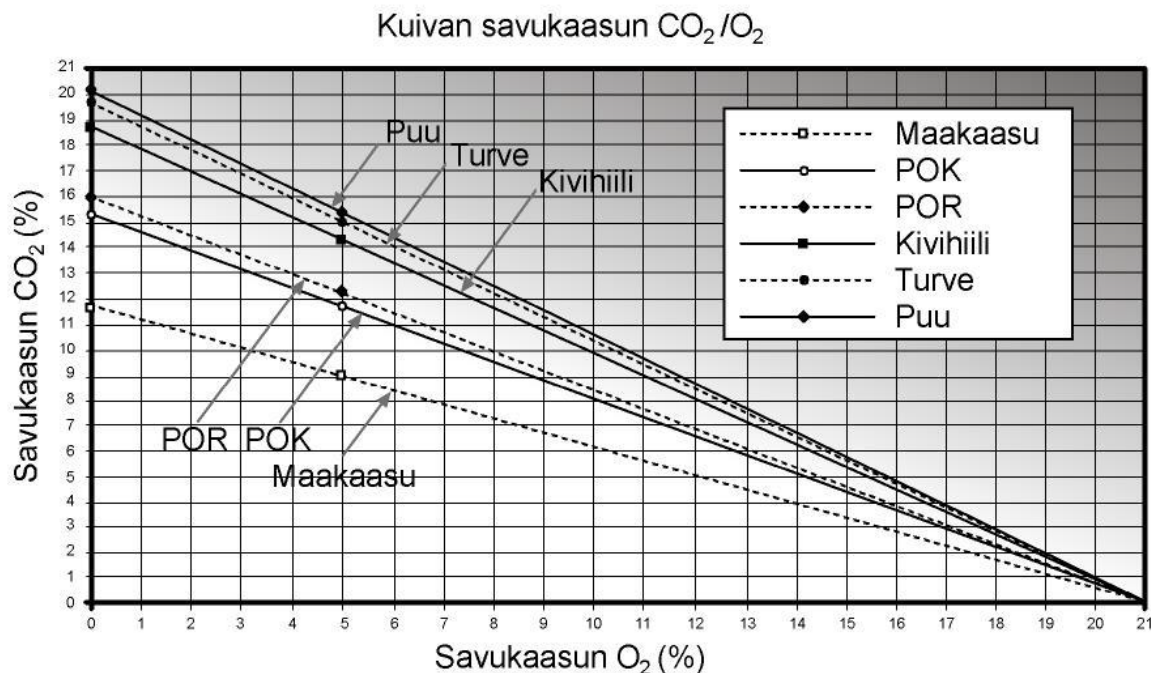
Water content can also be determined with the so called “dry-wet-temperature”, the example is shown in Annex 2 of the Finnish Manual. In this case, in order to perform the measurement with dry-wet-temperature, the temperature needs to be measured with thermo-element. The thermo-element is wrapped with wet towel. When it is placed in a duct, its temperature starts to rise. When the evaporation point is reached, the raise of the temperature shall stop until there is enough water to evaporate to reach thermic balance, where the temperature is conducted both ways. When the towel dries out the temperature shall start to rise again. Water content can also be measured continuously with IR or FTIR-instrument.

### 3.3 Determining the wet gas density

In order to determine the wet gas density we shall need the following data:

- temperature
- concentrations of gas components  $O_2$ ,  $CO_2$  etc.
- pressure difference between the stack and the ambient air
- ambient air pressure
- gas pressure in the stack
- water content

**The temperature** is usually measured with a thermo-element (as K-type thermo-element)  
**Gas concentrations  $O_2$ ,  $CO_2$**  or any other concentrations ( $> 2\%$ ) as significant gas component measured in accordance to paragraph 5.2. When measuring  $O_2$ ,  $CO_2$ , the so called “combustion triangle” can be used, meaning that when you measure the combustion processes and know the oxygen concentration, the carbon dioxide concentration can be determined (look at following image)



Information about ***the difference of pressure between the stack and the ambient air***, is prepared by taking the tube displaying the dynamic pressure and is connected to the part measuring the static pressure, the tube connected to the part measuring the static pressure in the Pitot tube is left outside the stack.

**Ambient pressure** is determined with a barometer or can be found on the internet, can be obtained from the local meteorological institute etc.

**The pressure of the gas in the stack** is measured in the following manner:

- when the stack has greater pressure:

- the pressure of the gas in the stack = pressure of the ambient air + difference of the pressure in the stack and the ambient air

- when the stack has too small pressure:

- the pressure of the gas in the stack = pressure of the ambient air - difference of the pressure in the stack and the ambient air

**Determining the water content** is explained in the previous chapter

## 4. Particulate measurement (dust)

### 4.1 General

This part is related to the MKC EN 13284-1 standard (Stationary source emissions - Determination of low range mass concentration of dust. Part 1: Manual gravimetric method) for particulate measurement.

## 4.2 Factors influencing the reliability of the particulate measurements

Most important factors are:

- Sampling must be representative
- No leaking in the sampling lines
- Avoid touching stack walls with the probe when inserting the probe in the duct or when taking it out (you will get more particles on the filter)
- Temperature control of the nozzle (opening), the probe and the filter in order to avoid condensation
- Control that the sampling is isokinetic
- Gas sample needs to be properly dried before it is taken to the gas meter

### 4.2.1 Filter material

It is usual that quartz fibers are used as particulate filter fabric, since they are relatively inert to external conditions and can tolerate temperatures up to 950 °C.

Glass fiber filters are usually cheaper compared to quartz fiber filters. However, when using glass fiber filters make sure that the flue gas does not contain high quantities of sulfur components, since they easily react with the glass fiber fabric and form sulfates, therefore increasing filter mass. Usually glass fiber filters tolerate temperatures up to 550 °C.

*Note! Prior to the measurements, the filters need to be treated in a furnace, at a temperature which depends on the standard method which is used. This “thermal treatment” makes the filters inert and they can tolerate the stack temperatures without braking.*

### 4.2.2 Weighing

Attention needs to be devoted to the precision in the weighing procedure! For example, the balance needs to be placed in rooms with stable temperatures, and the humidity of the ambient air is minimized.

Before measuring the filters, they need to be dried in desiccators.

The balance needs to be regularly calibrated with reference weights.

Several effects contributing to mistakes in weighing need to be taken into consideration, such as the insufficient temperature equilibrium, the effect of temperature variation, and the effect of barometric pressure variations. The uncertainty which may occur is usually not only related to the balance performance, but rather to the procedure applied.

### 4.2.3 Field blank

An overall field blank sample shall be taken after each measurement series or at least once a day, following the normal sampling procedure without starting the suction device. The sampling nozzle is recommended to be kept in the channel for 15 min at 180 ° from the direction of the flow. The measured mass variation provides an estimation of the

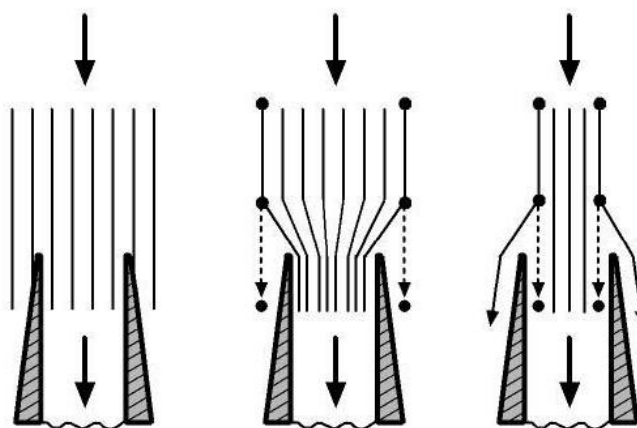
uncertainties. The overall blank value, divided by the average sampling volume of the measurement series, provides an estimation of the detection limit (in milligrams per cubic metre) of the whole measurement process, as carried out by the operators. The overall blank includes possible deposits on the filter and on all parts upstream.

The purpose of this sample is to check that there is no contamination of filters and of rinsing solutions during handling on site, transport, storage, handling in the laboratory and weighing procedures. Field blank is especially important when the measured dust concentrations are low.

Note! Field blank cannot be subtracted from the measured result. Field blank values shall be reported individually in the measurement report. No result below the overall blank value is valid.

#### 4.2.4 Isokinetic sampling

The isokinetic sampling is sampling where the direction and velocity of the gas entering the sampling nozzle (opening) is equal to the one of the gas in the duct at the measurement point.



Вшмукување	Изокинетичко	Хиперкинетичко	Хипокинетичко
Концентрација на прашина	точна	ниска	висока
Големината на честичките	точна	мала	глема

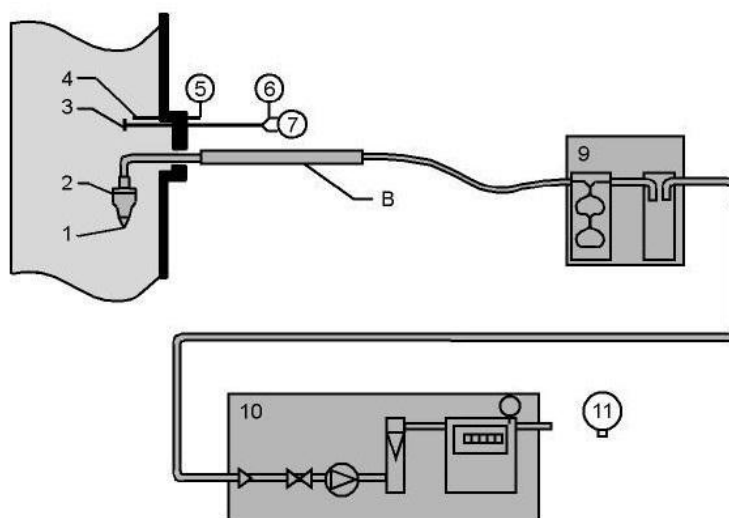
Image 10: Isokinetic effect in particulate sampling.

The permitted deviation during isokinetic sampling according to the 13284-1 standard is - 5% to + 15%.

#### 4.2.5 In-stack sampling method

The filtering method in the stack with the filter and the filter holder placed opposite of the probe nozzle (opening).

The in-stack method is used when the flue gas temperature is above the water or acid dew point, meaning that the gases are not saturated.



1. Ноздринката (отворот)

2. Држачот на филтерот

3. Питова сонда

4. Сонда за температура

5. Термометар

6. Сензор за статичен притисок

7. Сензор за динамичен притисок

8. Заштитна цевка на сондата

9. Систем за ладење и сушење нагасот

10. Пумпа, единица за управување и анализа на примерокот

11. Барометар.

Image 11: In-stack sampling method according to the MKC EN 13284-1 standard.

EN 13284-1 requires:

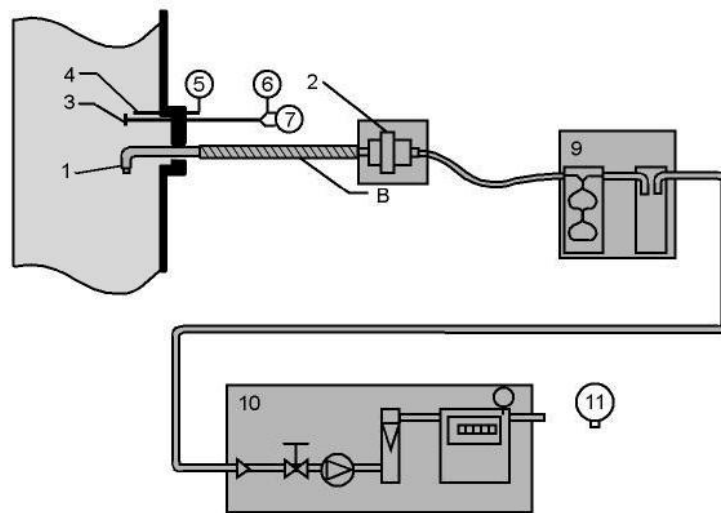
- a) The filters, before the measurements, need to be heated at minimum 180 °C and always at a temperature for at least 20 °C higher than the flue gas temperature (meaning, for example, if the flue gas temperature is 350 °C, the filter before the measurements need to be heated at a temperature of 370 °C).
- b) The sampling is also performed at the same flue gas temperature (since the filter itself is within the stack at the same temperature).

- c) The filter needs to be heated in a furnace after the measurements at temperatures of 160 °C

#### 4.2.6 Out-stack sampling method

Out-stack method is filtering out of the stack and its heated holder placed away from the nozzle, at the back side of the probe.

The out-stack method is usually used when flue gases are saturated, meaning that there is a possibility for condensation. The out-stack method can also be used when measuring non-saturated gases.



- |                                 |                                                          |
|---------------------------------|----------------------------------------------------------|
| 1. Ноздринка (отворот)          | 7. Сензор за динамичен притисок                          |
| 2. Држач на филтерот со греалка | 8. Зачитна цевка на сондата со греач                     |
| 3. Питова сонда                 | 9. Систем за ладење и сушење на гасот                    |
| 4. Сонда за температура         | 10. Пумпа, единица за управување и анализа на примерокот |
| 5. Термометар                   | 11. Барометар.                                           |
| 6. Сензор за статичен притисок  |                                                          |

Image 12: Out-stack sampling method according to the MKC EN 13284-1 standard.

When out-stack is used for non-saturated gases:

- a) The filters, before the measurement, need to be heated at minimum 180 °C and always at temperatures, at least, 20 °C higher than the flue gas temperatures (meaning, for example, if the flue gas temperature is 350 °C, the filter, prior to the measurements, need to be heated at temperatures of 370 °C.
- b) The sampling is performed at the temperature of the flue gas
- c) The filter, after the measurement, needs to be heated at a temperature of 160 °C.

When the out-stack method is used for saturated gases and the flue gas temperature is below 160 °C, than:



- a) The filter prior to the measurements needs to be heated at 180 °C minimum
- b) The sampling line temperature is 160 °C
- c) The filters after the measurements need to be heated in a furnace at a temperature of 160 °C

When the out-stack method is used for saturated gases and the flue gas temperature is above 160 °C, then:

- a) The filter, prior to the measurements, need to be heated, at least, 20 °C higher than the flue gas temperature
- b) The sampling is performed at the flue gas temperature
- c) The filters after the measurements need to be heated in a furnace at a temperature of 160 °C

Table 1 Overview of the methods used in different situations.

Method	Flue gas condition	Flue gas temperature	Sampling temperature	Filter pre-treatment	Filter post-treatment
"in-stack"	Non-saturated	Any	Flue gas temperature	Always at flue gas temperature + 20 °C, at least 180 °C	160 °C
"out-stack"	Non-saturated	Any	Flue gas temperature	Always at flue gas temperature + 20 °C, at least 180 °C	160 °C
"out-stack"	Saturated	< 160 °C	160 °C	180 °C	160 °C
"out-stack"	Saturated	> 160 °C	Flue gas temperature	Always at flue gas temperature + 20 °C	160 °C

## 5. Measurement of gaseous components- continuous methods

### 5.1 Sampling

Continuos measurements of gaseous components can be divided into different types based on the sampling:

- Extractive methods
- In-situ-methods
- Remote sensors

This text focuses on extractive methods and on their quality assurance.

### 5.1.1 Sampling line

Simplified figure on the extractive sampling line is presented below.

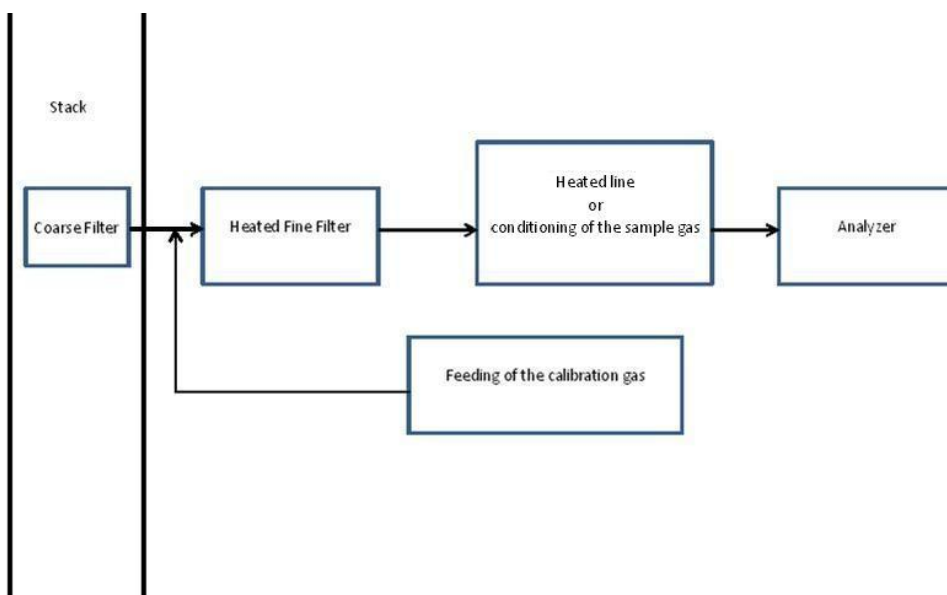


Figure 13. Extractive sampling line

Often the flue gas is hot and moist and it can contain lots of particulates. In order to prevent the condensation of the moisture in the sampling lines, heated lines and heated filter holders must be used in the sampling before the cooling unit.

The sampling line and filter must be made from inert material. Most common materials used in sampling lines are PTFE (Teflon) and polyethylene (PE).

**Note!** The use of silicone must be avoided because of its “non-inert” properties (it can e.g adsorb organic compounds quite easily).

Typically the calibration gas is fed to the beginning of the line, so that it follows the same route to the analyser as the actual sample gas. Then the effect of sampling line is similar both on the calibration gas and to the sample gas.

When the extractive sampling line is constructed, at least following things must be taken into account:

- Probe: length and material
- Filters: materials, not to cause pressure losses

- Sampling line: material, length, diameter
- Connections, valves
- Pressure meters: reading accuracy
- Calibration gases: accuracy, stability time
- Pumps: type, capacity
- Gas conditioning (drying) techniques

*It must be noted that all the cold spots must be eliminated in the whole sampling line in order to avoid any condensation and losses of components!*

### **5.1.2 Conditioning techniques**

There are several conditioning configurations the sample gas, such as:

1. Condensation method.
2. Permeation dryer
3. Dilution probes
4. Heated line and heated analyser

#### **1. Condensation methods**

These methods are easy to use, many different methods available on the market. However, you must make sure that you do not lose the components you are studying in the condensate. For example, SO<sub>2</sub> and NO<sub>2</sub> are easily absorbed in the water, however NO is not. So, make sure you select the right condensation method for your purpose!

*Note! It is required in many standards (e.g MKC EN14972) that the temperature of the sample gas at the exit of the cooling unit needs to be recorded and that it must be < 4 °C; then the gas can be considered to be dry!*

A maximum dew-point temperature of 4 °C shall not be exceeded at the outlet of the sample cooler.

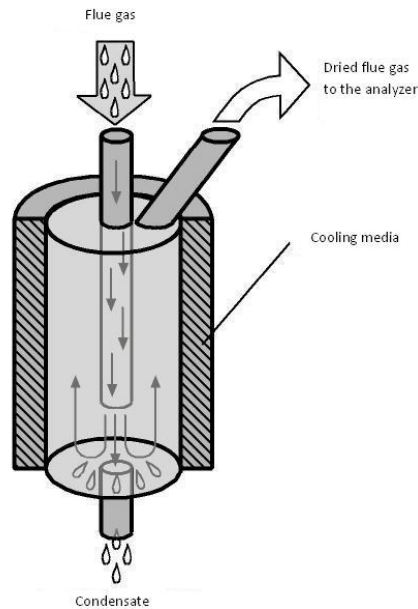


Figure 14. Jet stream condenser (source Finnish Handbook for Emission Measurements)

## 2. Permeation dryer

There is no need for condensation unit when using this method. On the other hand, there is a risk that the permeation dryer can be easily blocked if the sample gas contains lot of particulates or condensating components. Therefore, the sample gas must be filtered before it is led to the permeation dryer.

The gas temperature in the permeation dryer needs to be above the water dew point. The gas sample in the permeation dryer is dried while still in gas condition in order to avoid losses of the water dissolved components (i.e.  $\text{NO}_2$  and  $\text{SO}_2$ ) in the sample.

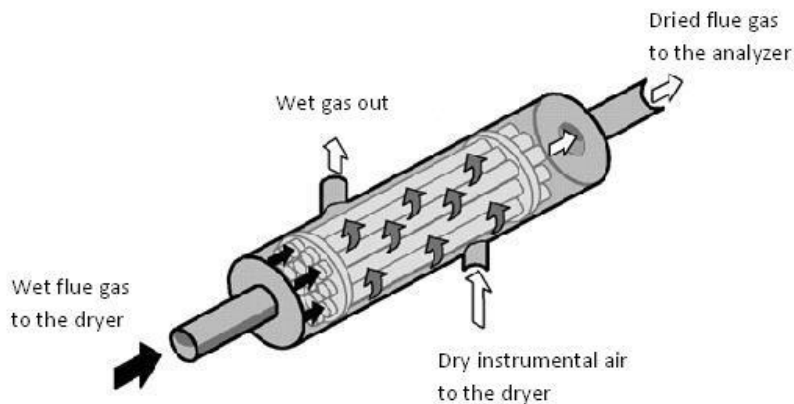


Figure 15. Permeation dryer (source Finnish Handbook for Emission Measurements)

### 3. Dilution probes

When using dilution probes the sample gas is dried with dry dilution air already when the sample is taken and as a consequence, there is no need for separate condensation removal.

Following factors can have an affect to the accuracy of the dilution probe:

- Changes in the flue gas pressure
- Changes in the flue gas density
- Changes in the flue gas temperature
- Quality of the dilution air (how clean it is!)

The dilution air must be clean enough, so that there is no mistake during measurement and in the result. During the measurements care must be taken that the dilution probe does not clog because this will change the dilution ratio. The critical orifices that are used for the control of dilution ratio can be cleaned with ultrasound wash.

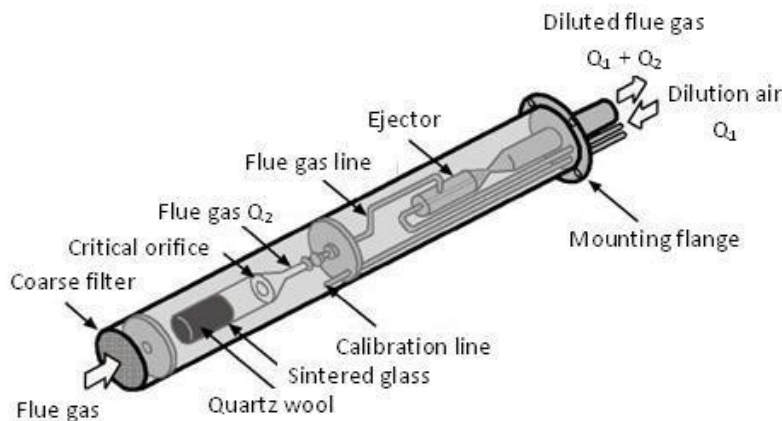


Figure 16. Dilution probe (source Finnish Handbook for Emission Measurements)

### 4. Heated line and heated analyser

The most preferable way is to lead the hot and moist sample gas directly to the analyser without cooling it. By doing this, the risk of losing components in the condensate will be eliminated. To avoid condensation the user shall maintain the temperature of the sampling line up to the measuring cell. The analyser itself must be also heated.

The concentrations are given on wet basis and shall be corrected so that they are expressed on dry basis. The correction shall be made from the water vapour concentration measured in the flue gases

**Note!** *As a summary, the measurer must choose the conditioning system that is fit for its purpose! For some cases, condensation method can be perfect, for some you need to choose another cooling system in order to avoid the loss of the sample gas in the condensate.*

## 5.2 Different measurement techniques for gaseous components

### 5.2.1 Most common techniques for the measurement of gaseous components

In the Table Z below the most common measurement techniques for different gaseous components are presented.

Component	Measurement method
O <sub>2</sub>	Zirkonium oxide cell, Paramagnetic methods, electrochemical cells
O <sub>3</sub>	UV, FTIR
H <sub>2</sub>	Thermal conductivity detectors, gas chromatographs
H <sub>2</sub> O	Measurement of dry/wet temperatures, heated IR, FTIR
N <sub>2</sub>	electrochemical cells, Chemiluminescence
CO <sub>2</sub>	IR, FTIR, Thermal conductivity detectors
CO	IR, FTIR, electrochemical cells
SO <sub>2</sub>	IR, FTIR, UV, UV –fluorescence, electrochemical cells
TRS	Converter with UV –fluorescence, converter with FTIR
H <sub>2</sub> SO <sub>4</sub>	Absorption into liquids, determination with colorimetric methods
H <sub>2</sub> S	UV, gas chromatographs, electrochemical cells
NO/NO <sub>2</sub>	Chemiluminescence, IR, FTIR, UV, electrochemical cells
N <sub>2</sub> O	IR, FTIR
NH <sub>3</sub>	UV, Chemiluminescence, IR, FTIR
HCN	IR, FTIR
HCl	IR, FTIR
HF	IR, FTIR
Cl <sub>2</sub>	UV absorption, Chemiluminescence
CH <sub>4</sub>	IR, FTIR,
Individual organic components	IR, FTIR, gas chromatographs
Total organic carbon (TOC)	Flame ionisation detector (FID)

## 5.2.2 Standard reference methods SRM for different components in EU

List for SRM-methods can be found in Annex 1 of this guideline.

When these European Standards are used as the SRM, the user shall demonstrate that:

- performance characteristics are better than the minimum performance criteria given for each method in the relevant standard; and
- overall uncertainty calculated by combining values of standard uncertainties associated to the performance characteristics given in relevant standard is less than the requirement stated in the standard

Overall expanded uncertainty for standard reference methods are defined in EN reference standards :

- NO<sub>x</sub>: < 10 % of the daily emission limit values (MKC EN 14792)
- CO: < 6 % of the daily emission limit values (MKC EN 15058)
- SO<sub>2</sub>: < 20 % of the daily emission limit values (MKC EN 14791)
- O<sub>2</sub>: < 6 % (relative) of the measured concentration (MKC EN 14789)
- H<sub>2</sub>O: < 20 % (relative) of the measured concentration (MKC EN 14790)

## 5.3 Factors affecting the measurement uncertainty

At least following factors have an effect to analyser's measurement uncertainty:

- Repeatability
- Linearity
- Drift (for zero and span)
- Noise
- Environmental conditions
- Interfering components
- Calibration (accuracy of the calibration gases)

Expert using the analyser must know the total effect of all possible factors which can have an influence on the results ! Typically, analyser manufacturer's give these performance characteristics in their manual but the user of the analyser must know his own instruments "behavior".

### 5.3.1 Calibration

Calibration of the gaseous analyser is one of the most important things in the QA and reliability of emission measurements. The aim in the calibration is to have information on the possible deviation between the concentration and the reading.



Typically the calibration is performed before the measurements by feeding into analyser a certain gas concentration of studied gas and also zero gas which is usually either nitrogen or synthetic air. This calibration must be performed at the site, before and after the measurements!!! The calibration of the analyzer needs to be added to the normal working procedure. Laboratory must define the criteria for the acceptable deviation between these calibrations. Meaning that if the deviation is larger, then in the worst case, the measurements have to be rejected.

- The calibration gases must be stored in proper temperature, not too cold, not too hot!
- The stability time given in the certificate must be respected
- When the pressure in the calibration gas bottle drops below critical limits, there might be changes in the gas concentrations. Therefore, the minimum pressure info needs to be respected also!
- It must be noted also that some components might react with each other, for example it is not possible to have mixture for NO and O<sub>2</sub> because NO will react with oxygen. However, gas manufacturers are experts on this...!
- In some cases the background gas in the calibration gas can have an effect to the results. For example, if you use UV-fluorescence for SO<sub>2</sub>-measurements the oxygen concentration in the calibration gas has an effect to the measured results. Thus, in this case, it is recommended that the background gas oxygen concentration should be as close as possible to the stack gas oxygen level.

### **5.3.2 Check for the linearity**

The linearity of the gas analyzer has to be checked on a regular basis, for example once in a year. It is checked by feeding different concentrations of the studied gas into the analyser (0, 20, 40, 60, 80, 100 % of the measurement range and all the ranges need to be checked).

### **5.3.3 Undertaken measures in studying interfering gases**

Below are listed few methods and typical interfering components:

- Measurement of CO with IR-technique => CO<sub>2</sub> will interfere
- Measurement of NO<sub>x</sub> with chemiluminescence => H<sub>2</sub>O and CO<sub>2</sub>
- Measurement of SO<sub>2</sub> with UV-fluorescence => some organic substances interfere and therefore, UV-fluorescence analysers have an unit to remove organic substances from the sample gas

*It must be emphasized, however, that these interferences do not mean that this measurement method could not be used when interfering components exist in the flue gas!!* You can minimize the effect of interfering substances by feeding the gas mixture with similar gas composition to the analyser. (However, this means that laboratory has to have a mixing system for different mixtures...). The test for interfering components must be performed at least when you take a new analyser into use and when new functional parts have been

changed to the analyser. The tests are performed by feeding the components separately to the analyser and the response of the analyser is registered.

$$S = \frac{100}{M_r} \sum_{i=1}^n R_i$$

Where

S = the sum response of interfering components

$R_i$  = response of individual component

$M_r$  = measurement range of the analyser

n = number of tested components

In many standards it is stated that S must be  $< \pm 4 \%$  of the measurement range studied.

### **5.3.4 Test for NO<sub>x</sub>-converter**

The NO<sub>x</sub>-converter efficiency needs to be checked when using the chemiluminescence method. Especially when the NO<sub>2</sub>-concentrations in the flue gas are expected to be high, it is of great importance that the converter is working properly. Converter must be tested on a regular interval, e.g once in a year. Instructions for this test can be found in the analyser's manual.

Typical requirement for the converter efficiency is  $> 95 \%$ .

### **5.3.5 Environmental conditions**

Users of the analyser must respect the recommended operational temperatures that are given in manuals. Typically, the operation temperatures are  $+ 5 \text{ C} - +35 \text{ C}$  and the relative humidity of the air 5-95 %. Measurer needs to take into account the conditions at the site (temperature, humidity, air pressure) and record them for example in the diary. It is important to mention also if there is lot of vibration, dust, draught etc because these might affect to the results.

## **6. Measurement of gaseous components- discontinuous methods**

## 6.1 Absorption methods

- Process where the gaseous air pollutant reacts with the liquid reactant to form a stable, nonvolatile and easily detected product in the liquid phase
- Often used as primary (reference) method
- Absorption solutions used for sampling can be divided into inorganic and organic dilutions. Most common inorganic solutions are water, different acids,  $\text{HNO}_3$  ( $\text{H}_2\text{SO}_4$ ) and bases (e.g.  $\text{NaOH}$ ). Alcohols, e.g. ethanol, are used as organic absorbing solutions.

### 6.1.1 Sampling for absorption methods

1. Isokinetic/Non isokinetic sampling => the choice depends on the flue gas. If there are droplets present or if the component is "attached" to the particles, then the sampling has to be performed using isokinetic sampling. For example, inorganic fluorine components and heavy metals can be combined with the particles present in the flue gas and therefore, particulates need to be filtered before the absorption sampling and also analyzed. Isokinetic sampling may be required e.g. in those cases when a wet scrubber is used without subsequent reheating.

Non-isokinetic sampling can be used if the component to be determined are not attached to the particles, sample gas is not saturated and there are no droplets.

Isokinetic sampling requires usually volume flow rates much higher than those which can be admitted by the washing bottles used for the collection of pollutants. Therefore, downstream of the filter, only a part of the gases is drawn through the washing bottle(s) through a secondary line, the main line and the secondary line having their own gas metering systems and suction devices. The ratio between the main and the secondary line volume flow rates shall be kept constant. Principles for this sampling is shown in Fig. X.

2. Selection of sampling point => representative sampling
3. Preparations before the measurements
  - rinsing of the sampling lines, gas impingers
  - velocity measurements
  - leak tests (also during sampling by measuring the  $\text{O}_2$ -concentrations at the end of the sampling line and comparing this information with the flue gas  $\text{O}_2$ !!)
- blanks; chemical blanks and field blanks. More information about these can be found e.g. from EN 14791:  $\text{SO}_2$ - measurement method, below an example of field

blank text from this standard:

➤ Field blank

- To check the sampling procedure, a field blank shall be performed at least before each measurement series or at least once a day, following the whole measurement procedure specified in this European Standard and including the sampling procedure described in 7.2.3 to 7.3 without the suction step i.e., without starting and operating the suction device.
- The average sampling time shall be used for calculation of the blank value expressed in mg/m<sup>3</sup>.
- If the equipment in contact with the measured substance is cleaned and reused in the field, a field blank shall also be taken after the measurement series. If several measurements are performed at the same industrial process or on several lines of the same industrial process, then only one single field blank at the beginning and one at the end of the series shall be performed.
- The field blank shall be less than 10 % of the emission limit value (ELV). If the calculated value of the measurement is less than the field blank, the measured value result shall be reported as less or equal to the field blank.
- The result of field blank shall not be subtracted to the result of measured value. However, it is necessary to take into account the value of the field blank in the calculation of the uncertainty of the measured value

4. Requirements for sampling:
- gas residence time should be minimized
  - probe, filter and sample lines must be heated
  - all parts in the sampling line must be resistant to corrosion and temperature
  - sampling line should not consist the elements which are collected (meaning that for example stainless steel probes cannot be used in heavy metal sampling because there will be contamination...)

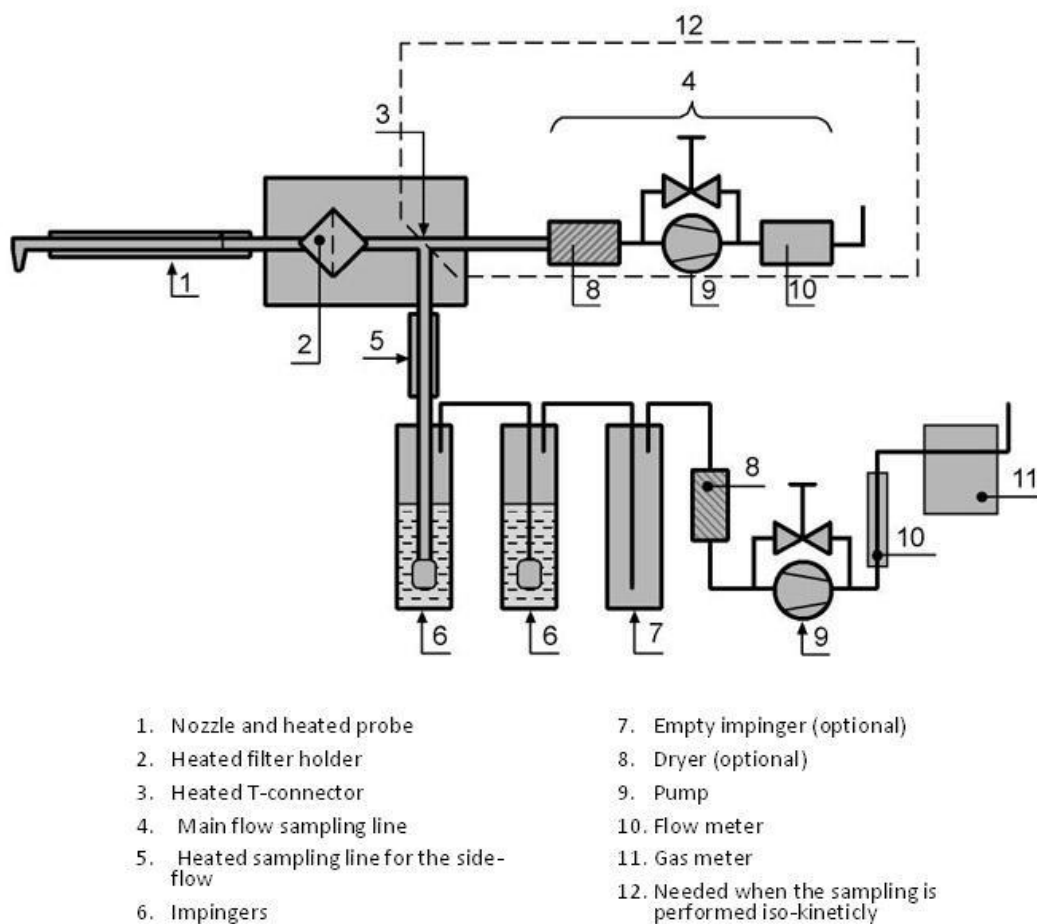


Figure 17. Sampling arrangement for iso/non-isokinetic sampling

In Table 2 examples of absorption measurement methods for different components are presented.

Table 2. Examples of absorption methods for different components

Component	Standard	Absorption liquid	Method for analysis
Ammonia (NH <sub>3</sub> )	SFS 3869	0,1 M H <sub>2</sub> SO <sub>4</sub>	NH <sub>3</sub> -specific

			electrode
Ammonia (NH <sub>3</sub> )	VDI 2461 Blatt 1 ja VDI 2461 Blatt 2	0,05 M H <sub>2</sub> SO <sub>4</sub>	Titration
Mercury (Hg)	EN 13211	4 % K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> + 20 % HNO <sub>3</sub>	Cold vapour- atomic absorption spectrometry (CV- AAS)
Ethanol and methanol (C <sub>2</sub> H <sub>5</sub> OH and CH <sub>3</sub> OH)	VDI 2457, Blatt 2	Methyldiglykol	Gas chromatography (GC)
Gaseous fluorine compounds	VDI 2470 Blatt 1	NaOH-liquid	Ion selective electrode
Formaldehyde (HCHO)	VDI 3862 Blatt 2	DNPH	Liquid chromatography
Hydrochloric acid (HCl)	EN 1911	H <sub>2</sub> O	Ion chromatography
Reduced sulfur compounds (TRS)	SFS 5727	Hydrogen peroxide liquid	Titration
Heavy metals (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sb, Tl, V)	EN 14385	4,5 % HNO <sub>3</sub> + 1,7 % H <sub>2</sub> O <sub>2</sub>	ICP-AES
Sulfur dioxide (SO <sub>2</sub> )	EN 14791	Hydrogen peroxide liquid	Titration
Hydrogen cyanide (HCN)	SFS 3869	1 M NaOH	Polarography

SFS = Finnish  
VDI= Verein  
EN = European standard produced by CEN

Standards  
Deutscher

Association  
Ingenieure

### 6.1.2 Methods for analysis

a list of typical analytical methods which are used:

- AAS; atomic absorption spectrometry
- HPLC; High-performance liquid chromatography
- GC; Gas chromatography
- ICE; Ion specific electrode
- IC; Ion chromatography
- titration methods
- gravimetric determination
- etc

## 6.2 Adsorption methods

Adsorption is merging or attaching of atoms, ions, or molecules of gas, liquid or dissolved solid substances on a certain area. This process creates an adsorbent film on the surface of the adsorbent.

There are several materials which are used in the adsorption sampling. The most typically used substances are active charcoal, Tenax-hartz, polyuretanfoam (PUF).

Typically for example PCDD/PCDF-components are measured using adsorption techniques.

- PCDDs / PCDFs can form in the combustion of organic materials (e.g. municipal waste incinerators)
- They also occur as undesirable byproducts in the manufacture or further processing of chlorinated organic chemicals
- Universally they are present in very small concentrations
- PCDDs (polychlorinated dibenzodioxins) consist of 75 individual substances (congeners)
- PCDFs (polychlorinated dibenzofurans) consist of 135 congeners
- 17 congeners are necessary to measure to calculate the total I-TEQ (International Toxic Equivalent)

European Standard EN 1948: 2006 specifies the sampling of PCDDs / PCDFs in stationary source emissions. The standard is also suitable for the determination of other low-volatile substances e.g. of dioxin-like PCBs. Standard consists of three parts which are necessary for the performance of the dioxin measurements

- Part 1: Sampling of PCDDs/PCDFs
- Part 2: Extraction and clean-up of PCDDs/PCDFs
- Part 3: Identification and quantification of PCDDs/PCDFs

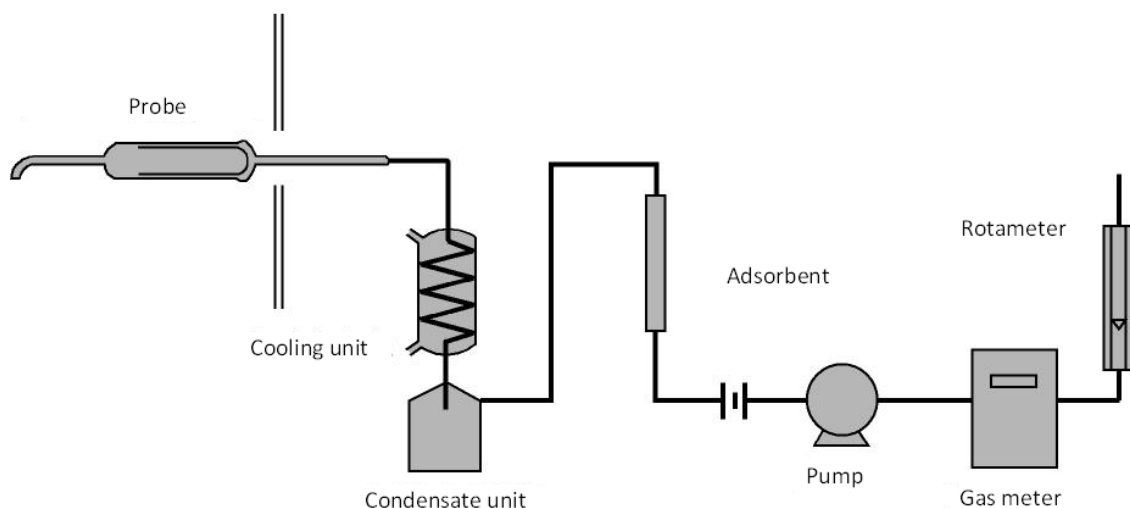




Figure 18. Principle of dioxin and furan sampling

## 7. Emission calculation

### 7.1 Calculation of the gas flow rate in stack according to the Finnish standard SFS 3866

Ratio of the dry gas flow ( $\text{m}^3/\text{s}$ ), NTP

Measurement data:

Gas composition

$$r_{\text{CO}_2} = 0,090 = 9,0 \% \text{ (vol)}$$

$$r_{\text{O}_2} = 0,088\% = 8,8 \% \text{ (vol)}$$

$$r_{\text{CO}} = 0,00 = 0,0 \% \text{ (vol)}$$

$$r_{\text{N}_2} = 0,82 (= 1 - r_{\text{CO}_2} - r_{\text{O}_2} - r_{\text{CO}})$$

-dynamic pressure

(16 measurement points)

$$p_{\text{дин}} = 40 \text{ Pa}, 50 \text{ Pa}, 60 \text{ Pa}, 100 \text{ Pa}, 95 \text{ Pa}, 80 \text{ Pa}, 70 \text{ Pa}, 60 \text{ Pa}, 60 \text{ Pa}, 80 \text{ Pa}, 100 \text{ Pa}, 115 \text{ Pa}, 100 \text{ Pa}, 80 \text{ Pa}, 70 \text{ Pa}, 55 \text{ Pa}$$

- mass of water condensate

$$m_{\text{KB}} = 100 \text{ g}$$

- gas volume

$$\text{achieved with the}$$

measurement rota-meter

$$V_{\text{гр}} = 0,375 \text{ m}^3$$

- ambient pressure

$$p_a = 101,9 \text{ kPa}$$

- under pressure

$$p_{\text{под}} = - 0,3 \text{ kPa}$$

- stack pressure

$$P_o = p_a - p_{\text{под}} = 101,9 \text{ kPa} - 0,3 \text{ kPa} = 101,6 \text{ kPa}$$

- gas temperature in the gas-meter

$$t_{\text{ГМ}} = 27 \text{ }^\circ\text{C}$$

- stack temperature

$$T_o = 131 \text{ }^\circ\text{C}$$

- measurement plane area

$$A = 2,269 \text{ m}^2$$

- water vapor density

$$\rho_{\text{вп}} = 0,8038 \text{ kg/m}^3$$

Calculation in NTP (normal temperature and pressure), 273 K and 101,3 kPa.

Calculation:

a) Dry gas density in standard conditions.

$$\rho_{\text{crey}} = r_{\text{CO}_2} \times \frac{M_{\text{CO}_2}}{V_{\text{CO}_2\text{n}}} + r_{\text{O}_2} \times \frac{M_{\text{O}_2}}{V_{\text{O}_2\text{n}}} + r_{\text{N}_2} \times \frac{M_{\text{N}_2}}{V_{\text{N}_2\text{n}}} \quad (1)$$

$$\Rightarrow \rho_{\text{crey}} = 0,090 \frac{44,01 \text{ kg/kmol}}{22,26 \text{ m}^3 / \text{kmol}} + 0,088 \frac{32,00 \text{ kg/kmol}}{22,39 \text{ m}^3 / \text{kmol}} + 0,82 \frac{28,02 \text{ kg/kmol}}{22,40 \text{ m}^3 / \text{kmol}} = 1,332 \text{ kg/m}^3$$

b) Mass relation between the water and the dry gas

$$x_s = \frac{m_{\text{KB}}}{V_{\text{rp}} \times \rho_{\text{crey}}} = \frac{m_{\text{KB}}}{V_{\text{rp}} \times \frac{T_{\text{H}}}{T_{\text{a}}} \times \frac{p_{\text{a}}}{p_{\text{H}}} \times \rho_{\text{crey}}} \quad (2)$$

$$\Rightarrow x_s = \frac{0,100 \text{ kg}}{0,375 \text{ m}^3 \times \frac{273 \text{ K}}{(273+0) \text{ K}} \times \frac{101,3 \text{ kPa}}{101,3 \text{ kPa}} \times 1,332 \text{ kg/m}^3} = 0,200 \text{ kg/kg}$$

Note! The above mentioned calculation presumes that the values from the roto-meter are already expressed as NTP, therefore there is no need to correct the temperature or pressure!!!

And the dry density of the gas, NTP

$$\rho_{\text{BFH}} = \rho_{\text{crey}} \frac{1 + x_s}{1 + \frac{x_s \times \rho_{\text{crey}}}{\rho_{\text{BH}}}} \quad (3)$$

$$\Rightarrow \rho_{\text{BFH}} = 1,332 \text{ kg/m}^3 \frac{1 + 0,200 \text{ kg/kg}}{1 + \frac{0,200 \text{ kg/kg} \times 1,332 \text{ kg/m}^3}{0,8038 \text{ kg/m}^3}} = 1,201 \text{ kg/m}^3$$

c) Wet gas density in the stack

$$\rho_{\text{BFO}} = \rho_{\text{BFH}} \times \frac{T_{\text{H}}}{T_{\text{c}}} \times \frac{p_{\text{c}}}{p_{\text{H}}} \quad (4)$$

$$\Rightarrow \rho_{\text{BrO}} = 1,201 \text{ kg/m}^3 \times \frac{273 \text{ K}}{(273 + 131) \text{ K}} \times \frac{101,6 \text{ kPa}}{101,3 \text{ kPa}} = 0,814 \text{ kg/m}^3$$

**Wet density is needed for Pitot tube measurements!**

Wet gas velocity in the stack (measured with L-pitot tube)

$$v_{\text{Br}(1-i)} = \sqrt{\frac{2 \times p_{\text{дин}(1-i)}}{\rho_{\text{BrO}}}} \quad (5)$$

$$\Rightarrow v_{\text{Br}1} = \sqrt{\frac{2 \times 40 \text{ kPa}}{0,814 \text{ kg/m}^3}} = 9,91 \text{ m/s} \quad \text{(first point velocity)}$$

Average stack velocity:

$$\bar{v}_{\text{Br}} = \frac{v_{\text{Br}1} + \dots + v_{\text{Br}i}}{n} = 13,53 \text{ m/s}$$

d) Ratio of the wet gas flow in the stack

$$\bar{q}_{\text{Br}} = v_{\text{Br}} \times A \quad (6)$$

$$\Rightarrow \bar{q}_{\text{Br}} = 13,53 \text{ m/s} \times 2,269 \text{ m}^2 = 30,70 \text{ m}^3 / \text{s}$$

e) Ratio of the wet gas flow, NTP

$$\bar{q}_{\text{BFH}} = q_{\text{BF}} \times \frac{T_{\text{H}}}{T_{\text{O}}} \times \frac{p_{\text{O}}}{p_{\text{H}}} \quad (7)$$

$$\Rightarrow \bar{q}_{\text{BFH}} = 30,70 \text{ m}^3 / \text{s} \times \frac{273 \text{ K}}{(273 + 131) \text{ K}} \times \frac{101,6 \text{ kPa}}{101,3 \text{ kPa}} = 20,81 \text{ m}^3 / \text{s}$$

f) Ratio of the dry gas flow, NTP

$$\bar{q}_{\text{GFH}} = \bar{q}_{\text{BFH}} \times \frac{1}{1 + \frac{x_{\text{s}} \times \rho_{\text{crey}}}{\rho_{\text{BFH}}}} \quad (8)$$

$$\Rightarrow \bar{q}_{\text{GFH}} = 20,81 \text{ m}^3 / \text{s} \times \frac{1}{1 + \frac{0,200 \text{ kg/kg} \times 1,332 \text{ kg/m}^3}{1,201 \text{ kg/m}^3}} = 15,63 \text{ m}^3 / \text{s}$$

7.2 Calculation of the particulates and the emission according to the Finnish standard SFS 3866

**Particulate concentration, mg/m<sup>3</sup>, NTP**

**Particulate emission, g/h**

Measurement data:

- particulate mass (including the deposition)	m = 5,30 mg
- gas temperature in the gas meter	t <sub>ΓM</sub> = 27 °C
- data taken from the gas meter	V <sub>ΓM</sub> = 1,346 m <sup>3</sup>
- ambient pressure	P <sub>a</sub> = 101,9 kPa (= p <sub>a</sub> )
- sampling duration	T = 48 min
- ratio of the dry gas flow	$\bar{q}_{\text{GFH}}$ = 15,63 m <sup>3</sup> /s

Calculation in NTP (normal temperature and pressure), 273 K and 101,3 kPa.

Calculation:

g) Sampled dry gas volume, NTP

$$V_{\text{cr}} = V_{\text{ΓM}} \times \frac{T_{\text{H}}}{T_{\text{ΓM}}} \times \frac{p_{\text{a}}}{p_{\text{H}}} \quad (9)$$

$$\Rightarrow V_{\text{cr}} = 1,346 \text{ m}^3 \times \frac{273 \text{ K}}{(273 + 27) \text{ K}} \times \frac{101,9 \text{ kPa}}{101,3 \text{ kPa}} = 1,232 \text{ m}^3$$

Particulate concentration in the dry gas, NTP

$$c_{\text{crH}} = \frac{m}{V_{\text{cr}}} \quad (10)$$

$$\Rightarrow c_{\text{crH}} = \frac{5,3 \text{ mg}}{1,232 \text{ m}^3} = 4,3 \text{ mg/m}^3$$

Emission of particulates in stack

$$q_o = c_{\text{crH}} \times \bar{q}_{\text{crH}} \quad (11)$$

$$\Rightarrow q_o = 4,3 \text{ mg/m}^3 \times 15,63 \text{ m}^3 / \text{s} = 67,21 \text{ mg/s} = 242 \text{ g/h}$$

*For particulate concentration, for more than one gas sample (and filtration) in the measurement plane*

$$\bar{C}_{\text{crH}} = \frac{\sum_{i=1}^k m_i}{\sum_{i=1}^k V_{\text{cri}}} \quad (12)$$

where

$m_i$  particulate mass [g] on filter + deposition  
 $V_{\text{cri}}$  sampled dry gas volume, NTP [m<sup>3</sup>] during sampling

*(isokinetic sampling and sampling duration at each measurement point is the same)*

To ensure the calculated emission

$$q_{\text{осигурање}} = \frac{A_{\text{пмп}}}{A_{\text{пн}}} \times \frac{m}{T} \quad (13)$$

where

$q_e$  = particulate emission = 242 g/h (calculated normally)  
 $A_{\text{пмп}}$  = measurement plane area = 2,269 m<sup>2</sup>  
 $A_{\text{пн}}$  = nozzle area =  $\pi d^2 / 4 = 3,14 \times 0,0084^2 / 4 = 0,0000554 \text{ m}^2$   
 $m$  = sampled particulate + deposit = 3,5 mg = 0,00350 g  
 $T$  = sampling duration = 48 min

$$\Rightarrow q_{\text{осигурање}} = \frac{2,269 \text{ m}^2}{0,0000554 \text{ m}^2} \times \frac{0,00530 \text{ g}}{48 \text{ min}} \times 60 \frac{\text{min}}{\text{h}} = 271,4 \frac{\text{g}}{\text{h}}$$

factors to consider in isokinetic sampling

$$q_{\text{осигурање, корегиран}} = \frac{q_{\text{осигурање}}}{k} \quad (14)$$

Where

k = isokinetic ratio (in this example k = 1,12)

$$\Rightarrow q_{\text{осигурање, корегиран}} = \frac{271,4 \text{ g}}{1,12 \text{ h}} = 242 \frac{\text{g}}{\text{h}}$$

**The emission result is same as calculated normal way!**

### 7.3 Changes between different gas component units

Gas density

$$c_{\text{mg/m}^3} = c_{\text{ppm}} \times \frac{M}{22,4} \quad (15)$$

where

$$\begin{array}{llll} c_{\text{mg/m}^3} & = & \text{concentration} & \text{in units mg/m}^3 \\ c_{\text{ppm}} & = & \text{concentration in units ppm} & \\ M & = & \text{molar mass (g/mol)} & \end{array}$$

Volume of ideal gases 22,4 m<sup>3</sup>/kmol (NTP; 101,3 kPa, 0 °C)

### 7.4 Conversions between dry and wet concentrations and standardisation to reference oxygen concentration

Wet concentration in dry concentrations:

$$c_{\text{сув}} = \frac{c_{\text{влажн}}}{1 - \frac{c_{\text{H}_2\text{O}}}{100}} \quad (16)$$

where

$c_{\text{влажн}}$  = we concentrations  
 $c_{\text{H}_2\text{O}}$  = water vapor (%)vol.

Dry concentrations in wet concentrations:

$$c_{\text{влажн}} = c_{\text{сув}} \times \left(1 - \frac{c_{\text{H}_2\text{O}}}{100}\right) \quad (17)$$

Where we appropriately refer the concentration to specific concentration gas component of gas mixture for example oxygen concentration.

$$c_{\text{O}_2 - \text{редукция}} = c_{\text{сув}} \times \frac{20,9 - \text{O}_{2, \text{селектиран}}}{20,9 - \text{O}_{2, \text{измерен}}} \quad (18)$$

## 8. Calculation of measurement uncertainty

A National Physical Laboratory NPL-document “A beginner’s guide to uncertainty of measurements” introduces the subject of measurement uncertainty. Below you can find text from this document describing for example the sources of uncertainties, as well as types of uncertainties.

Many things can undermine a measurement (Bell, Stephanie, 2001, NPL). Flaws in the measurement may be visible or invisible. Because real measurements are never made under perfect conditions, errors and uncertainties can come from:

- **The measuring instrument** - instruments can suffer from errors including bias, changes due to ageing, wear, or other kinds of drift, poor readability, noise (for electrical instruments) and many other problems.
- **The item being measured** - which may not be stable. (Imagine trying to measure the size of an ice cube in a warm room.)
- **The measurement process** - the measurement itself may be difficult to make. For example, measuring the weight of small but lively animals presents particular difficulties in getting the subjects to co-operate.
- **“Imported” uncertainties** - calibration of your instrument has an uncertainty which is then built into the uncertainty of the measurements you make. (But remember that the uncertainty due to not calibrating would be much worse.)
- **Operator skill** - some measurements depend on the skill and judgement of the operator. One person may be better than another at the delicate work of setting up a measurement, or at reading fine detail by eye. The use of an

instrument such as a stopwatch depends on the reaction time of the operator. (But gross mistakes are a different matter and are not to be accounted for as uncertainties).

- **Sampling issues** - the measurements you make must be properly representative of the process you are trying to assess. If you want to know the temperature at the work-bench, don't measure it with a thermometer placed on the wall near an air conditioning outlet. If you are choosing samples from a production line for measurement, don't always take the first ten made on a Monday morning.
- **The environment** - temperature, air pressure, humidity and many other conditions can affect the measuring instrument or the item being measured

The effects that give rise to uncertainty in measurement can be either:

- *random* - where repeating the measurement gives a randomly different result. If so, the more measurements you make, and then average, the better estimate you generally can expect to get or
- *systematic*- where the same influence affects the result for each of the repeated measurements (but you may not be able to tell). In this case, you learn nothing extra just by repeating measurements. Other methods are needed to estimate uncertainties due to systematic effects, e.g. different measurements, or calculations

There are two approaches to estimating uncertainties: 'Type A' and 'Type B' evaluations. In most measurement situations, uncertainty evaluations of both types are needed.

- Type A evaluations - uncertainty estimates using statistics (usually from repeated readings)
- Type B evaluations - uncertainty estimates from any other information. This could be information from past experience of the measurements, from calibration certificates, manufacturer's specifications, from calculations, from published information, and from common sense.

From NPL (National Physical Laboratory) - webpages you can find some excel-sheets where calculation examples for gaseous components and particulates are given. Here is the web-address .

<http://www.npl.co.uk/environmental-measurement/products-and-services/emissions-measurement-guidance-and-training>

In the appendix II you can find examples of NPL calculation sheets as well as an example on the calculation of the measurement uncertainty for gaseous analyser with the use of EN ISO 14956 standard.



## 9. Reporting of emission measurements

### 9.1 Reporting of the emission measurement teams

The working team performing the measurements prepares a report for all activities according to the measurement plan. The working team hands over the report to the responsible person in the laboratory. That person verifies the report and sends it to the installation and the competent authorities.

### 9.2 Reporting of the emission data by the installations

The reporting of the installations that are sources of ambient air pollution towards MEPP is defined in article 45 of the Law on ambient air quality (Official gazette of RM num 67/2004, 92/2007, 35/2010, 47/2011). In this article the frequency of data submission to MEPP by installations as well as manner on which emission data are gained is defined.

The form and content of the forms for submitting data of emissions in the ambient air from stationary sources, the manner and the time period for submission in accordance with the capacity of the installation, the content and manner of keeping the emission diary are prescribed in the Rulebook on the form and the content of the forms for submitting data and the form, the content and the manner for keeping the diary for emissions in the air (Official gazette of RM num 79/2011) which is available on the following web side [www.moepp.gov.mk](http://www.moepp.gov.mk).

### 9.3 International reporting by MEPP

The emission data reported by the installations (previous chapter) are used and will be used for international reporting by MEPP.

Type of reporting	Legal acts	Institution	Deadline	Web page of available report	Available reports
<b>CLRTAP reporting</b>	Ratified CLRTAP convention	CLTRP	15.02 each year for the year-2	<a href="http://cdr.eionet.europa.eu/">http://cdr.eionet.europa.eu/</a>	From 2003

Ratified Gothenburg protocol			
<b>LCP reporting</b>	EU	1 January each year	<a href="http://cdr.eionet.europa.eu/">http://cdr.eionet.europa.eu/</a>
<b>NEC reporting</b>	EEA	31 March each year	<a href="http://cdr.eionet.europa.eu/">http://cdr.eionet.europa.eu/</a>

## 10. Standardisation of emission measurement

The focus areas of TC17-Air quality are methods for air quality characterization of emissions, ambient air, indoor air- gases in and from the ground and deposition- in particular measurement methods for air pollutants (for example particles, gases, odours, micro organisms) - methods for the determination of the efficiency of gas cleaning systems. TC17 committee consist of 7 members (from the relevant institutions IPH and HMA and the major industries) under leadership of MEEP. The duty of this committee is to translate the standards titles and adopt the air quality and air emission standards by the method of endorsement. Regarding the different types of standards in EU Member Countries it is mandatory to use EN-standards if they are available. In case, EN-standards do not exist, it is allowed to use ISO-standards if they exist. In non candidate countries the both type of standards for emission measurements are used. The national standards are also allowed to be used. However, it must be ensured that the data will have equivalent scientific quality when other than EN-methods are used. The list of the adopted MKC EN emission standards and MKC ISO emission standards by the TK17 that we refer to in this guidebook are specified in Annex of the Rulebook, as well as Technical Specifications (TS)- and Technical References (TR)- referred in this guidelines are given in Annex I of this guidelines. The updated list of standards and information how to purchase them is available on the following web side of the institute for standardisation of the Republic of Macedonia [www.isrm.gov.mk](http://www.isrm.gov.mk).

## REFERENCES

A beginner's guide to uncertainty of measurement, Stephanie Bell, Centre for Basic, Thermal and Length Metrology, National Physical Laboratory, NPL, Measurement Good Practice Guide No. 11 (Issue 2), 41 p., 2001

Finnish Handbook on Emission Measurements, 2004, 57 p. + appendices, <http://www.isy.fi/osa1.pdf>

## ANNEX I

### MKC EN emission standards

**EN 1911-1:1998-04** Air quality – Stationary source emissions – Manual method of determination of HCl – Part 1: Sampling of gases

**EN 1911-2:1998-04** Air quality – Stationary source emissions – Manual method of determination of HCl – Part 2: Gaseous compounds absorption

**EN 1911-3:1998-04** Air quality – Stationary source emissions – Manual method of determination of HCl – Part 3: Absorption solution analysis and calculations

**EN 1948-1:2006-03** Stationary source emissions – Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs - Part 1: Sampling of PCDDs/PCDFs

**EN 1948-2:2006-03** Stationary source emissions – Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs – Part 2: Extraction and clean-up of PCDDs/PCDFs

**EN 1948-3:2006-03** Stationary source emissions – Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs – Part 3: Identification and quantification of PCDDs/PCDFs

**EN 12619:1999-06** Stationary source emissions – Determination of the mass concentration of total gaseous organic carbon at low concentrations in flue gases – Continuous flame ionisation detector method

**EN 13211:2001-01** Air quality - Stationary source emissions - Manual method of determination of the concentration of total mercury

**EN 13284-1:2001-11** Stationary source emissions – Determination of low range mass concentration of dust – Part 1: Manual gravimetric method

**EN 13284-2:2004-09** Stationary source emissions – Determination of low range mass concentration of dust – Part 2: Automated measuring systems

**EN 13526:2001-11** Stationary source emissions – Determination of the mass concentration of total gaseous organic carbon at high concentrations in flue gases – Continuous flame ionisation detector method

**EN 13649:2001-11** Stationary source emissions – Determination of the mass concentration of individual gaseous organic compounds – Activated carbon and solvent desorption method

**EN 13725:2003-04** Air quality – Determination of odour concentration by dynamic olfactometry

**EN 13725:2003/AC** Corrigendum of EN 13725:2003

**EN 14181:2004-07** Stationary source emissions – Quality assurance of automated measuring systems

**EN 14385:2004-02** Stationary source emissions – Determination of the total emission of As, Cd, Cr, Co, Cu, Mn, Ni, Pb, Sb, Tl and V

**EN 14789:2005-11** Stationary source emissions – Determination of volume concentration of oxygen (O<sub>2</sub>) – Reference method – Paramagnetism

**EN 14790:2005-11** Stationary source emissions – Determination of the water vapour in ducts

**EN 14791:2005-11** Stationary source emissions – Determination of mass concentration of sulphur dioxide – Reference method

**EN 14792:2005-11** Stationary source emissions – Determination of mass concentration of nitrogen oxides (NO<sub>x</sub>) – Reference method: Chemiluminescence

**EN 14884:2005-12** Air quality – Stationary source emissions – Determination of total mercury: Automated measuring systems

**EN 15058:2006-05** Stationary source emissions – Determination of the mass concentration of carbon monoxide (CO) – Reference method: Nondispersive infrared spectrometry

**EN 15259:2007-10** Air quality – Measurement of stationary source emissions – Requirements for measurement sections and sites and for the measurement objective, plan and report

**EN 15267-1:2009-03** Air quality – Certification of automated measuring systems – Part 1:

**EN 15267-2:2009-03** Air quality – Certification of automated measuring systems – Part 2: Initial assessment of the AMS manufacturer's quality management system and post certification surveillance for the manufacturing process

**EN 15267-3:2007-12** Air quality – Certification of automated measuring systems – Part 3: Performance criteria and test procedures for automated measuring systems for monitoring emissions from stationary sources

**EN 15445:2008-01** Fugitive and diffuse emissions of common concern to industry sectors – Qualification of fugitive dust sources by Reverse Dispersion Modelling

**EN 15446:2008-01** Fugitive and diffuse emissions of common concern to industry sectors – Measurement of fugitive emission of vapours generating from equipment and piping leaks

## **MKC ISO emission standards**

**EN ISO 23210:2009-08** Stationary source emissions – Determination of PM10/PM2,5 mass concentration in flue gas – Part 1: Measurement at low concentrations by use of impactors (ISO 23210:2009)

**EN ISO 14956:2002-08** Air quality – Evaluation of the suitability of a measurement method by comparison with a stated measurement uncertainty (ISO 14956:2002)

**EN ISO 9169:2006-07** Air quality – Definition and determination of performance characteristics of an automatic measuring system (ISO 9169:2006)

**ISO 10780** Stationary source emissions – measurement of velocity and volume flow rate of gas streams in ducts;

**ISO 9096 Stationary source emissions** – Manual Determination of Mass Concentration of Particulate Matter;

**ISO 12039 Stationary source emissions**-Determination of carbon monoxide, carbon dioxide and oxygen – Performance characteristics and calibration of automated measuring systems;

**ISO 7935 Stationary source emissions**-Determination of the mass concentration of sulphur dioxide – Performance characteristics of automated measuring methods;

**ISO 10849 Stationary source emissions**- Determination of the mass concentration of nitrogen oxides – Performance characteristics of automated measuring methods.

## **Technical specifications**

**CEN/TS 15675:2007-10** Air quality – Measurements of stationary source emissions – Application of EN ISO/IEC 17025:2005 to periodic measurements

**CEN/TR 15983:2010-01** Stationary source emissions – Guidance on the application of EN 14181:2004

**CEN/TS 15674:2007-10** Air quality – Measurement of stationary source emissions – Guidelines for the elaboration of standardised methods

**CEN/TS 14793:2005-03** Stationary source emissions – Intralaboratory validation procedure for an alternative method compared to a reference method

**CEN/TS 1948-4:2007-07** Stationary source emissions – Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs – Part 4: Sampling and analysis of dioxin-like PCBs

## **ANNEX II**

NPL- Spreadsheets for uncertainty calculations in accordance with the referred standards

According to the requirements laid down in the standard MKC EN 13284

Uncertainty calculation for EN 13284 Determination of low range mass concentration of dust, Manual Gravimetric Method					Users of this spreadsheet should validate their own calculations				
v10	Draft								
Limit value	10	mg.m <sup>-3</sup>	Reference oxygen	11	% by volume	Measurement Equation			
Measured concentration	9.74	mg.m <sup>-3</sup>				$c = \frac{m}{V} f_c$			
Measured Quantities	Symbol	Value	Standard uncertainty	Units	Uncertainty as percentage	Uncertainty at lv	Requirement of std		
Sampled Volume	V <sub>m</sub>	0.5	uV <sub>m</sub>	0.001 m <sup>3</sup>	0.20		<=2%		
Sampled gas Temperature	T <sub>m</sub>	299	uT <sub>m</sub>	2 K	0.67		<=1%		
Sampled gas Pressure	p <sub>m</sub>	101.3	up <sub>m</sub>	1 kPa	0.99		<=1%		
Sampled gas Humidity	H <sub>m</sub>	0	uH <sub>m</sub>	1 % by volume	1.00		<=1%		
Oxygen content	O <sub>2,m</sub>	12	uO <sub>2,m</sub>	0.1 % by volume	0.83		<=5%		
Mass particulate	m	4	um	0.1 mg	2.50	2.43	<5% of limit value		
Note - Sampled gas humidity, temperature and pressure are values at the gas meter									
Leak	L	2		%	2.00		<=2%		
Uncollected Mass	UCM	0		mg	0		<=10%		
(Instack filter - no rinse)									
Intermediate calculations									
Factor for std cond	fs	0.91							
uncertainty components	symbol	sensitivity coeff	u (in units of fs)						
	p <sub>m</sub>	0.009	0.009						
	H <sub>m</sub>	0.009	0.009						
	T <sub>m</sub>	0.003	0.006						
	ufs		0.014			1.56			
Corrected volume	V	0.46	uV	0.007 m <sup>3</sup>					
						1.57			
Factor for O2 correction	fc	1.11							
uncertainty components	symbol	sensitivity coeff	u						
	O <sub>2,m</sub>	0.12	0.012						
Factor for O2 Correction	ufc	1.11	0.012			1.11			
Parameter	Uncertainty, Value	Units	Sensitivity coeff	Uncertainty in Result	Uncertainty as %				
Volume(standard conditions)V		0.46 m <sup>3</sup>	21.33	0.15 mg.m <sup>-3</sup>	1.57 %				
Mass	m	4.00 mg	2.43	0.24 mg.m <sup>-3</sup>	2.50				
Factor for O2 Correction	fc	1.11	8.76	0.11 mg.m <sup>-3</sup>	1.11 %				
Leak	L	0.11 mg.m <sup>-3</sup>	1.00	0.11 mg.m <sup>-3</sup>					
Uncollected mass	UCM	0.00 mg	2.43	0.00 mg.m <sup>-3</sup>					
Combined uncertainty				0.33 mg.m <sup>-3</sup>					
Expanded uncertainty	expressed with a level of confidence of 95%		6.72	%					
Expanded uncertainty	expressed with a level of confidence of 95%		0.65	mg.m <sup>-3</sup>					
Note:	Enter values into green boxes								

According to the requirements laid down in the standard MKC EN 14789

Uncertainty calculation for Gaseous Measurement Oxygen prEN14789					Users of this spreadsheet should validate their own calculations				
v1	Draft								
Limit value		%vol	Calibration gas	12	%vol				
Measured concentration	11.00	%vol	Full Scale	100	%vol				
Performance characteris	Value			specification					
Response time	120	seconds		180					
Number of readings in measurement	60								
Repeatability at zero	0.15	% by volume	stdev						
Repeatability at span level	0.8	% by volume	stdev						
Deviation from linearity	2	% of value	+/-						
Zero drift	0.1	% vol at zero level	+/-	<2% of value					
Span drift	0.1	% vol at span level	+/-						
volume or pressure flow dependence	0.5	% of fs / 10l/h	+ 5 l/h	<1% range	flow	min	5	15	10
atmospheric pressure dependence	0.2	% of fs/kPa	+ 2kPa	< 1.5 % range	pressure	99.00	100	100	
ambient temperature dependence	0.3	% by volume /10K	+ 15K	<3% volume 10 K	temp	283	308	285	
CO2 (10%)	0.003	% by volume			CO2 range	8	15	0	
NO(300)	0.05	% by volume			NO range	300	400	0	
NO2(30)	0.02	% by volume			NO2 range	5	7.5	0	
dependence on voltage	0.1	% by volume /10V	+ 5%	< 0.1%vol /10 volt	Voltage	218.5	241.5	240	
losses in the line (leak)	2	% of value							
Uncertainty of calibration gas	0.5	% of value							
Measurement performance related to stationary conditions									
Performance characteristic	Uncertainty		Value of uncertainty quantity						
Standard deviation of repeatability at zero	u <sub>0</sub>		for mean		just use rep at span				
Standard deviation of repeatability at span level	u <sub>s</sub>		for mean		0.10				
Lack of fit	u <sub>fit</sub>				0.13				
Drift	u <sub>dr</sub>				0.11				
volume or pressure flow dependence	u <sub>ppres</sub>				0.14				
atmospheric pressure dependence	u <sub>apres</sub>				0.12				
ambient temperature dependence	u <sub>temp</sub>				0.38				
CO2 (15%)					0.00				
NO(300)					0.06				
NO2(30)					0.00				
dependence on voltage	u <sub>volt</sub>				0.12				
losses in the line (leak)	u <sub>leak</sub>				0.13				
Uncertainty of calibration gas	u <sub>calib</sub>				0.03				
Measurement uncertainty	Result	11.00	%vol						
Combined uncertainty		0.51	%vol						
% of value		4.59	%						
Expanded uncertainty	expressed with a level of confidence of 95%	9.19	% of value						
Expanded uncertainty	expressed with a level of confidence of 95%	1.01	% vol						
Note:	Enter values into green boxes								
	Dark blue boxes indicate information that can be obtained from MCERTS tests								

According to the requirements laid down in the standard MKC EN 14792

Uncertainty calculation for Gaseous Measurement EN 14792 Nox				Users of this spreadsheet should validate their own calculations																																	
v4	Draft																																				
Limit value	100	mg.m <sup>-3</sup> (corrected) NO2	Gas	NO	<table><tr><th colspan="5">Correction for reference conditions</th></tr><tr><td></td><td>02, %</td><td>Moisture, %</td><td>Pressure, KPa</td><td>Temperature, K</td></tr><tr><td>ref</td><td></td><td></td><td>101.30</td><td>273.0</td></tr><tr><td>measured</td><td></td><td></td><td>101.30</td><td>273.0</td></tr><tr><td>Factors</td><td>1.00</td><td>1.00</td><td>1.00</td><td>1.0</td></tr><tr><td>Correction Factor</td><td>1.00</td><td></td><td></td><td></td></tr></table>			Correction for reference conditions						02, %	Moisture, %	Pressure, KPa	Temperature, K	ref			101.30	273.0	measured			101.30	273.0	Factors	1.00	1.00	1.00	1.0	Correction Factor	1.00			
Correction for reference conditions																																					
	02, %	Moisture, %	Pressure, KPa	Temperature, K																																	
ref			101.30	273.0																																	
measured			101.30	273.0																																	
Factors	1.00	1.00	1.00	1.0																																	
Correction Factor	1.00																																				
Measured concentration	15.00	ppm	Full Scale	100	ppm																																
Measured concentration	30.75	mg.m <sup>-3</sup> (273K, 101.3kPa) NO2	Cal gas conc	80	ppm																																
Ratio NO/NO2	5.00		Conversion	2.05																																	
			Full Scale	205	mg.m <sup>-3</sup> (NO2)																																
			Cal gas conc	164	mg.m <sup>-3</sup> (NO2)																																
Performance characteristics		Value		specification																																	
Response time		60	seconds	180.000																																	
Number of readings in measurement		120																																			
Repeatability at zero		0.15	% full scale	0.200																																	
Repeatability at span level		0.8	% full scale	2.000																																	
Deviation from linearity		0.4	% of value	2.000																																	
Zero drift		0.01	% full scale	2.000																																	
Span drift		1	% full scale	2.000																																	
volume or pressure flow dependence		0.02	% of full scale/kPa	0.033																																	
atmospheric pressure dependence		0.8	% of value/kPa	0.750																																	
ambient temperature dependence		0.01	% full scale/10K	0.300																																	
NH3 (20 mg/m3)		1.2	mg/m3																																		
CO2 (15%)		1.2	% by vol																																		
H2O (30%)		1.2	% by vol	4.000																																	
dependence on voltage		0.1	% full scale/10V	2.000/10V																																	
converter efficiency		95	%	95%																																	
losses in the line (leak)		2	% of value	2% of value																																	
Uncertainty of calibration gas		2	% of value																																		
Measurement performance related to stationary conditions																																					
Performance characteristic		Uncertainty		Value of uncertainty quantity																																	
Standard deviation of repeatability at zero		U <sub>0</sub>		for mean	use rep at span																																
Standard deviation of repeatability at span level		U <sub>2</sub>		for mean	0.07																																
Lack of fit		U <sub>fit</sub>			0.47																																
Drift		U <sub>dr</sub>			0.19																																
volume or pressure flow dependence		U <sub>pres</sub>			0.00																																
atmospheric pressure dependence		U <sub>atm</sub>			0.19																																
ambient temperature dependence		U <sub>temp</sub>			0.00																																
NH3 (20 mg/m3)		U <sub>inh</sub>			0.00																																
CO2 (15%)					0.02																																
H2O (30%)					0.01																																
Dependence on voltage		U <sub>v</sub>			0.03																																
Converter efficiency		U <sub>eff</sub>			0.04																																
losses in the line (leak)		U <sub>leak</sub>			0.36																																
Uncertainty of calibration gas		U <sub>calib</sub>			0.36																																
Measurement uncertainty		Result	30.75	mg/m <sup>3</sup>																																	
Combined uncertainty			0.75	mg/m <sup>3</sup>																																	
Expanded uncertainty		k = 2	1.49	mg/m <sup>3</sup>																																	
Uncertainty corrected to std conds			1.49	mg.m-3 (corrected)																																	
Expanded uncertainty		expressed with a level of confidence of 95%	1.49	% ELV																																	
Expanded uncertainty		expressed with a level of confidence of 95%	1.49	mg.m-3 at ELV																																	

## ISO 14956, "EVALUATION OF THE SUITABILITY OF A MEASUREMENT PROCEDURE BY COMPARISON WITH A REQUIRED MEASUREMENT UNCERTAINTY" (1)

Combined standard uncertainty is sum of all partial standard uncertainties:

$$u_c = \sqrt{\sum_p u_p^2}$$

where  $u_p$  = partial standard uncertainty

For example



$$u_c = \sqrt{u_{lin}^2 + u_r^2 + u_d^2 + u_t^2 + u_p^2 + u_{hv}^2 + u_k^2 + u_{cal}^2}$$

where  $u_{lin}$  = the standard uncertainty of the nonlinearity of the analyser  
 $u_r$  = the standard uncertainty of the repeatability  
 etc....

PRINCIPLES OF ISO14956 (2)

**The expanded uncertainty is:**

$$U_c = k \cdot u_c$$

Where

- $k$  = the coverage factor (= 2 (normal distribution, 95 % confidence level of))
- $u_c$  = combined standard uncertainty

PRINCIPLES OF ISO14956 (3)

The upper and lower bounds of deviations of an influence quantity are known, the standard uncertainty can be calculated:

where  $\Delta x_{j,p}$  = maximum positive difference of  $x_j$  between measurement and corresponding calibration  
 $\Delta x_{j,n}$  = maximum negative difference of  $x_j$  between measurement and corresponding calibration

Here it is assumed that the probability distribution function is uniform

Often this calculation formula is used for such parameters which might vary during measurements (such as temperature, selectivity etc...)

PRINCIPLES OF ISO14956 (4)

Example: the interfering effect of NO to O<sub>2</sub>-measurement:

- fluctuation of NO-concentration in the sample gas: 100 – 150 mg/m<sup>3</sup>
- studied in the laboratory that 300 mg/m<sup>3</sup> NO has an effect of + 0,05 % (abs.) to O<sub>2</sub>-results

=> equation (1) is applied here:

$$\frac{0,05}{300} \times \sqrt{\frac{150^2 + 150 \times 100 + 100^2}{3}} = 0,021$$

The interfering gases can have either a positive or negative impact to the result. When calculating the uncertainty, these parameters are taken into account following:

- calculate all standard uncertainties
- sum all standard uncertainties of interferences with positive impact
- sum all standard uncertainties of interferences with negative impact
- retain the highest sum as the representative value for all interferences

## PRINCIPLES OF ISO14956 (5)

If the extremes are symmetric about zero, standard uncertainty can be presented as:

$$u(x_j) = \frac{\Delta x_{j,p}}{\sqrt{3}}$$

Performance characteristic that is not able to create a standard uncertainty of more than 20% of the highest standard uncertainty of the others may be excluded from the selections

## EXAMPLE OF CALCULATION OF MEASUREMENT UNCERTAINTY ACCORDING TO ISO 14956 (1)

Measurement range: 0 – 100 ppm CO

Measured value: 70 ppm CO

Environmental conditions during the measurements:

- temperature (at the measurement site) during the calibration: 25 °C
- variation of the temperature during the measurements: 5 °C
- barometric pressure during calibration: 99 kPa
- variation of barometric pressure during measurements: 0,5 kPa
- calibration gas and its accuracy: 80 ppm CO ± 2 % (rel.)

## EXAMPLE OF CALCULATION OF MEASUREMENT UNCERTAINTY ACCORDING TO ISO 14956 (2)

Performance characteristics_	Obtained	value
- Non-linearity	± 2% of range	
- Pressure dependence	± 1% / kPa	
- Drift	1 % of range / 8h	
- Temperature dependence	± 0,3% / °C	
- Repeatability standard deviation	0,5 % of reading	
- Uncertainty of calibration gas	2 % of reading	
- Drying of sample gas	2 % of reading	
- Selectivity (gas interferences)	1 % of range	

## EXAMPLE OF CALCULATION OF MEASUREMENT UNCERTAINTY ACCORDING TO ISO 14956 (3)

Performance characteristics		$u_p$	$u_p^2$
Non-linearity	$\frac{2}{100} \times \frac{100}{\sqrt{3}} =$	1,15	1,33
Pressure dependence	$\frac{1}{100} \times 0,5 \times \frac{70}{\sqrt{3}} =$	0,20	0,04
Drift	$\frac{1}{100} \times \frac{100}{\sqrt{3}} =$	0,58	0,33

Temperature dependence	$\frac{0,3}{100} \times 5 \times \frac{70}{\sqrt{3}} =$	0,61	0,37
Repeatability	$\frac{0,5}{100} \times \frac{70}{\sqrt{3}} =$	0,20	0,04
Uncertainty of calibration gas	$\frac{2}{100} \times \frac{70}{2} =$	0,70	0,49
Drying of sample gas	$\frac{2}{100} \times \frac{70}{\sqrt{3}} =$	0,81	0,65
Selectivity (interfering gases)	$\frac{1}{100} \times \frac{100}{\sqrt{3}} =$	0,58	0,33
<b>SUM</b>		<b>3,68 ppm</b>	

#### EXAMPLE OF CALCULATION OF MEASUREMENT UNCERTAINTY ACCORDING TO ISO 14956 (4)

The combined uncertainty is thus:

$$u_c = \sqrt{1,15^2 + 0,58^2 + 0,61^2 + 0,70^2 + 0,81^2 + 0,58^2}$$

$$= 1,87 \text{ ppm}$$

The expanded uncertainty  $U_c = 2 \times u_c = 3,74 \text{ ppm}$

Note! The effect of pressure dependence and repeatability is not taken into account in the calculations because their uncertainties are below 20 % of the highest standard uncertainty

#### EXAMPLE OF CALCULATION OF MEASUREMENT UNCERTAINTY ACCORDING TO ISO 14956 (5)

When calculating if the analyser fulfills the criteria which is set for it, the relative expanded uncertainty is calculated at the selected concentration.

For example, emission limit value is  $200 \text{ mg/m}^3 (=c)$  and previously calculated expanded uncertainty was  $= 3,74 \text{ ppm} \Rightarrow 1,25 \times 3,74 = 4,67 \text{ mg/m}^3$  (conversion factor :  $1 \text{ ppm CO} = 1,25 \text{ mg/m}^3$ )

=>                      Relative                      expanded                      uncertainty                      is                      thus:  
 $= (U_c/c) \times 100 \% = 2,3 \%$

