

## Air Quality Reference Centre and the Hungarian Air Quality Monitoring Network

### General:

In Hungary, compliance of the air quality levels and air pollution limits are officially investigated by only the Hungarian Air Quality Monitoring Network (306/2010. (XII. 23.) Government regulation 9§ (1))

The Hungarian Air Quality Monitoring Network provides current and historical air quality monitoring data nationwide. The network consists of two major parts: automatic monitoring stations with continuous measure of wide range of air pollutants in ambient air, and manual system with sampling points and consecutive laboratory analysis.

All instruments are complied (or equivalent with) the EU reference measurement methods in the Hungarian Air Quality Monitoring Network:

- **MSZ EN 12341:2014** Ambient air. Standard gravimetric measurement method for the determination of the PM<sub>10</sub> or PM<sub>2,5</sub> mass concentration of suspended particulate matter
- **MSZ ISO 12884:2003** Ambient air. Determination of total (gas and particle-phase) polycyclic aromatic hydrocarbons. Collection on sorbent-backed filters with gas chromatographic/mass spectrometric analyses
- **MSZ EN 14211:2013** Ambient air. Standard method for the measurement of the concentration of nitrogen dioxide and nitrogen monoxide by chemiluminescence
- **MSZ EN 14212:2013** Ambient air. Standard method for the measurement of the concentration of sulphur dioxide by ultraviolet fluorescence Ambient air. Standard method for the measurement of the concentration of sulphur dioxide by ultraviolet fluorescence
- **MSZ EN 14625:2013** Ambient air. Standard method for the measurement of the concentration of ozone by ultraviolet photometry
- **MSZ EN 14626:2013** Ambient air. Standard method for the measurement of the concentration of carbonmonoxide by non-dispersive infrared spectroscopy
- **MSZ EN 14662-3:2005** Ambient air. Standard method for the measurement of benzene concentrations. Part3: Automated pumped sampling with in situ gas chromatography
- **MSZ EN 14902:2006** Ambient air quality. Standard method for the measurement of Pb, Cd, As and Ni in the PM<sub>10</sub> fraction of suspended particulate matter

The web page ([www.levegominoseg.hu](http://www.levegominoseg.hu)) contains data from automatic network within one/some hours (historical data back to 2004). Data from manual system are updated at least every quarter years (historical data back to 2002). There are also annual assessment reports for both systems as well as for particulate matter (PM<sub>10</sub>) components (now only in Hungarian).

The tasks of the **Air Quality Reference Centre** (Department of the Hungarian Meteorological Service) is also regulated by the 306/2010 Government regulation 9§ (2) and other legislation.

The Air Quality Reference Centre as a calibration laboratory has been registered by the National Accreditation Board

The main tasks of the National Air Quality Reference Centre and Laboratory:

- Management of the Hungarian Air Quality Monitoring Network (HAQM) operation according to the requirements of the Ministry of Agriculture.
- Coordination and regulation of the used methods and procedures in the HAQM according to the EU legislation.
- Determining the QA/QC aims for the HAQM and checking these.
- Ensure the traceability of the measurements with operating an accredited Calibration Laboratory.
- Participation in the national and international standardisation.
- Participation in the work of the international organisation of the National Reference Centers (AQUILA).
- Collection, validation and evaluation of the data from the HAQM.
- Operation of the National Public Information System for air quality.
- Coordination of the central public procurements for the HAQM.
- Data transmission for the European Environment Agency (EEA-AirBase).
- Organisation of workshops to solve actual problems and answering questions coming up during the operation, especially according to the new legislations, programs and methods.
- Organisation of the intercalibrations for the analytical laboratories.

The Air Quality Reference Centre (AQRC) can be found at HMS / OMSZ György Marcell Main Observatory. Our accredited activities is working according to the regulation of EN ISO/IEC 17025 standard. Since AQRC work is closely linked to the Hungarian Air Quality Monitoring Network, its up-to-date status and appropriate operation are our common target.

Thanks to some projects (Swiss-Hungarian Cooperation Program (No. *SH/3/9 project*) and KEOP – No. 6.3.0/09-11 project), the local *Inspectorates for Environmental Protection and Nature Conservation* received new instruments, since they ensure the appropriate operation of the air quality measuring stations. Specifically, their analytical laboratories and measuring stations were renewed with new instruments and softwares. These softwares guarantee the data transmission between measuring stations and AQRC Data Centre. This new IT system was successfully connected to the network of Hungarian Meteorological Service and Ministry of Agriculture, as well. Moreover, a new web site for sharing air quality datas of the Hungarian Air Quality Monitoring Network was created, which you can find at [levegominoseg.hu](http://levegominoseg.hu). We purchased an ICP-OES spectrometer, a gas chromatograph mass spectrometer (GC-MS) and a discrete photometric analyser to our newly created analytical laboratory within the framework of the tender. Calibration laboratory instruments fleet expanded a CO analyser, a PM<sub>10</sub> / PM<sub>2.5</sub> monitors, a calibration tower, and a mass flow meter calibration system within the framework of the tender. The combined value of these systems is more than 150 million HUF.

The Calibration Laboratory use to execute calibrations for our own purposes (about 70 per year) and further 250 calibrations in the laboratory and on field for the Monitoring Network (HAQMN) and our clients.

We use to organize and executed interlaboratory comparisons, including an emission test and an immission test. With equivalence field test we started to study the new particulate matter monitors and samplers for PM<sub>10</sub>/PM<sub>2.5</sub> fraction which had been obtained by the Air Quality Monitoring Network.

We use to participate and well suited at inter laboratory comparison measurements organized by the JRC ERLAP (Joint Research Centre under the egis of the European Commission's air pollution reference laboratory) for PM<sub>2.5</sub>, PM<sub>10</sub>, BTEX, CO, NO, NO<sub>2</sub>, NO<sub>x</sub>, SO<sub>2</sub>, and O<sub>3</sub> components.

Staff of the Data Centre have prepared an annual assessment report of the air quality in the year 2014, based on data of both automatic and manual measuring network system, and has been honoured with the changed national and EU reporting obligations as well. As a result of the amendment of Government Decree about air protection no. 306/2010. (XII.23.), the data management from law about self-determination right of data, and freedom of data, and data management from law public data re-use carry out the Air Quality Reference Centre, as tasks defined public administrations.

We carried out the national background level measurement of the heavy metals, elemental and organic carbon, and the polycyclic aromatic hydrocarbons (PAH) from PM<sub>2.5</sub> aerosol samples of K-pusztá measuring point. We prepared the field-test report about the demonstration of equivalence of PM<sub>10</sub>, PM<sub>2.5</sub> monitors which are measuring aerosols based on nonreference methods.

We participated in the “Fűts Okosan” (Heat wisely) campaign together with the Ministry of Agriculture and the Herman Otto Institute, we backed it up with measurement data

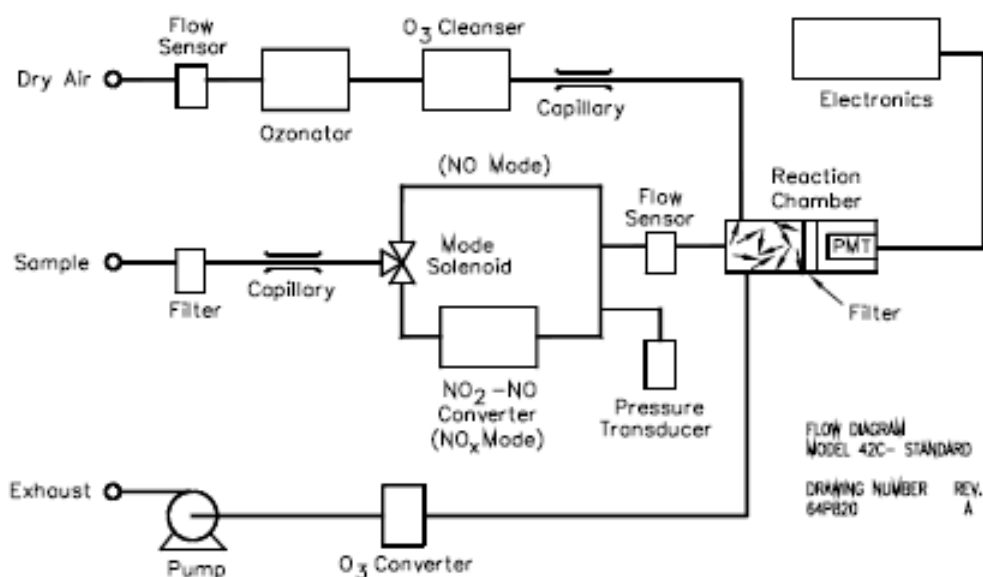
### **The standard measurement of NO<sub>x</sub>**

The NO<sub>x</sub> measurement based on the principle that nitric oxide (NO) and ozone (O<sub>3</sub>) react to produce a characteristic luminescence with an intensity linearly proportional to the NO concentration. Infrared light emission results when electronically excited NO<sub>2</sub> molecules decay to lower energy states. Specifically,



Nitrogen dioxide (NO<sub>2</sub>) must first be transformed into NO before it can be measured using the chemiluminescent reaction. NO<sub>2</sub> is converted to NO by a molybdenum NO<sub>2</sub>-to-NO converter heated to about 325 °C.

The sample flows through a particulate filter, a capillary, and then to the mode solenoid valve. The solenoid valve routes the sample either straight to the reaction chamber (NO mode) or through the NO<sub>2</sub>-to-NO converter and then to the reaction chamber (NO<sub>x</sub> mode). A flow sensor prior to the reaction chamber measures the sample flow.



Schematic figure of a NO<sub>x</sub> analyser

Dry air enters through the DRY AIR bulkhead, through a flow sensor, and then through a silent discharge ozonator. The ozonator generates the necessary ozone concentration needed for the chemiluminescent reaction. The ozone reacts with the NO in the ambient air sample to produce electronically excited NO<sub>2</sub> molecules. A photomultiplier tube (PMT) housed in a thermoelectric cooler detects the NO<sub>2</sub> luminescence.

The NO and NO<sub>x</sub> concentrations calculated in the NO and NO<sub>x</sub> modes are stored in memory. The difference between the concentrations are used to calculate the NO<sub>2</sub> concentration.

**The calibration** technique is based on the rapid gas phase reaction between NO and O<sub>3</sub> which produces stoichiometric quantities of NO<sub>2</sub> in accordance with the reaction:



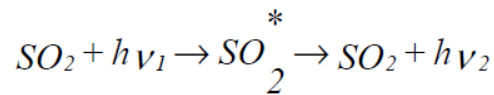
The quantitative nature of this reaction is such that when the NO concentration is known, the concentration of NO<sub>2</sub> can be determined. Ozone is added to excess NO in a dynamic calibration system, and the NO channel of the chemiluminescence NO-NO<sub>2</sub>-NO<sub>x</sub> analyzer is used as an indicator of changes in NO concentration. Upon the addition of O<sub>3</sub>, the decrease in NO concentration observed on the calibrated NO channel is equivalent to the concentration of NO<sub>2</sub> produced. The amount of NO<sub>2</sub> generated may be changed by adding variable amounts of O<sub>3</sub> from a stable O<sub>3</sub> generator.

**NO Concentration Standard.** A cylinder containing 50 to 100 ppm NO in N<sub>2</sub> with less than 1 ppm NO<sub>2</sub> is usually used as the concentration standard. The cylinder must be NO in N<sub>2</sub> Standard Reference Material or NO<sub>2</sub> Standard Reference Material.

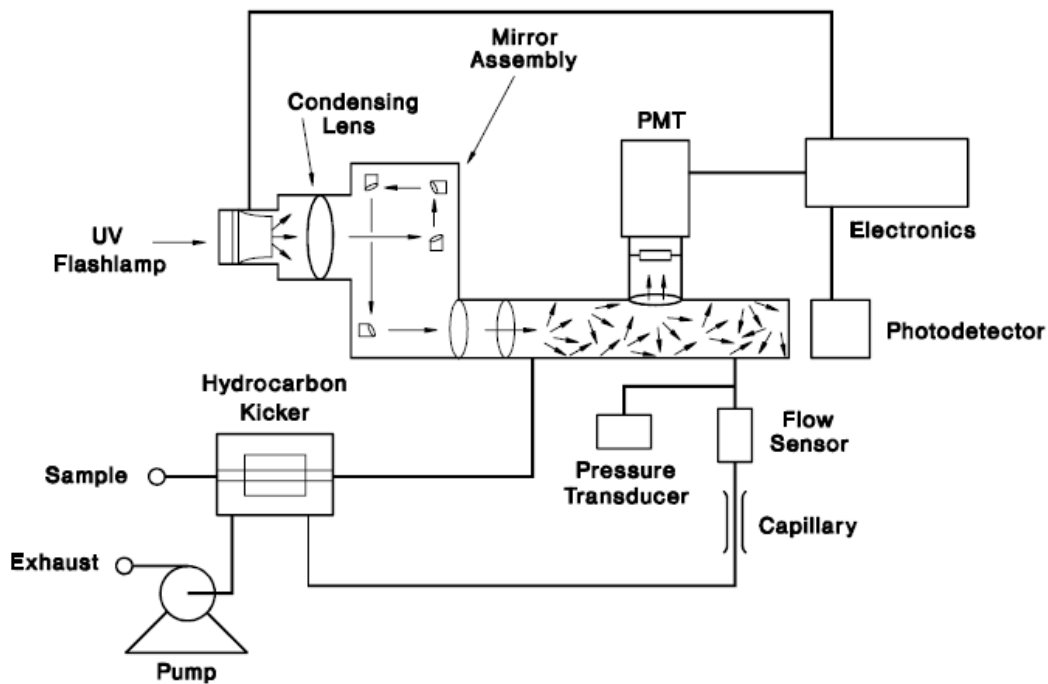
### The standard measurement of SO<sub>2</sub>

The SO<sub>2</sub> measurement is based on the principle that SO<sub>2</sub> molecules absorb ultraviolet (UV) light and become excited at one wavelength, then decay to a lower energy state emitting UV

light at a different wavelength. Specifically,



The sample flows through a hydrocarbon “kicker,” which removes hydrocarbons from the sample by forcing the hydrocarbon molecules to permeate through the tube wall. The SO<sub>2</sub> molecules pass through the hydrocarbon “kicker” unaffected. The sample flows into the fluorescence chamber, where pulsating UV light excites the SO<sub>2</sub> molecules. The condensing lens focuses the pulsating UV light into the mirror assembly. The mirror assembly contains four selective mirrors that reflect only the wavelengths which excite SO<sub>2</sub> molecules.



Schematic figure of a SO<sub>2</sub> analyser

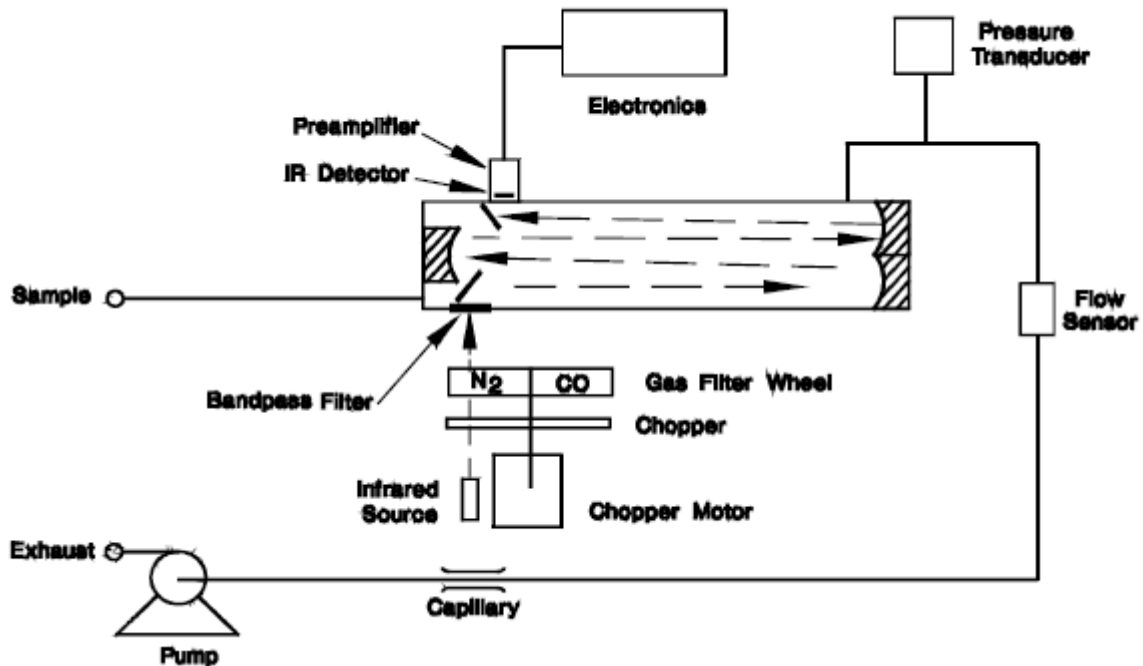
As the excited SO<sub>2</sub> molecules decay to lower energy states they emit UV light that is proportional to the SO<sub>2</sub> concentration. The bandpass filter allows only the wavelengths emitted by the excited SO<sub>2</sub> molecules to reach the photomultiplier tube (PMT). The PMT detects the UV light emission from the decaying SO<sub>2</sub> molecules. The photodetector, located at the back of the fluorescence chamber, continuously monitors the pulsating UV light source and is connected to a circuit that compensates for fluctuations in the UV light. The sample then flows through a flow sensor, a capillary, and the shell side of the hydrocarbon “kicker.” The Model 43C outputs the SO<sub>2</sub> concentration to the front panel display and the analog outputs.

### The standard measurement of CO

The CO measurement is based on the principle that carbon monoxide (CO) absorbs infrared adiation at a wavelength of 4.6 microns. Because infrared absorption is a non-linear measurement technique, it is necessary for the instrument electronics to transform the basic analyzer signal into a linear output. The instrument uses an exact calibration curve to

accurately linearize the instrument output over any range up to a concentration of 10,000 ppm.

The sample flows through the optical bench. Radiation from an infrared source is chopped and then passed through a gas filter alternating between CO and N<sub>2</sub>. The radiation then passes through a narrow bandpass interference filter and enters the optical bench where absorption by the sample gas occurs. The infrared radiation then exits the optical bench and falls on an infrared detector.



Schematic figure of a CO analyser

The CO gas filter acts to produce a reference beam which cannot be further attenuated by CO in the sample cell. The N<sub>2</sub> side of the filter wheel is transparent to the infrared radiation and therefore produces a measure beam which can be absorbed by CO in the cell. The chopped detector signal is modulated by the alternation between the two gas filters with an amplitude related to the concentration of CO in the sample cell. Other gases do not cause modulation of the detector signal since they absorb the reference and measure beams equally. Thus the GFC system responds specifically to CO.

### The standard measurement of O<sub>3</sub>

The Model 49C is based on the principle that ozone (O<sub>3</sub>) molecules absorb UV light at a wavelength of 254 nm. The degree to which the UV light is absorbed is directly related to the ozone concentration as described by the Beer-Lambert Law:

$$\frac{I}{I_0} = e^{-KLC}$$

where:

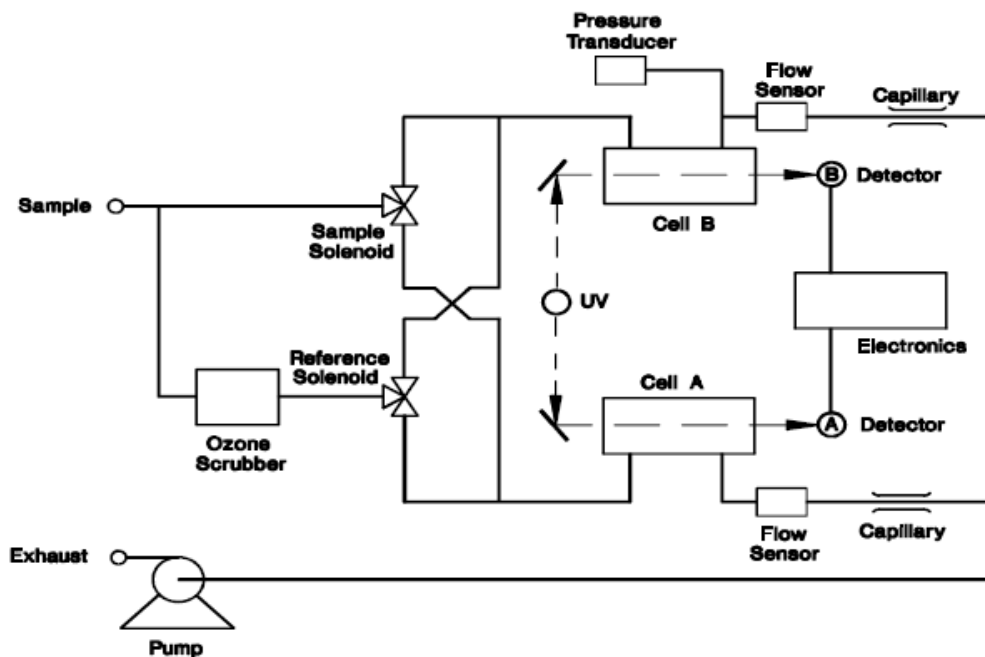
K = molecular absorption coefficient, 308 cm<sup>-1</sup> (at 0°C and 1 atmosphere)

L = length of cell, 38 cm

C = ozone concentration in parts per million (ppm)

$I$  = UV light intensity of sample with ozone (sample gas)  
 $I_0$  = UV light intensity of sample without ozone (reference gas)

One gas stream flows through an ozone scrubber to become the reference gas ( $I_0$ ). The reference gas then flows to the reference solenoid valve. The sample gas ( $I$ ) flows directly to the sample solenoid valve. The solenoid valves alternate the reference and sample gas streams between cells A and B every 10 seconds. When cell A contains reference gas, cell B contains sample gas and vice versa. The UV light intensities of each cell are measured by detectors A and B. When the solenoid valves switch the reference and sample gas streams to opposite cells, the light intensities are ignored for several seconds to allow the cells to be flushed. The instrument calculates the ozone concentration for each cell and outputs the average concentration to both the front panel display and the analog outputs.



Schematic figure of a O3 analyser

### The standard measurement of BTEX and VOC

VOCs are organic molecules (C<sub>2</sub> - C<sub>12</sub>) (based on carbon chemistry) present in ambient outdoor air at low concentration (typically in the low ppb range). In accordance with EN 14662-3 standard for benzene measurement, is based on gas chromatography (GC) for the separation of the measured compounds coupled with a Flame Ionization Detector (FID) or photo-ionization detector (PID). The compact and fully automated analyser provides equal performance to the laboratory chromatographs and is particularly well-suited for fixed or mobile ambient air quality monitoring stations. The BTEX (Benzene, Toluene, Ethyl-Benzene and m-p-o-Xylene) are measured separately because of the highly risk of health (toxic, carcinogenic, mutagenic),

The Instrument is a high performance gas chromatograph with flame ionisation detection (FID) and an on-line sample preparation. It is designed for the analysis of volatile organic compounds: VOC in gaseous samples, in ambient (100 ppt) to emission (ppm) concentration

ranges. The miniaturisation, the inertia to chemical compounds, the mobility and flexibility of this analyser have been optimised.

### **Sampling and on-line sampling preparation**

The trap phases are chosen so as to trap from the selected compounds.

Analyse: the sample is first in contact with Carbotrap where the higher molecular weight compounds are trapped and then with Carboxen where the non retained compounds are trapped. The C2 compounds get adsorbed on Carboxen phase to a temperature inferior to the ambient one. Therefore the trap is cooled by a cell with Peltier effect during the sampling. It is a thermo electrical module with a semi conductor elements set between two heat conductor flanges. When the power goes through the cell, it shows a decrease in the temperature for the cold panel and an increase in the temperature for the hot panel. The temperature for the cold is set at  $-8^{\circ}\text{C}$ . The set is installed in a box swept by dry air. It is possible, if required, to add to the sample flow an exactly known amount of reference standard compounds. The volume of gas sample is measured downstream of the adsorption section, at the level of a critical orifice. At the end of the sampling, a relay commutes, directing the sample flow to the event and making hydrogen flush the sampling circuit (in an way opposed to the sampling way) so as to purge this circuit.

### **Injection of the sample in the analytical column (trap and desorption)**

The 6-ways pneumatic valve that was in "sampling" position gets in "injection" position, thereby inserting the sampling tube in the carrier gas circuit. At the same time, a relay is activated to stop the carrier gas during the desorption time. Simultaneously, the trap is heated to desorb the compounds. The thermodesorption is fixed during 180 s. After the desorption, immediately the trap is flushed with hydrogen in the way opposite to the sampling way. Thermodesorption is fixed at  $220^{\circ}\text{C}$  during 180s. The now gaseous sample is introduced in the analytical column by the carrier gas flow.

### **Chromatographic separation**

The analytical column is situated in an oven of which temperature is programmed with a gradient that starts at the end of the trap thermodesorption (injection step). The sample components elute in the column at a characteristic rate (depending of their boiling point and of their interactions with the column stationary phase). Generally, the retention time of the compounds increases with their molecular mass (boiling point). However, if the hydrocarbons are not saturated, their retention time increases. For example, acetylene (a C2 with a treble carbon-carbon bond), elutes close to the isobutane, a C4 molecule with not unsaturated bond.

### **Detection and data treatment**

At the extremity of the column, a flame ionisation detector (FID) generates an electrical signal proportional to the flow of the sample components as they elute from the column. This electrical signal is digitised to be transferred to the CPU card where the microprocessor treats the data (integration, mass or concentration calculation, peak identification...). All parameters (data results, chromatograms, integration reports...) are then transferred via a RS-232 output where they can be displayed and retreated by shared software. The data acquisition starts after the trap thermodesorption ends. The complete cycle (sampling, focusing of the compounds, injection, chromatographic analysis, detection) is repeated. The on-board microprocessor stores the data, calculates the selected compound concentrations and stores them. The compound identification is made on the basis of their retention times, and concentrations are calculated in reference to standard compound analyses.



## **The standard measurement of dust (PM<sub>10</sub> or PM<sub>2,5</sub>)**

Ambient air is passed through a size-selective inlet at a known, constant flow rate. The relevant PM fraction is collected on a filter for a known period of nominally 24 h. The mass of the PM material is determined by weighing the filter at pre-specified, constant conditions before and after collection of the particulate matter.

The requirements for the connecting pipe work between the inlet and the filter holder are to minimize deposition losses of particulate matter by kinetic processes, as well as losses due to thermal, chemical or electrostatic processes.

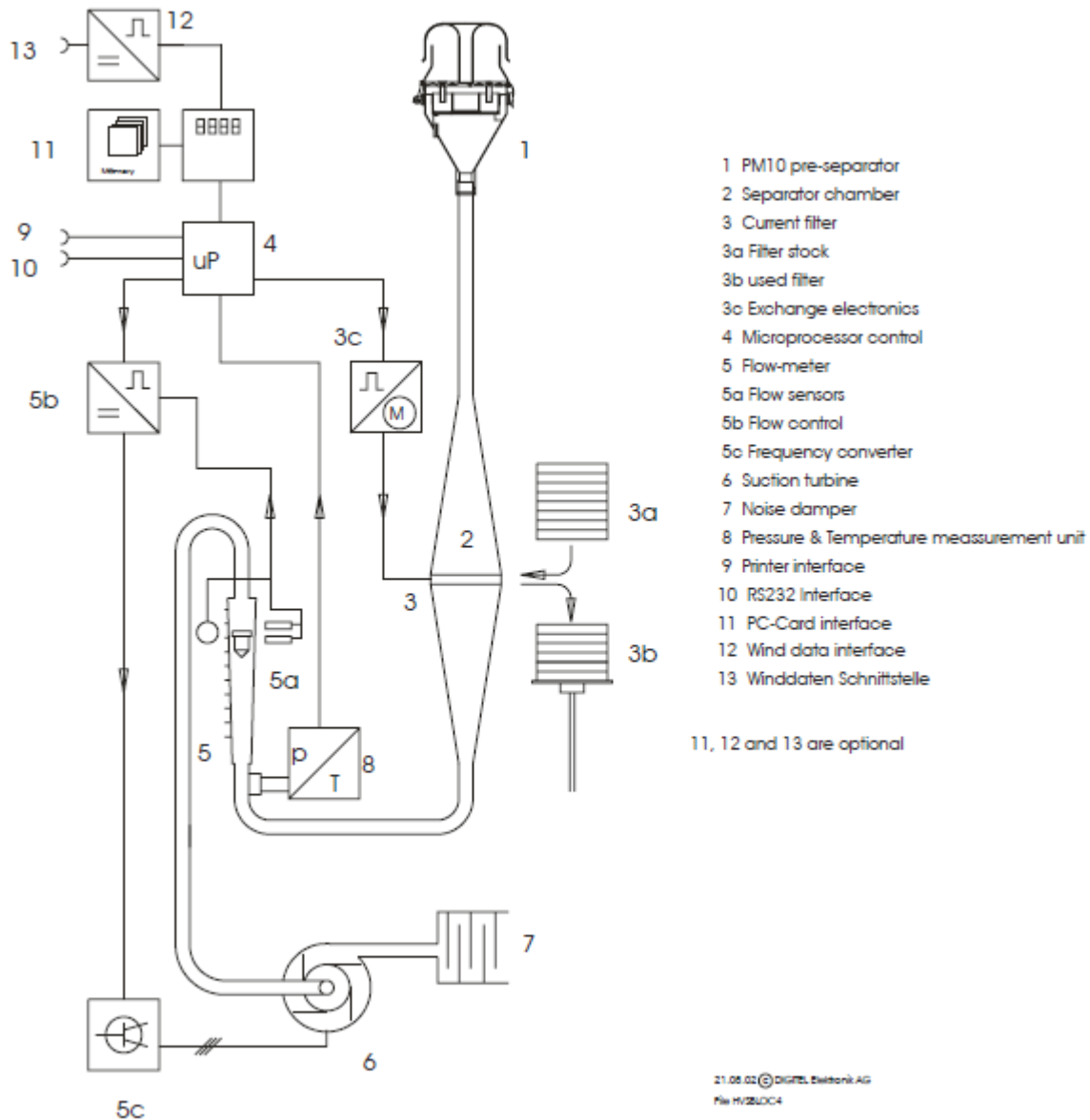
The sampling period shall be  $(24 \pm 1)$  h, and shall be recorded with an accuracy of  $\pm 5$  min. The sampler shall be able to provide information on start and stop times of sampling for each individual filter.

For a correct size-selective sampling of PM<sub>10</sub> and PM<sub>2,5</sub> the sampling flow shall be kept at a nominal flow rate of  $2,3 \text{ m}^3/\text{h} = \text{LVS}$  –Low Volume Sampler (or alternatively  $30 \text{ m}^3/\text{h} = \text{HVS}$ -High Volume Sampler)

**High Volume Samplers (HVS):** Various models of samplers are available from different applications. In general, they are differentiated by the number of filters processed and by the type of remote control via various interface protocols. Air-borne-dust parts in the sucked air are separated by round measurement filters of the diameter 150 mm. The filter diameter flown is 140 mm. Resulting gravimetric and analytical methods remain preserved, so the flown filters - depending on assignment, are assessed for dust quantity and various dust admixtures. Selection of the filter material and filter structure (deep filters, porous filters, glass fibres, silica fibres, pulp, Quartz, Teflon, porosity....) depends on the purpose of the analysis. Conditioning of such measurement filters is important in order to achieve an exact reproducible result of measurement. Sampler has a container of 15 filters stretched in filter holders. They are changed automatically to the flow position at the pre-set time.

The necessary air flow rate is selected by a rotameter. This value should be first calibrated at the beginning of a measurement session, using a gasmeter or by a secondary standard, e.g. by an additional rotameter. During air sampling, sucking capacity of the pump is dynamically controlled, so that this value is kept at good reproducibility and at a long-term stability. It is the case especially in respect of variation of flow resistance of the deposited filter as well of variation of pressure and temperature of ambient air sucked.

The air is sucked via a suction probe (1), using a sampling tube, vertically from the top to the bottom through the filter (3) placed in the flowing chamber (2). Changing of filters is done automatically. After the filter, the transported air quantity is measured using a rotameter with a floater (5). Its double photo-sensor (5a) optically senses the position of the floater. In connection with control electronics (5b, 5c), capacity of the suction unit (6) is made using the rpm control, so that the air quantity kept the set-point value. Air pressure and temperature are measured before the flow meter and continuously determined by a controller. A real-time protocol states sampling volumes yielding from the sampling time and controlled volume flow as the core information. The air is released from the device with reduced noise through noise damper (7).



Schematic figure of a HVS sampler

**Low volume sampler (LVS):**

The LVS sampler is a sequential automatic sampling device for particulate matter in the ambient air. The particles are sampled at constant flow rate (2,3 m<sup>3</sup>/hour) and collected on Ø 47-mm filters for gravimetric weighing and possible physicochemical analysis.

The dust-sampling device meets the requirements of EN 12341 standards. It uses a temperature regulated sampling line, in order to obtain representative samples of the atmospheric dust to be measured. This line can be equipped with any standard sampling head: TSP, PM10, PM2.5, PM1.

## Weighing room

A climate-controlled facility shall be used for conditioning and weighing the filters. This facility will be referred to within this European Standard as the “weighing room”, although it may be either a suitable room or cabinet. The temperature and the relative humidity shall be continuously monitored and controlled according to the requirements

### Requirements for weighing facilities

Performance characteristic	Requirement
Weighing room temperature	19 °C to 21 °C measured as hourly mean value
Weighing room relative humidity	45 % RH to 50 % RH measured as hourly mean value
Balance resolution	≤ 10 µg
Uncertainty (95 % confidence) of balance calibration	≤ 25 µg for a range of 0 mg to 200 mg
Recording of operational parameters	The following parameters shall be recorded to demonstrate fulfilment of the above requirements: – results of weighing room temperature measurements; – results of weighing room relative humidity measurements

It is of particular importance that the facilities used for the weighing of the filters before and after sampling fulfil the requirements of this European Standard.

**Loss of semi-volatile particulate matter between collection and weighing:** It is known that substantial fractions of PM mass may be composed of semi-volatile components, such as ammonium nitrate Organic matters, which can volatilize at any time between entry to the sample inlet and weighing of the sampled filter. Key factors in the rate of volatilization are the temperatures of the sampling system and the filter, relative humidity, filter material, and the flow rate.

**Change in filter mass due to water content:** It is known that the mass of filters, without any collected particulate matter, varies with humidity in a way which varies between filter materials, and also between filters nominally of the same material. For the purpose of this European Standard only changes in the effect of humidity between the unsampled and sampled weighings are relevant. This effect is controlled by the conditioning requirements for unsampled and sampled filters.

**Variation in mass of particulate matter due to water content:** A second function of the conditioning constraints is to bring the collected particulate matter to a standard level of water content by prescribing the temperature and relative humidity before and during weighing. Hygroscopic constituents of PM, e.g. ammonium salts and sodium chloride, will sorb amounts of water that will vary with air relative humidity

**Changes in buoyancy effects between the unsampled and sampled weighings:** The density of the surrounding air, which causes a buoyancy effect on the weight of the filters, is predominantly determined by the air pressure and temperature. Of these only the temperature is controlled. The expected effects of buoyancy changes can be calculated from physical principles to be less than 3 µg.

**Effects of static electrical forces during weighing:** Static electrical charge is known to have a potentially significant effect on the weighing of PTFE filters. However, the correct use of a static discharger as required to control this.

**Contamination or loss of filter material between unsampled and sampled weighings:**

It is possible to introduce significant errors in the weight of collected particulate matter because of the loss of filter or particulate material during handling and transport, or the addition of matter not collected during sampling. The procedures for handling, storage and transport in Clause 6 are designed to control these factors.

**Artefacts due to interactions between the filter material and gases:** In addition to water, filter materials may adsorb volatile compounds present in the sampled air. Examples are: ammonia, nitrogen dioxide and organic gases. Contributions to the filter mass will vary with concentrations of the gases and the chemical nature of the filter material. Adsorption may even lead to a reduction of losses of semi-volatile constituents of PM.

**Flow rate ( $\phi_a$ )**

The flow measurement can be based on several different physical principles, which have different influencing factors. However, the uncertainty is controlled by the requirements on the flow system set out and the parameters needing to be controlled shall be established by the operator in each case.

**Non standard (but can be equivalent) measurement method of dust:**

**1.)  $\beta$ -gauge method:**

The system is used to measure suspended particulate matter in the ambient air. Sampled air can also be monitored continuously for possible natural radioactivity, with programmed alarm in the event of a threshold overshoot. The system is available in the form of an indoor cabinet for installation in a closed room, or an outdoor, heated and ventilated enclosure. This monitor can operate separately or be included into supervision and warning networks.

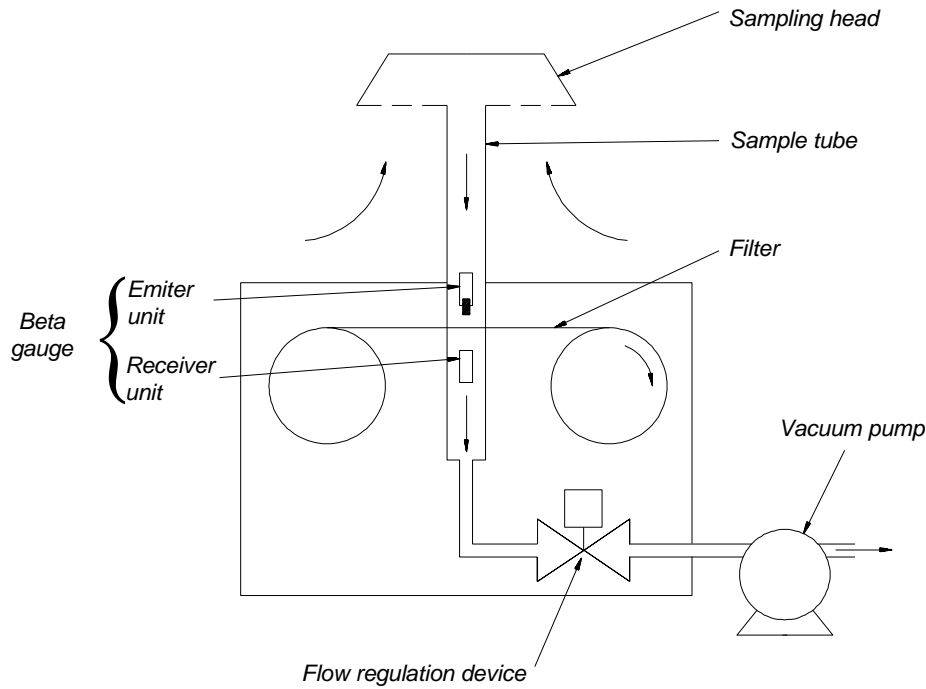
The particles measuring device using Beta gauge. The suspended particles are gathered by sampling a defined volume of air on a glass fiber filter. The filter is automatically unrolled between the Beta source and a Geiger-Müller counter (GM) according to defined sequences.

The difference in the radiation counting before and after gathering of the particles represents the measurement of the mass on the filter. Sampling is carried out with a vacuum pump through a sampling head connected to the top of the analyzer.

The Carbon 14 source ( $^{14}\text{C}$ ) is a low-intensity source with half-life of about 5730 years.

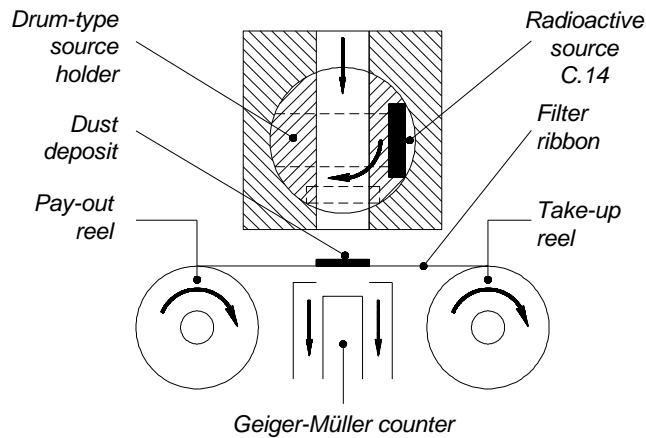
The filter ribbon used allows for a high number of sampling events (1200).

By the high-reliability of its components and its ease of use, and requires very limited maintenance.



**Figure: General functional diagram**

A BETA gauge consists of a Carbon 14 source ( $^{14}\text{C}$ ) emitting soft Beta radiation and a radioactive radiation detector: Geiger-Müller (G.M.) tube. The G.M. is mounted at a given distance downstream of the filter ribbon which gathers the particles suspended in the air.



**Figure: Beta gauge**

When determining a mass deposit, at the end of each period or cycle, the source is aligned with the dust deposit and the counter (G.M.). The low-energy Beta rays are absorbed by the matter by collision with the electrons whose number will be proportional to the density. The matter consists of the glass fibre filter, the dust deposited and the air between the source and the G.M. The absorption is governed by an exponential law and is independent of the physico-chemical nature of the matter. The measurement consists in calculating the difference in absorption observed on the blank filter at the start of the cycle and on the charged filter at the end of the period or cycle.

This differential measurement is used to compensate for the non-uniformity of the filter when calculating the mass of the deposited dust. The monitor also compensates for the variation in temperature of the weight of the air knife.



(1) reference gauge, (3) source holder, (4) flexible channel, (5) capstan, (6) disengageable pinch roller, (7) take-up reel, (8) Geiger-Müller tube detector, (9) pressure assembly, (10) pay-out reel.

**Figure Front face, overview of collector assembly and beta gauge**

## **2.) Optical method**

The CPM or Continuous Particulate Measurement is a measurement module dedicated to the continuous measurement of particles. Its measurement principle is based upon the scattering of a laser beam by the fine particles in the ambient air.

REMARK: as the laser is confined, the user cannot have access to the laser. Consequently, the device is graded as class 1, and is of no hazard for the user under standard operating conditions.

The CPM module is fixed between its sample inlet and the RST line (regulated sampling tube). The regulated sampling tube (RST) line fulfils the requirements of the standards relating to sampling and measurement of suspended particles PM10 (EN 12341) and PM2.5 (EN 14907). The method of particles sampling on filter must be equivalent to the reference method. Consequently, sampling must be carried out at a temperature close to the ambient temperature, in order to avoid any phenomenon of condensation inside the sampling line and any loss of weight due to the volatile and semi volatile compounds (as ammonium nitrate) which pass into gaseous phase at about 40 °C.

This system enables to count particles in real time and to obtain a classification by size range. The CPM module is an optical analyzer for the continuous measurement of particles. Since it enables to count particles and to calculate the corresponding mass concentration in continuous and in real time, it is additional to the sequential measurement (in general, one measurement each 2 hours). In practice, the data are memorized with a minimum time step of 1 minute.

Every time a particle passes in the laser beam and scatters the light, the photo detector (located at 15° from the incidental beam) measures the intensity of the scattered light. With this specific angle, the scattered light is independent of the particles nature. It is proportional to the particles size (the bigger the particle is, the more important the light intensity is).

Most of the optical counters measure the light scattered by the particles at 90°. With this angle, light scattering depends on the particles nature. Thus, some very absorbing particles cannot be detected by these counters.

Concentration is stated in µg/m<sup>3</sup>:

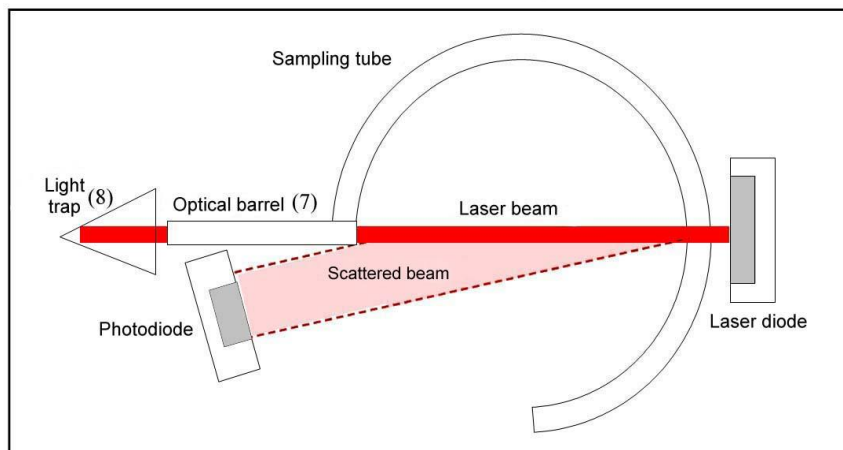
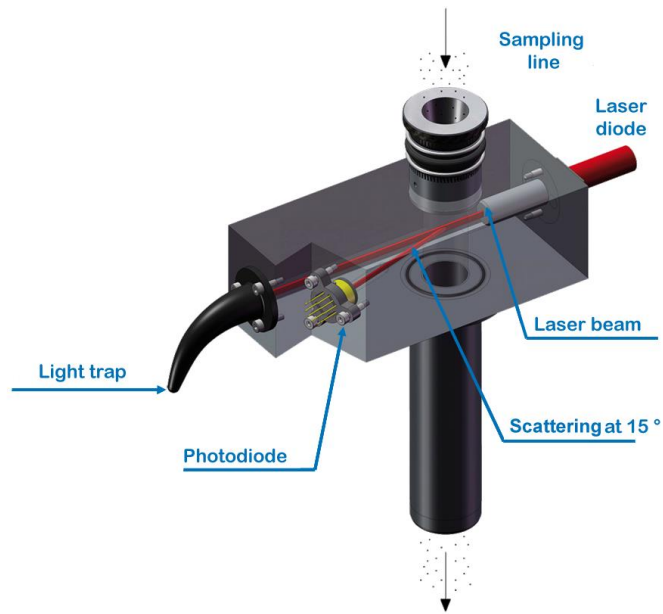
To convert the number of counted particles into a mass concentration, a relation is applied which takes into account the sampled air volume, the particles number per size range (stated in number/litre), and a calibration factor.

This calibration factor is calculated for each new measurement of the β-method. Then, it is applied to the calculation of the CPM concentration until the next measurement of beta attenuation occurs. It enables to adjust the value of the average density of the particles which is likely to change in time.

The sampling temperature control is managed by the software of the device in the following way:

- Sampling is carried out at atmospheric temperature.
- A continuous measurement of external relative humidity is carried out,
- When the RH value exceeds the empirical threshold of 60%, the line is heated and controlled (with a PID standard integration) at a temperature equal to the atmospheric temperature + 5 °C, in order to avoid condensation inside the line.





$$T_{\text{head}} = T_{\text{atmospheric}} + 5 \text{ °C.}$$



**Figure: Diagram of the optical measurement principle of the CPM**



## Colour code of the cylinders:

Gas property	colour	
Toxic and/or corrosive	Yellow	
Flammable	Red	
Oxidising	Light Blue	
Inert <sup>1</sup>	Bright Green	

Note: Students have to know the signals can be found on a cylinder, the pressure regulator assembly and how it is working. They also able to calculate dilutions from the concentration of the cylinder and also able to convert the dimension from any of the following: % V/V – ppm – ppb –  $\mu\text{g}/\text{m}^3$

## MFC (Mass Flow Controller):

The thermal mass flow sensing technique used in dilutor system as follows: A precision power supply provides a constant power heat input (P) at the heater which is located at the midpoint of the sensor tube. Refer to Figure 3-1. At zero, or no flow conditions, the heat reaching each temperature sensor is equal. The temperatures T1 and T2, therefore, are equal. When gas flows through the tube, the upstream sensor is cooled and the downstream sensor is heated which produces a temperature difference. The temperature difference T2-T1 is directly proportional to the gas mass flow. The equation is:

$$DT = A * P * C_p * m$$

Where:

DT = Temperature difference T2 - T1 ( $^{\circ}\text{K}$ )

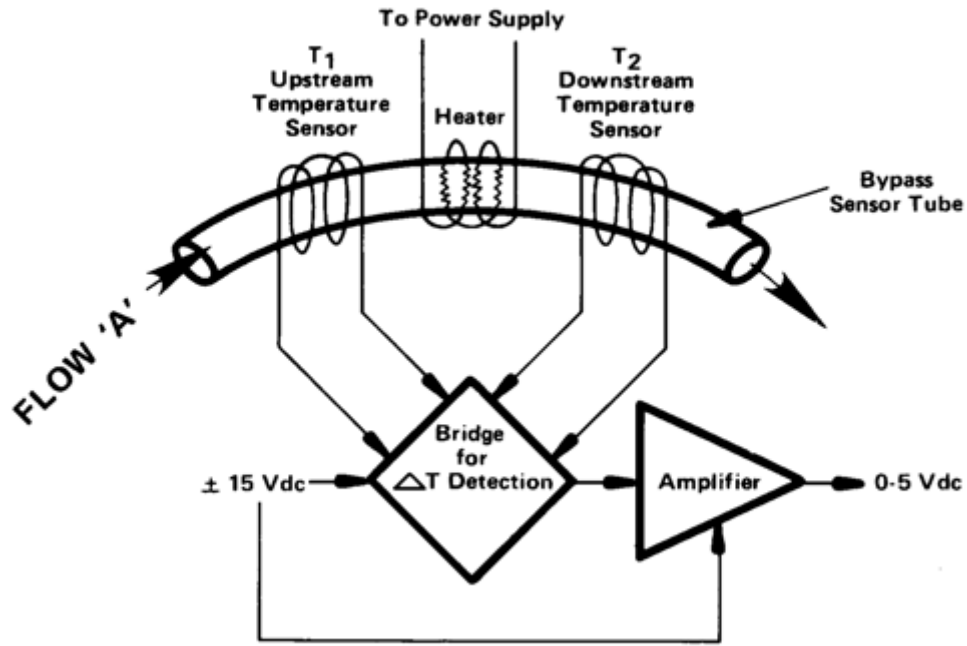
Cp = Specific heat of the gas at constant pressure ( $\text{kJ}/\text{kg}\text{-}^{\circ}\text{K}$ )

P = Heater power ( $\text{kJ}/\text{s}$ )

m = Mass flow ( $\text{kg}/\text{s}$ )

A = Constant of proportionality ( $\text{S}^2\text{-}^{\circ}\text{K}^2/\text{kJ}^2$ )

A bridge circuit interprets the temperature difference and a differential amplifier generates a linear 0-5 Vdc signal directly proportional to the gas mass flow rate. The flow restrictor shown in Figure performs a ranging function similar to a shunt resistor in an electrical ammeter. The restrictor provides a pressure drop that is linear with flow rate. The sensor tube has the same



Flow Sensor Operational Diagram

linear pressure drop/flow relationship. The ratio of the restrictor flow to the sensor tube flow remains constant over the range of the meter. Different restrictors have different pressure drops and produce controllers with different full scale flow rates. The span adjustment, in the electronics, affects the fine adjustment of the controller's full scale flow. In addition to the mass flow sensor, the Mass Flow Controller has an integral control valve and control circuit. The control circuit senses any difference between the flow sensor signal and adjusts the current in the modulating solenoid valve to increase or decrease the flow.

## Basic definitions about the measurement:

### International System of Units SI

**system of units**, based on the **International System of Quantities**, their names and symbols, including a series of prefixes and their names and symbols, together with rules for their use, adopted by the General Conference on Weights and Measures (CGPM)

Note 1: The SI is founded on the seven **base quantities** of the **ISQ** and the names and symbols of the corresponding **base units** that are contained in the following table.

Table: the seven basic SI unit

<b>Base quantity</b> <b>Grandeur de base</b>	<b>Base unit</b> <b>Unité de base</b>	
<b>Name</b> <b>Nom</b>	<b>Name</b> <b>Nom</b>	<b>Symbol</b> <b>Symbole</b>
length longueur	metre mètre	m
mass masse	kilogram kilogramme	kg
time temps	second seconde	s
electric current courant électrique	ampere ampère	A
thermodynamic temperature température thermodynamique	kelvin kelvin	K
amount of substance quantité de matière	mole mole	mol
luminous intensity intensité lumineuse	candela candela	cd

All other units (dimension) can be created by the combination of the seven basic unit.

Example: velocity: (m/s), concentration: (mol/liter), atmospheric mass concentration ( $\mu\text{g}/\text{m}^3$ )

### True quantity value:

**quantity value** consistent with the definition of **aquantity**

Note 1: In the Error Approach to describing **measurement**, a true quantity value is considered unique and, in practice, unknowable. The Uncertainty Approach is to recognize that, owing to the inherently incomplete amount of detail in the definition of a quantity, there is not a single true quantity value but rather a set of true quantity values consistent with the definition. However, this set of values is, in principle and in practice, unknowable. Other approaches dispense altogether with the concept of true quantity value and rely on the concept of **metrological compatibility of measurement results** for assessing their validity.

Note 2: In the special case of a fundamental constant, the quantity is considered to have a single true quantity value.

Note 3: When the **definitional uncertainty** associated with the **measurand** is considered to be negligible compared to the other components of the **measurement uncertainty**, the measurand may be considered to have an “essentially unique” true quantity value. This is the approach taken by the GUM and associated documents, where the word “true” is considered to be redundant.

### **Measurement accuracy:**

closeness of agreement between a **measured quantity value** and a **true quantity value** of a **measurand**

Note 1: The concept ‘measurement accuracy’ is not a **quantity** and is not given a **numerical quantity value**. A **measurement** is said to be more accurate when it offers a smaller **measurement error**.

Note 2: The term “measurement accuracy” should not be used for **measurement trueness** and the term “measurement precision” should not be used for ‘measurement accuracy’, which, however, is related to both these concepts.

Note 3: ‘Measurement accuracy’ is sometimes understood as closeness of agreement between measured quantity values that are being attributed to the measurand.

### **Measurement precision:**

closeness of agreement between **indications** or **measured quantity values** obtained by replicate **measurements** on the same or similar objects under specified conditions

Note 1: Measurement precision is usually expressed numerically by measures of imprecision, such as standard deviation, variance, or coefficient of variation under the specified conditions of measurement.

Note 2: The ‘specified conditions’ can be, for example, **repeatability conditions of measurement**, **intermediate precision conditions of measurement**, or **reproducibility conditions of measurement**

Note 3: Measurement precision is used to define **measurement repeatability**, **intermediate measurement precision**, and **measurement reproducibility**.

Note 4: Sometimes “measurement precision” is erroneously used to mean **measurement accuracy**.

### **Measurement error:**

**measured quantity value** minus a **reference quantity value**

Note 1: The concept of ‘measurement error’ can be used both a) when there is a single reference quantity value to refer to, which occurs if a **calibration** is made by means of a **measurement standard** with a **measured quantity value** having a negligible **measurement uncertainty** or if a **conventional quantity value** is given, in which case the measurement error is known, and b) if a **measurand** is supposed to be represented by a unique **true quantity value** or a set of true quantity values of negligible range, in which case the measurement error is not known.

Note 2: Measurement error should not be confused with production error or mistake.

### **Systematic measurement error:**

component of **measurement error** that in replicate **measurements** remains constant or varies in a predictable manner

Note 1: A **reference quantity value** for a systematic measurement error is a **true quantity value**, or a **measured quantity value** of a **measurement standard** of negligible **measurement uncertainty**, or a **conventional quantity value**.

Note 2: Systematic measurement error, and its causes, can be known or unknown. A **correction** can be applied to compensate for a known systematic measurement error.

Note 3: Systematic measurement error equals measurement error minus **random measurement error**.

**Measurement bias:**

estimate of a **systematic measurement error**

**random measurement error**

component of **measurement error** that in replicate **measurements** varies in an unpredictable manner

Note 1: A **reference quantity value** for a random measurement error is the average that would ensue from an infinite number of replicate measurements of the same **measurand**.

Note 2: Random measurement errors of a set of replicate measurements form a distribution that can be summarized by its expectation, which is generally assumed to be zero, and its variance.

Note 3: Random measurement error equals measurement error minus **systematic measurement error**.

**Repeatability condition of measurement:**

condition of **measurement**, out of a set of conditions that includes the same **measurement procedure**, same operators, same **measuring system**, same operating conditions and same location, and replicate measurements on the same or similar objects over a short period of time

Note 1: A condition of measurement is a repeatability condition only with respect to a specified set of repeatability conditions.

Note 2: In chemistry, the term “intra-serial precision condition of measurement” is sometimes used to designate this concept.

**Measurement repeatability:**

**measurement precision** under a set of **repeatability conditions of measurement**

**Reproducibility condition of measurement:**

condition of **measurement**, out of a set of conditions that includes different locations, operators, **measuring systems**, and replicate measurements on the same or similar objects

Note 1: The different measuring systems may use different **measurement procedures**.

Note 2: A specification should give the conditions changed and unchanged, to the extent practical.

**Measurement reproducibility:**

**measurement precision** under **reproducibility conditions of measurement** Note Relevant statistical terms are given in ISO 5725-1:1994 and ISO 5725-2:1994.

**Measurement uncertainty:**

non-negative parameter characterizing the dispersion of the **quantity values** being attributed to a **measurand**, based on the information used

Note 1: Measurement uncertainty includes components arising from systematic effects, such as components associated with **corrections** and the assigned quantity values of **measurement standards**, as well as the **definitional uncertainty**. Sometimes estimated systematic effects are not corrected for but, instead, associated measurement uncertainty components are incorporated.

Note 2: The parameter may be, for example, a standard deviation called **standard measurement uncertainty** (or a specified multiple of it), or the half-width of an interval, having a stated **coverage probability**.

Note 3: Measurement uncertainty comprises, in general, many components. Some of these may be evaluated by **Type A evaluation of measurement uncertainty** from the statistical distribution of the quantity values from series of **measurements** and can be characterized by standard deviations. The other components, which may be evaluated by **Type B evaluation of measurement uncertainty**, can also be characterized by standard deviations, evaluated from probability density functions based on experience or other information.

Note 4: In general, for a given set of information, it is understood that the measurement uncertainty is associated with a stated quantity value attributed to the measurand. A modification of this value results in a modification of the associated uncertainty.

**Standard measurement uncertainty:**

standard uncertainty **measurement uncertainty** expressed as a standard deviation

**Combined standard measurement uncertainty:**

**standard measurement uncertainty** that is obtained using the individual standard measurement uncertainties associated with the **input quantities in a measurement model**

**Relative standard measurement uncertainty:**

**standard measurement uncertainty** divided by the absolute value of the **measured quantity value**

**Expanded measurement uncertainty:**

product of a **combined standard measurement uncertainty** and a factor larger than the number one

Note 1: The factor depends upon the type of probability distribution of the **output quantity in a measurement model** and on the selected **coverage probability**.

Note 2: The term “factor” in this definition refers to a **coverage factor**.

Note 3: Expanded measurement uncertainty is termed “overall uncertainty”

**Calibration:**

operation that, under specified conditions, in a first step, establishes a relation between the **quantity values** with **measurement uncertainties** provided by **measurement standards** and corresponding **indications** with associated measurement uncertainties and, in a second step, uses this information to establish a relation for obtaining a **measurement result** from an indication

Note 1: A calibration may be expressed by a statement, calibration function, **calibration diagram, calibration curve**, or calibration table. In some cases, it may consist of an additive or multiplicative **correction** of the indication with associated measurement uncertainty.

Note 2: Calibration should not be confused with **adjustment of a measuring system**, often mistakenly called “self-calibration”, nor with **verification** of calibration.

Note 3: Often, the first step alone in the above definition is perceived as being calibration.

**Calibration hierarchy:**

sequence of **calibrations** from a reference to the final **measuring system**, where the outcome of each calibration depends on the outcome of the previous calibration

Note 1: **Measurement uncertainty** necessarily increases along the sequence of calibrations.

Note 2: The elements of a calibration hierarchy are one or more **measurement standards** and measuring systems operated according to **measurement procedures**.

Note 3: For this definition, the ‘reference’ can be a definition of a **measurement unit** through its practical realization, or a measurement procedure, or a measurement standard.

Note 4: A comparison between two measurement standards may be viewed as a calibration if the comparison is used to check and, if necessary, correct the **quantity value** and measurement uncertainty attributed to one of the measurement standards.

### **Metrological traceability:**

property of a **measurement result** whereby the result can be related to a reference through a documented unbroken chain of **calibrations**, each contributing to the **measurement uncertainty**

Note 1: For this definition, a ‘reference’ can be a definition of a **measurement unit** through its practical realization, or a **measurement procedure** including the measurement unit for a non-ordinal quantity, or a **measurement standard**.

Note 2: Metrological traceability requires an established **calibration hierarchy**.

Note 3: Specification of the reference must include the time at which this reference was used in establishing the calibration hierarchy, along with any other relevant metrological information about the reference, such as when the first calibration in the calibration hierarchy was performed.

Note 4: For **measurements** with more than one **input quantity in the measurement model**, each of the input **quantity values** should itself be metrologically traceable and the calibration hierarchy involved may form a branched structure or a network. The effort involved in establishing metrological traceability for each input quantity value should be commensurate with its relative contribution to the measurement result.

Note 5: Metrological traceability of a measurement result does not ensure that the measurement uncertainty is adequate for a given purpose or that there is an absence of mistakes.

Note 6: A comparison between two measurement standards may be viewed as a calibration if the comparison is used to check and, if necessary, correct the quantity value and measurement uncertainty attributed to one of the measurement standards.

Note 7: The ILAC considers the elements for confirming metrological traceability to be an unbroken **metrological traceability chain** to an **international measurement standard** or a **national measurement standard**, a documented measurement uncertainty, a documented measurement procedure, accredited technical competence, metrological traceability to the SI, and calibration intervals (see ILAC P-10:2002).

Note 8: The abbreviated term “traceability” is sometimes used to mean ‘metrological traceability’ as well as other concepts, such as ‘sample traceability’ or ‘document traceability’ or ‘instrument traceability’ or ‘material traceability’, where the history (“trace”) of an item is meant. Therefore, the full term of “metrological traceability” is preferred if there is any risk of confusion.

### **Metrological traceability chain:**

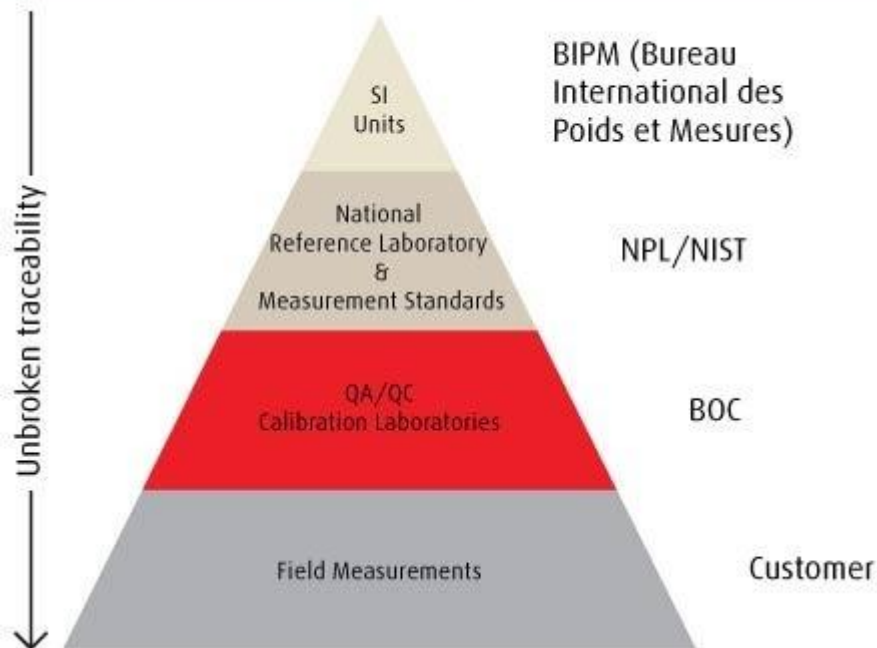
sequence of **measurement standards** and **calibrations** that is used to relate a **measurement result** to a reference

Note 1: A metrological traceability chain is defined through a **calibration hierarchy**.

Note 2: A metrological traceability chain is used to establish **metrological traceability** of a measurement result.

Note 3: A comparison between two measurement standards may be viewed as a calibration if the comparison is used to check and, if necessary, correct the **quantity value** and **measurement uncertainty** attributed to one of the measurement standards.

## Hierarchy of Gas Calibration Standards



### Verification:

provision of objective evidence that a given item fulfils specified requirements

Example 1: Confirmation that a given **reference material** as claimed is homogeneous for the **quantity value** and **measurement procedure** concerned, down to a measurement portion having a mass of 10 mg.

Example 2: Confirmation that performance properties or legal requirements of a **measuring system** are achieved.

Example 3: Confirmation that a **target measurement uncertainty** can be met.

Note 1: When applicable, **measurement uncertainty** should be taken into consideration.

Note 2: The item may be, e.g. a process, measurement procedure, material, compound, or measuring system.

Note 3: The specified requirements may be, e.g. that a manufacturer's specifications are met.

Note 4: Verification in legal metrology, and in conformity assessment in general, pertains to the examination and marking and/or issuing of a verification certificate for a measuring system.

Note 5: Verification should not be confused with **calibration**. Not every verification is a **validation**.

Note 6: In chemistry, verification of the identity of the entity involved, or of activity, requires a description of the structure or properties of that entity or activity.

### Validation:

**verification**, where the specified requirements are adequate for an intended use

Example: **measurement procedure**, ordinarily used for the **measurement** of mass concentration of nitrogen in water, may be validated also for measurement of mass concentration of nitrogen in human serum.

**Measurement standard** = etalon:

realization of the definition of a given **quantity**, with stated **quantity value** and associated **measurement uncertainty**, used as a reference



Example 1: 1 kg mass measurement standard with an associated **standard measurement uncertainty** of 3  $\mu\text{g}$ .

Note 1: A “realization of the definition of a given quantity” can be provided by a **measuring system**, a **material measure**, or a reference material.

Note 2: A measurement standard is frequently used as a reference in establishing **measured quantity values** and associated measurement uncertainties for other quantities of the same **kind**, thereby establishing **metrological traceability** through **calibration** of other measurement standards, **measuring instruments**, or measuring systems.

Note 3: The term “realization” is used here in the most general meaning. It denotes three procedures of “realization”. The first one consists in the physical realization of the **measurement unit** from its definition and is realization *sensu stricto*. The second, termed “reproduction”, consists not in realizing the measurement unit from its definition but in setting up a highly reproducible measurement standard based on a physical phenomenon, as it happens, e.g. in case of use of frequency-stabilized lasers to establish a measurement standard for the metre, of the Josephson effect for the volt or of the quantum Hall effect for the ohm. The third procedure consists in adopting a material measure as a measurement standard. It occurs in the case of the measurement standard of 1 kg.

Note 4: A standard measurement uncertainty associated with a measurement standard is always a component of the **combined standard measurement uncertainty** in a **measurement result** obtained using the measurement standard. Frequently, this component is small compared with other components of the combined standard measurement uncertainty.

Note 5: Quantity value and measurement uncertainty must be determined at the time when the measurement standard is used.

Note 6: Several quantities of the same kind or of different kinds may be realized in one device which is commonly also called a measurement standard.

Note 7: The word “embodiment” is sometimes used in the English language instead of “realization”.

Note 8: In science and technology, the English word “standard” is used with at least two different meanings: as a specification, technical recommendation, or similar normative document (in French “norme”) and as a measurement standard (in French “*étalon*”). This Vocabulary is concerned solely with the second meaning.

Note 9: The term “measurement standard” is sometimes used to denote other metrological tools, e.g. ‘software measurement standard’

#### **International measurement standard:**

**measurement standard** recognized by signatories to an international agreement and intended to serve worldwide

Example 1: The international prototype of the kilogram.

#### **National measurement standard:**

**measurement standard** recognized by national authority to serve in a state or economy as the basis for assigning **quantity values** to other measurement standards for the **kind of quantity** concerned

#### **Primary measurement standard:**

**measurement standard** established using a **primary reference measurement procedure**, or created as an artifact, chosen by convention

Example 1: Primary measurement standard of amount-of-substance concentration prepared by dissolving a known amount of substance of a chemical component to a known volume of solution.

Example 2: Primary measurement standard for pressure based on separate **measurements** of force and area.

Example 3: Primary measurement standard for isotope amount-of-substance ratio measurements, prepared by mixing known amount-of-substances of specified isotopes.

Example 4: Triple-point-of-water cell as a primary measurement standard of thermodynamic temperature.

Example 5: The international prototype of the kilogram as an artifact, chosen by convention.

### **Reference measurement standard:**

**measurement standard** designated for the **calibration** of other measurement standards for **quantities** of a given **kind** in a given organization or at a given location

### **Reference material RM:**

material, sufficiently homogeneous and stable with reference to specified properties, which has been established to be fit for its intended use in **measurement** or in examination of **nominal properties**

Note 1: Examination of a nominal property provides a nominal property value and associated uncertainty. This uncertainty is not a **measurement uncertainty**.

Note 2: Reference materials with or without assigned **quantity values** can be used for **measurement precision** control whereas only reference materials with assigned quantity values can be used for **calibration** or **measurement trueness** control.

Note 3: 'Reference material' comprises materials embodying **quantities** as well as nominal properties.

Note 4: A reference material is sometimes incorporated into a specially fabricated device.

Note 5: Some reference materials have assigned quantity values that are metrologically traceable to a **measurement unit** outside a **system of units**. Such materials include vaccines to which International Units (IU) have been assigned by the World Health Organization.

Note 6: In a given **measurement**, a given reference material can only be used for either calibration or quality assurance.

Note 7: The specifications of a reference material should include its material traceability, indicating its origin and processing

### **Certified reference material CRM:**

**reference material**, accompanied by documentation issued by an authoritative body and providing one or more specified property values with associated uncertainties and traceabilities, using valid procedures

Example: Human serum with assigned **quantity value** for the concentration of cholesterol and associated **measurement uncertainty** stated in an accompanying certificate, used as a **calibrator** or **measurement trueness** control material.

Note 1: In this definition, "uncertainty" covers both 'measurement uncertainty' and 'uncertainty associated with the value of a **nominal property**', such as for identity and sequence. "Traceability" covers both '**metrological traceability** of a quantity value' and 'traceability of a nominal property value'.

Note 2: Specified quantity values of certified reference materials require metrological traceability with associated measurement uncertainty