

Methods for online monitoring of air pollution concentration

Ionel Ioana and Francisc Popescu
"Politehnica" University of Timisoara
Romania

1. Introduction

In this chapter some major considerations of an environmental management by direct on line monitoring of the air quality, illustrated by examples, as experienced by the authors, are discussed. First the *standard (reference) methods* for the main pollutants are indicated, further some *non-standard methods*.

Atmospheric pollution is a major problem facing all nations of the world. Rapid urban and industrial growth has resulted in vast quantities of potentially harmful waste products being released into the atmosphere. The atmosphere is the largest imaginable chemical reactor in which pollutants may be converted into more harmful or harmless substances. Societies have been reluctant to accept, or have simply failed to recognise the limitations of the cleaning properties of the atmosphere and self-adaptation of the ecosystem Planet, with no remnant damages or preventing a non-equilibrium status. The consequences has been that air pollution has affected the health and wellbeing of people, has caused widespread damage to vegetation, crops, wildlife, materials, buildings and climate, and has resulted in depletion of the scarce natural resources needed for long-term economic development. In the past, the earth was considered virtually infinite, and little thought was given to the polluting effects of our dumping wastes. The atmosphere felt to be so vast that it could absorb any amount. However, over the past decades, several factors have come together to bring this attitude into sharp question. Along with the realisation that we are on an all too finite spaceship - the earth - the *increasing population* and *technological base for our way of life* and the *increased sensitivity of our instruments for measuring pollution* have all played a role in bringing about an awareness regarding the environment and its quality.

Air pollution adversely affects soil, water, crops, vegetation, human-made materials, buildings, animals, wildlife, weather, climate, and transportation, as well as reduce economic values, personal comfort and well being. More and more, in the present time of the society of knowledge, the population and the policy makers are convinced and engaged for preserving the biodiversity that is fundamental to human welfare and economic development, and plays a critical role in meeting human needs by maintaining the ecological processes on which our survival depends. Broad-scale ecological systems provide benefits such as clean air and fresh water that are needed by everyone, whether in urban or rural settings.

As main sources for the pollution of air one recognises: *the natural sources*, and the *man-made sources*, in direct dependency to the energy consumption that is driven from the standard of comfort and industrial development, being influenced by the number of population, as well. It is not difficult to see that all of us are either directly or indirectly polluters and all of us share the disadvantages and cleanup costs of pollution generating activities, although often not in an equal and equitable manner.

In order to keep control over the quality of air the policy makers, in international co-operation mostly, decided to introduce specific regulations attesting the maximum admitted values as well the alert values. Thus, one controls both the emissions and the air quality, that represents a result of the transport in the air of the pollutants, in direct dependence to the topography and the weather conditions. *Primary pollutants* are those released directly from the source into the air in a harmful form. They are mostly result from combustion of classic C - containing non-renewable fuels, and not only even the combustion is perfect, according to thermodynamic concepts. *Secondary pollutants*, by contrast, are modified to a hazardous form after they enter the air or are formed by chemical reactions as components of the air mix and interactive. *Fugitive emissions* are those that do not go through a smokestack. By far the most massive example of this category is dust from soil erosion, strip mining, rock crushing, and building construction (and destruction). Fugitive industrial emissions are also an important source of air pollution.

2. Present state of art

2.1 Significance of the locations and sampling

When carrying out air quality measurements it is important to define the problem precisely (measuring plan) and to choose accordingly the site locations, measuring stations and methods. Applying the most expensive measuring instrument is of no use if, e.g., the pollutant to be investigated is influenced during its sampling to such a degree that it either cannot reach the measuring instrument at all or not in its original state. When measuring pollutant gases in the air a difference between mobile measurements and stationary measurements stations is necessary. Mobile stations (laboratories) are measuring at random and changing locations, according to a plan, to determine the spatial distribution of the air pollutants, whereas stationary measurements continuously record the temporal distribution in few fixed points of a certain area. Stationary measurements must be carried out at representative points of the investigated area. It is recommended to know the spatial distribution of the ambient air pollutants which might be determined only with mobile measurements at the corner points of a 1 x 1 km grid over the area to be investigated (Erste allg., 1986). Special guidelines have been drawn up so that the site locations for automatic measuring stations are chosen according to standardized criteria. Selection of the right sampling site can be of great importance for stationary as well as for mobile measurements. Guidelines have been drawn up so that in the measuring networks the site locations for automatic measuring stations are chosen according to standardized criteria. These guidelines are very important especially when planning on line in real time air quality measuring networks, i.e., when data are continuously transferred to a central station (RdSchr, 1983). Thus, selecting the site locations for ambient air quality measuring stations means to respect important guidelines in order to meet the general goal that the ambient air meaning that sample is representative of the area (Immissionsmessnetze in der

Bundesrepublik Deutschland, 1987), (Projektgruppe Bayern, GSF-Bericht 25/87). Generally speaking, these conditions are specified by legislation, in each country, but general rules are at their origin. Some of these general rules refer to: (i) distance of measuring site to the closest flow obstacle must be twofold height or width of the obstacle's, (ii) sample suction should be placed below half of the mean building height, (iii) influence of local emission sources must be kept low meaning the distance to sources (industry, domestic furnaces, streets with heavy traffic) should be more than regularly 20 m, and special investigation when industrial sources are situated nearby, are necessary. Further, a free flow accessibility of the sampling systems within a radius of less than 10 m and no flow obstacles such as trees or buildings must be assured, excluding by this mean the influence on measuring site by topographically caused local circulation. EU guideline requires that special aggressive pollutant gases (i.e. NO), must be measured continuously, particularly in locations with the suspected highest load risk, i.e., also near roads with heavy traffic, in street canyons, etc. The sampling system for gaseous pollutants consists generally of a sampling nozzle, a guidance tube, a central sampling tube, sampling connections leading from the central sampling tube to the individual measuring instruments and a fan or a pump. The sampling nozzle might be constructed as a pre-separator for particles and precipitation. The sampling line should extend generally 1 m beyond the station roof. In the standard measuring stations particle filtering in the sampling system is not provided in order to avoid possible reactions of the gases on the filters. Particle filters are only installed at the input of the instruments themselves (Laskus & Bake 1976).

Within air quality investigations, pollutant concentration profiles must frequently be measured. Examples for this are the determinations of pollutant concentrations in and over special sites at different altitudes (Baumbach et al., 1987), (Kost & Baumbach, 1985) or the registration of the concentration decline in the vicinity of streets, industrial areas with heavy traffic or intensive emissions (Esser, 1982), (Baumann, 1987). To be able to simultaneously or quasi-simultaneously measure the gas concentrations at several locations there is the possibility of sucking the air in via tubes and to conduct it to a set of measuring instruments with the help of a measuring gas change-over in short periods of alternation.

During measuring the gas (air) probe is sucked in through tubes, and an influencing of gaseous substances is generally to be expected even if the tube wall material is inert, e.g., from Teflon. Also it is best to use warmed up tubes, in order to avoid the condensation of vapor. This depends on the reactivity of the gases to be investigated. Examinations with long tube lines have shown that the component ozone is most prone to losses in the tube system whereby a clear dependency on the rate of flow through the tube is to be observed. The air sucked in must be filtered to avoid dust depositions on the admission section.

According to national standards and general international methods the main pollutants to be measured are: NO_x (NO, NO₂), CO, SO₂, PM₁₀, O₃, TOC (Total organic carbon) respectively VOC (Volatile organic compounds).

Fig. 1 shows a scheme of a set-up of such a measuring station. The measuring gas suction hoods and different meteorological measuring instruments are installed on a 10 m high altitude. The management and working methods are respecting the international standards SR EN ISO/CEI 17025:2005 (General features and competences), according to the fundamentals and definitions imposed by SR EN ISO 9000:2006. In addition to the instruments for the specific measurement of pollutants there are numerous other instruments for the recording of meteorological parameters such as wind direction and wind

speed, temperatures, global radiation, duration of rain and bedewing, amount of rain etc., as well as an electronic controlled computer, to record, calculate and memorise the values. The computer also controls the valve timing and correctly stores the measured values according to the given valve position. Half-hourly mean values (or other mean values) are calculated and are stored in the memory or/and printed out. Further evaluation of the data is then carried out on a larger computing system. Some measuring stations work with direct data transmission to a central computing station. For reasons of safety the measured values are additionally recorded by multi-channel continuous-line recorders or multipoint recorders independently of the computer controlled measured value recording system. If the computer breaks down these recorder graphs can be evaluated if necessary.

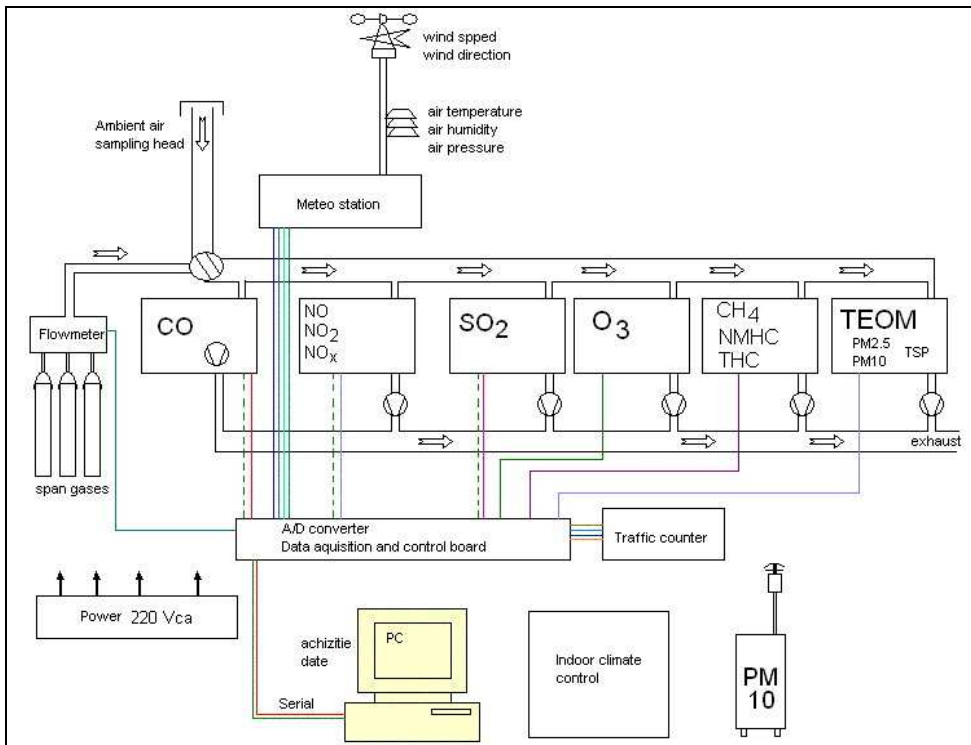


Fig. 1. Set-up of the sampling system of an air quality station with air suction through tubes and with calibration gas switching (www.mediu.ro).

In the example (Fig. 1.) also an optic open path device is included; this is an option not compulsory, for supplementary measuring possibilities, according non standardised methods. Monitors for NO_x detection from ambient air, based on the chemiluminescence's principle, according ISO 7996/1985, Monitor for the SO₂ ambient air concentration, working in UV by applying the fluorescence method, according ISO/FDIS 10498, instruments for CO detection applying ND spectroscopy in IR, according ISO 4224, Sampling analyser LVS3 for the PM₁₀ specie, based on the filtration and mass determination of a specific suspension by

means of gravimetric principles, according EN 12341 are the basic standard main components. Mostly available are also an O₃ measuring devices applying as measurement principle the UV photometry, according reference method: EN 14625:2005, and CH₄, NMHC and THC instruments using the measurement principle of FID (flame ionization detection), reference method EN 12619:2002.

Calibration and adjusting are of major importance for the correctness of the measurements. *Adjusting* means setting or trimming a measuring instrument as accurately as possible, while calibrating signifies determining the deviation measured as compared to the accurate value or the value considered as such (DIN 1319, 1985). In air pollution measurements calibration conditions are set up with the help of *calibration* (ready made by special companies) *gas mixtures*. These are gas or gas mixtures having a composition predetermined with sufficient certainty by measuring basic parameters such as mass, volume, time, amount of substance (molar number) by applying independent analysis methods (Hartkamp et al., 1983). During calibration the calibration gas are entered into the measuring setup (measuring instrument), the values indicated are read and compared with the values of the calibration gases assumed correct, then the deviations are recorded. Frequently, calibrating a measuring instrument is accompanied by other measures such as maintenance, function control, trimming and others.

According (Hartkamp et al., 1983) the total of all calibration processes consists either of basic calibration, or routine calibration, and control calibration. The basic calibration provides the fundamental relationship between given calibration gas concentrations and recorded signals, and is called calibration function. In many instruments linear calibration functions are indicated. Routine and control calibrations ensure the validity of the calibration data of the basic calibration. This control verifies whether the data obtained by the basic calibration carried out last are still valid. The results of routine and control calibrations are yes-no-decisions. The principle of calibration gas production is based on the procedure of adding a known amount of the gas of interest to a known volume or volume flow of carrier gas (mostly N₂ or air) in certain amount. The most convenient way of calibrating is with commercially available calibration gases in pressure gas cylinders (produced with static methods).

Basically, the instruments are connected to a common sample line and the measurements are taking place in the same time and for the same spot for all species. Because of the instruments high precision and accuracy the station must be equipped with calibration gases with a minimum of $\pm 1\%$ uncertainty. The numeric values provided by instruments are collected by an PC data acquisition system and stored continuously for interpretation. The station indoor environment must be controlled in order to maintain a constant temperature for instruments.

The data acquisition system of the station is automatic and the data are stored in an ASCII file type format. The operator is using the data mainly to perform graphics for each pollutant and to compare their concentration with law regulated concentrations.

2.2 Physical and Chemical Measuring Principles

For the *physical measuring methods* a specific physical property of the pollutant is made use of as quantity to be measured. The air sample does not change materially during its measurement. Specific physical properties of the substances to be investigated are applied to which other components of the sample do not contribute. In *chemical measuring methods* the quantity to be

measured is transformed into a condition with characteristic; measurable properties by a chemical reaction; during this chemical reaction the measured quantity changes.

Measuring processes based on a physical principle can generally be automated better for continuous processes, chemical methods usually being suitable for discontinuous measurements. Chemo-physical measuring principles are also applied. An essential principle which is primarily applied in the continuous measurement of gaseous pollutants is the *excitation of molecules* by adding energy. Excitation can be caused by exposure to radiation in different wave lengths, by generating high temperatures, e.g., via combustion, or by chemical reactions. Either the energy used for excitation or the energy released in another form is exploited for measurement. There are still further methods of excitation, e.g., excitation by electric, magnetic or nuclear forces. Methods of this type can be used for laboratory analyses of air pollutant samples collected. They are used less frequently, however, for direct measuring.

Passive sampling methods provide reliable, cost-effective air quality analysis, which gives a good *indication* of average pollution concentrations over a period of weeks or months. Passive samplers are so-called because the device does not involve any pumping. Instead the flow of air is controlled by a physical process, such as diffusion. Active sampling methods use *physical or chemical methods* to collect polluted air, and analysis is carried out later in the laboratory. Typically, a known volume of air is pumped through a collector (such as a filter, or a chemical solution) for a known period of time. The collector is later removed for analysis.

2.3 Units

A number of different units are used in expressing the concentrations of various species in the atmosphere (Ionel, 2000).

For gas phase species, the most commonly used units are *parts per million (ppm)*, *parts per hundred million (pphm)*, *parts per billion (ppb)*, and *parts per trillion (ppt)*. These units express the number of molecules of pollutant found in a million (10^6), a hundred million (10^8), a billion (an *American billion* is 10, a *British billion* is 10^{12}) or a trillion (10^{12}) molecules of air, respectively (Finlayson-Pitts & Pitts, 1986).

Alternatively because numbers of molecules (or moles) are proportional to their volumes according to the ideal gas law ($pV = mRT$, where p - pressure in Pa, V - volume in m^3 , m - mass in kg, R is the gas constant expressed in J/(kg K), T - temperature in K), one uses also the *mass concentration*. The conversion is carried out as follows:

$$1 \text{ mg/m}^3 = 1 \text{ cm}^3/\text{m}^3 \cdot \rho = 1 \cdot \frac{\text{cm}^3 \text{ pollutant} \cdot \text{mg pollutant}}{\text{m}^3 \text{ air} \cdot \text{cm}^3 \cdot \text{pollutant}}$$

$$\rho = \text{gas density} = \frac{m}{V} \text{ kg/m}^3$$

$$\rho = \frac{\text{molar mass}}{\text{molar volume}} \text{ kg/m}^3 \text{ or g/l or mg/cm}^3$$

$$\rho = \frac{\text{molar mass}}{22.4} \text{ kg/m}^3 \text{ or mg/cm}^3 \text{ (at } 0^\circ\text{C, 1,013 mbar)}$$

$$\rho = \frac{\text{molar mass}}{24} \text{ kg/m}^3 \text{ or mg/cm}^3 \text{ (at } 20^\circ\text{C, 1,013 mbar)}$$

The molar mass is specific to each chemical gas specie, according to its chemical formula. The molar volume is depending on the pressure and temperature values, considered by law as reference.

3. Standard Measuring Methods for Air Pollutants

3.1 Photometry

Photometry uses the absorption of infrared (IR), visible (VIS) or ultraviolet (UV) radiation by the gases as measuring effect. Wave length ranges are: IR (1,000 - 10,000 nm), VIS (400 - 800 nm), UV (approx. 200 - 400 nm). In the visible and UV electrons are excited by radiation, in the IR range predominantly molecule vibrations but also rotations are activated. During this, the gases absorb energy in certain wave length ranges (absorption bands). The loss of radiation intensity caused by this is consequently measured.

Fig.2 shows the principle of a photometer that consists of a radiation source (lamp), having a focused beam of light falling through a cell on a radiation detector. The latter transforms the beam into an electric signal of proportional intensity. The loss of radiation intensity due to the absorption of the measuring gas is - when frame conditions are constant - a measure for its concentration.

The interrelationships of radiation absorption are described by the Lambert-Beer law:

$$I = I_0 \cdot e^{-\varepsilon \cdot C \cdot l} \quad (1)$$

$$\frac{I}{I_0} = T = \frac{1}{E} \quad (2)$$

$$E = \ln \frac{I_0}{I} = \varepsilon \cdot C \cdot l \quad (3)$$

where I_0 is the intensity of entering radiation (intensity of light for the reference), I the intensity of exiting radiation (intensity of light for the sample), T stands for the transmission, ε for the extinction coefficient (dependent on wave-length), C for the concentration of gas or pollutant, l for optical path-length of the cell measurement, E for extinction (non-dimensional) of the absorbing substance inverse logarithm of the transmission T .

Most IR photometers function as so-called non-dispersive instruments (NDIR), i.e., radiation is emitted in the entire IR range. There is no spectral splitting of the IR radiation emitted by the radiation source. Selectivity is achieved by installing a radiation detector filled with the component to be measured. This type of detector is possible only in the IR range, as the lifespan of the molecules excited by IR radiation is so long that the excitation energy can be released via molecule collisions as thermal energy.

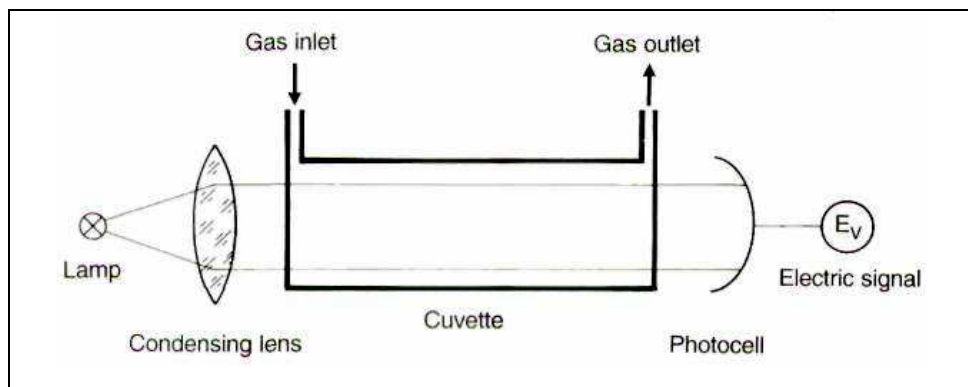


Fig. 2. Principle of a photometer (Baumbach, 1997).

Extinction E as a measure of the radiation absorption of a gas (or also of a liquid) is thus dependent on the properties of the gas (extinction coefficient ϵ), on the concentration c and on the optical path-length l which the beam of light must pass through. If ambient conditions are constant, ϵ for a gas is constant. If l is also kept constant, then extinction E is directly dependent on the concentration of the gas to be measured.

In practice it is not sufficient to form the logarithm of the ratio of intensity I_0 in and intensity I out and to thus determine extinction E . Even without the presence of the component to be measured the instruments absorb radiation, e.g., via optical windows and the gases to be investigated. Thus, even without the presence of the component to be measured, radiation in is not equal to radiation I_0 out. This blank absorption must generally be determined experimentally.

NDIR instruments are primarily used for emission measurements; analyzers are mainly suitable for the determination of the gases CO , CO_2 , NO , SO_2 , H_2O , CH_4 , C_2H_6 , and many other hydrocarbons. For CO and CO_2 , NDIR photometry is the most commonly used measuring technique, which is also unrivalled in its application for the measurement of these gases in the ambient air range.

As shown in the Fig. 3, the instruments for CO measurements uses the modulation effect that occurs with infrared absorption of sample gas itself when sample gas and zero gas are alternately sent to its cell at a certain flow rate using a solenoid valve which is actuated at a frequency of 1 Hz. Unless the gas concentration of the measured component is changed in the cell, the output from the detector essentially becomes zero, therefore, the zero drift does not occur. Since the instrument also uses the AS-type detector, extremely high-accuracy results are obtained without any effect of the interference component.

The radiation source is an infrared radiation emitter. The radiation - modulated by a chopper - passes a chamber containing the probe and in parallel a chamber containing a reference gas. To reduce the influence of interfering gases optical filters are used. The content of the measurement cell receives periodically infrared radiation with different strength, which results in different temperature and pressure effects. The pressure effects are hence transferred to electrical signals by a sensor, and this signal correlates to the measured CO concentration. Some systems use the pressure waves for detection, while others use directly the IR receiving an optical detector to measure the CO concentration.

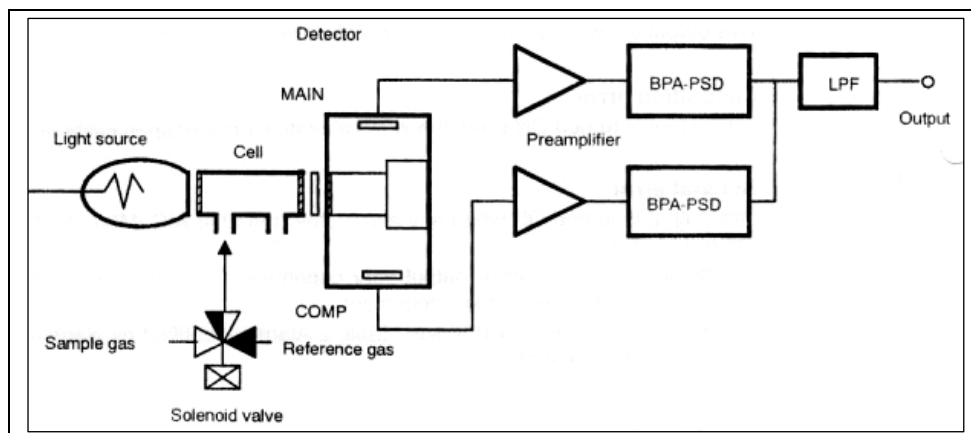


Fig. 3. CO monitoring device schematic (Horiba, User manual)

There are gases with relatively narrow UV absorption bands, e.g., NO and NH₃. Other gases, however, absorb UV radiation in a wider band. To be able to obtain selective measurements certain stratagems are to be applied. A first selection is made by choosing the right UV lamp. Depending on their metal or gas fillings UV lamps have certain emission spectra. Therefore one uses lamps with emission bands which best correspond to the absorption bands of the measuring components or which lie within the absorption bands as clearly defined lines. Besides soiled cells and lamps with fluctuating intensities, they also lead to high and fluctuating reference values I_0 of the radiation and thus to high blank values of extinction. There are different possibilities of compensating for the blank extinctions and of receiving corrected reference radiation intensity I_0 and will be outlined using the example of UV-photometric measurement of NO.

An UV absorption photometer for NO was developed as shown schematically in Fig. 4 (Hartmann & Braun, 1982), (FVLR, 1979). In a hollow cathode lamp filled with nitrogen and oxygen at reduced pressure, excited NO molecules are formed in an electrical discharge. The energy of the excited molecules is dissipated by emission of characteristic luminescence radiation. The source of radiation is selective; it produces an emission range which corresponds precisely to the absorption range of NO in the measuring cell. This is called resonance absorption. One peculiarity of the radiation excited by electrical discharge is that two groups of NO-specific lines are emitted, i.e.: (i) "cold" emission lines - this is the group absorbed by the NO to be determined in the measuring cell (measuring radiation), (ii) "hot" emission lines - that group of radiation showing lines in the neighboring range and meeting the detector not influenced by NO (reference radiation).

The radiation is modulated by a chopper wheel and passed through the measuring cell via a condensing lens. It reaches the radiation detector, a photomultiplier, via an interference filter where interfering radiation is removed. If NO is present in the measuring cell, then the radiation is reduced by resonance absorption (extinction E) according to the Lambert-Beer law. For this measuring technique the blank value of extinction E_0 is compensated for by alternately setting the chopper wheel to a position where all radiation (hot and cold emission lines) is passed through and to a position with a gas filter.

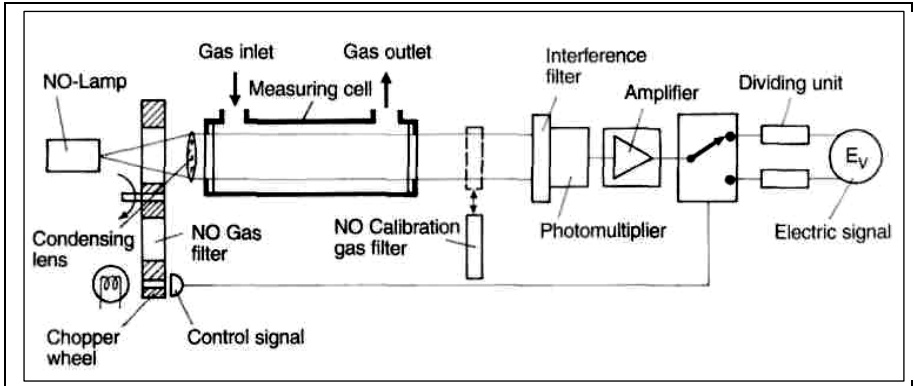


Fig. 4. Diagram of a UV gas analyzer for the detection of NO with blind value compensation by wavelength comparison (FVLR, 1979).

The gas filter contains NO in high concentrations which completely absorbs the cold emission lines. The hot emission lines, however, which are in the immediate neighborhood range, pass through it as reference radiation. Just like the measuring radiation they are influenced by the in-line optics, by the cell windows but mainly by the wide-banded interfering components to produce the intensity reference value I_0 at the photomultiplier. Fig 5 presents an ozone instrument that performs a dry analysis of ozone, on continuous basis.

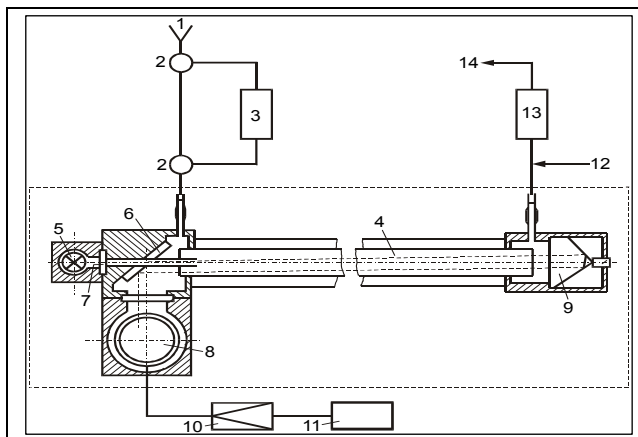


Fig. 5. O₃ monitoring device schematic (Horiba, User manual) 1 - Sample intake, 2 - Three way valve, 3 - Ozone generator (internal calibration), 4 - Measurement cell, 5 - Hg-Low pressure lamp, 6 - Mirror, 7 - Interference filter, 8 - Photo multiplier, 9 - Quartz - triple prisms, 9 - Amplifier, 10 - Display, 11 - Exit gas sample, 12 - Charcoal, 13 - Excess air exit, 14 - Excess air exit.

3.2 UV Fluorescence

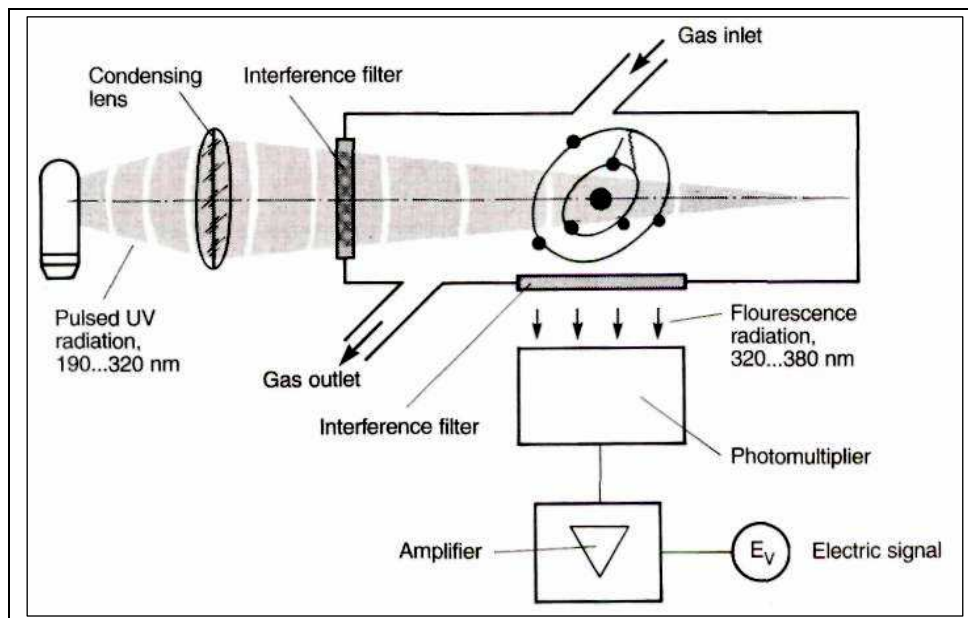


Fig. 6. Principle of UV fluorescence measurement (Zolner, 1984).

UV fluorescence is a measuring technique related to photometry. The measuring gas is also exposed to radiation. However, it is not the radiation absorption which is measured but a luminous phenomenon (fluorescence) which is caused by the excitation of molecules through UV radiation of a certain wavelength. The measuring principle is, e.g., applied in SO_2 ambient air measurement, presented in Fig. 6.

The air sample is exposed to UV radiation in the wavelength range of 190-320 nm. If present, SO_2 gives off a fluorescence radiation of 320-380 nm. Due to an interference filter only a radiation of this wavelength is recorded by the detector (photomultiplier); thus, the measuring principle is strictly selective. The higher the SO_2 concentration, the greater the fluorescence.

One interference in this measuring technique is that other components can absorb the energy of the excited SO_2 molecules, thus reducing the fluorescence yield. This interfering effect is known particularly from water vapor and hydrocarbons. By interposing a permeation gas exchanger an elimination of the interfering components from the measuring gas is attempted. Measuring instruments operating according to this principle are used for both SO_2 air quality measurements as well as for SO emission measurements. In emission measurements the interferences are higher due to the higher concentrations of the interfering components. Air quality measurement instruments operate very stably as far as zero point and sensitivity drift are concerned and as long as the intensity of the UV lamp remains constant.

The reference method for SO_2 measurements is the ultraviolet fluorescent method (UVF).

When a sample is irradiated with ultraviolet ray (215 nm), SO₂ emits the light of a different wavelength (peak: 320 nm, range: 240 nm to 420 nm) from that irradiated. The former, irradiated light is referred to as excitation light, and the later, emitted light is referred to as fluorescence. The method to obtain sample concentrations by measuring the fluorescence intensity is called the fluorescence method. In the fluorescence method, fluorescence, which radiates in all directions, is usually detected at the right angles to the excitation light in order to prevent interference by the excitation light.

When excitation light is irradiated and absorbed following processes take place:

Process 1: Absorbing and process excitation.



There are three ways by which the SO₂* loses its excitation energy.

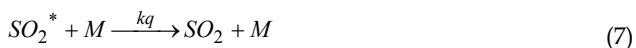
Process 2: Fluorescence process: Excitation energy is emitted as fluorescence.



Process 3: Dissociation process: Excitation energy is used for dissociation.



Process 4: Quenching process: Excitation energy is lost by collision with surrounding molecules, M.



Practically, the excitation energy is lost resulting from the confluence of these three processes. Fig. 7 presents the schematic diagram of a SO₂ measurement device.

The sample gas is continuously drawn into a cylindrical Teflon-coated reaction cell at near ambient pressures. The atmospheric gas is irradiated by UV light that has been mechanically modulated and filtered to 214 nm. The fluorescent secondary emission of the SO₂ molecules present in the gas is measured by a photo-multiplier tube (PMT). The PMT is located at 90° from the UV lamp source on the axial centre line of the reaction cell. The filtered UV light passes through a collimating lens that focuses the light energy at the centre of the cell. The PMT is optically tuned to measure the fluorescent emission and outputs the signal through an amplifier to a synchronous demodulator. Simultaneously, the UV light source constancy is measured by a reference photo-detector tube, located directly across the reaction cell from the lamp. The light travel down an optically-designed dump to the photo tube, whereupon is output is amplified and processed through a nearly identical synchronous demodulator. The mixer board electronics then uses this signal to compensate for any variation in the UV light source.

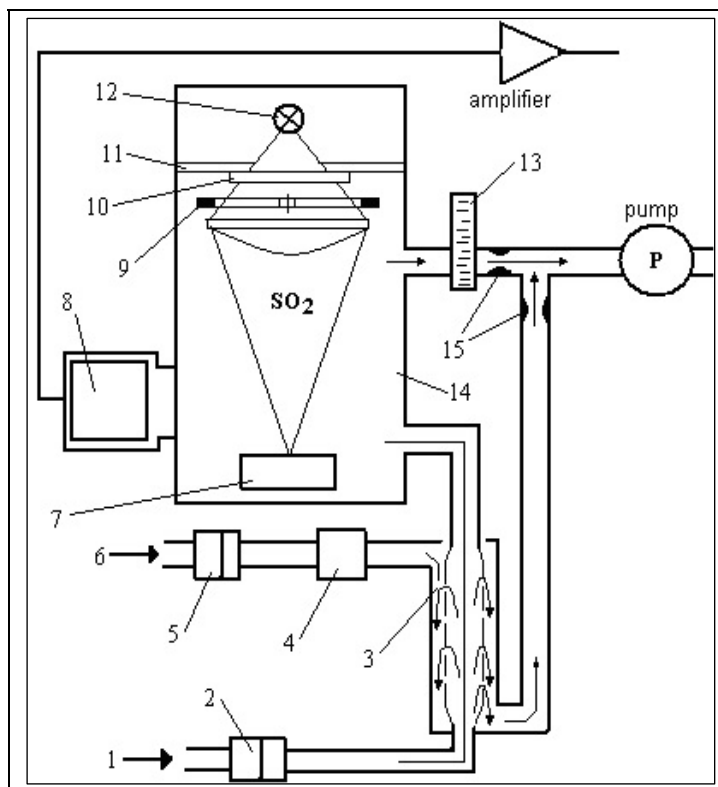


Fig. 7. SO₂ monitoring device schematic according UV fluorescence principle (Baumbach, 1997).

3.3 Chemiluminescence

Chemiluminescence is related to UV fluorescence. The difference between the two is that in chemiluminescence molecules are not excited by UV radiation, but are excited by a chemical reaction. Thus, the measuring principle is a chemo-physical one. The intensity of the radiation created is a measure for the concentration of the reacting gas in a mixture of gases, if the external conditions (pressure, temperature and volume flow of the measuring gas) are kept constant. Just as is the case in UV fluorescence, the radiation created is recorded by a photomultiplier acting as radiation detector and is transformed into an electric signal. This method is used mainly for measuring NO, NO+NO₂ (i.e., NO_x) and O₃.

To measure the NO and NO₂ concentration into the atmosphere the TÜV (EU) and U.S. EPA requirements are fulfilled only by chemiluminescence's method. The instrument must provide continuous and unattended monitoring of NO, NO₂ and NO_x with individual determinations and high reliability and accuracy. An internal NO₂ to NO converter permit NO_x analysis and an integral ozone supply system which puts filtered, dehumidified ambient air through an ozonator to generate the ozone necessary for reaction with NO to give chemiluminescence's reaction. The instrument must have a flow-chopping modulation system to give continuous NO_x and NO analysis. With this system, the sample gas is divided into two separate lines. One sample gas line passes through the NO₂ to NO

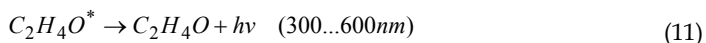
converter, while the other leads directly to the detector. Also a permeation tube in which only moisture is passed through is used for the sample line is needed. This tube functions so that an influence from the moisture is reduced by minimizing difference of moisture concentration between sample gas and reference gas.

Inside the reaction chamber NO reacts with ozone to form NO₂. The NO₂ is excited to a higher electronic state. This chemiluminescence's is measured through an optical filter by a photodiode. The modulated hybrid signal from the detector is demodulated to give continuous NO_x and NO signals at the same time. The NO₂ concentration is given by subtraction of NO from NO_x.



Filtered sample gas is divided into lines 1 and 2. In line 1, the sample gas flows through an integral converter which reduces NO₂ to NO. In line 2, the sample gas remains as it is. The sample gas is switched to NO line, reference line, NO line and to reference line again by the solenoid valve with 0.5 sec interval. Then it is introduced into respective reaction chamber. Luminescence due to reaction of the sample and O₃ occurred in the chamber is detected by a photodiode. By electrically processing the output of photodiode, it is possible to take out continuous signal in NO line and NO line respectively. Flow to the detector unit is controlled by capillaries. Ozone is supplied to the reaction chamber at a constant rate by an internal ozonator which uses dehumidified ambient air as feed gas. The dryer unit has two dryer cylinders. When one cylinder is under operation, the other is regenerated. For regeneration, first heat the tube to 120°C for 135 minutes to evaporate all the water, and then cool the tube for 45 minutes. It is possible to perform continuous drying by changing over the line of use and regeneration every 180 minutes.

According to the same chemiluminescence reaction as in the case of the NO measurement, ozone could be measured by its reaction with NO. A better and more inexpensive reaction partner for ozone, however, is ethane (C₂H₄):



During this reaction chemiluminescence radiation is once again formed to be measured analogous to NO determination. The sole disadvantage of this ozone measuring technique is that ethane is required which is only available from a gas cylinder. As it is a flammable gas, this measuring technique is regarded with disfavor in air quality measuring stations and has given way increasingly to UV photometry. In the matter of interference and susceptibility to faults the chemiluminescence method is superior to UV photometry.

Fig. 8 gives the basic schematic of one NO_x analyzer.

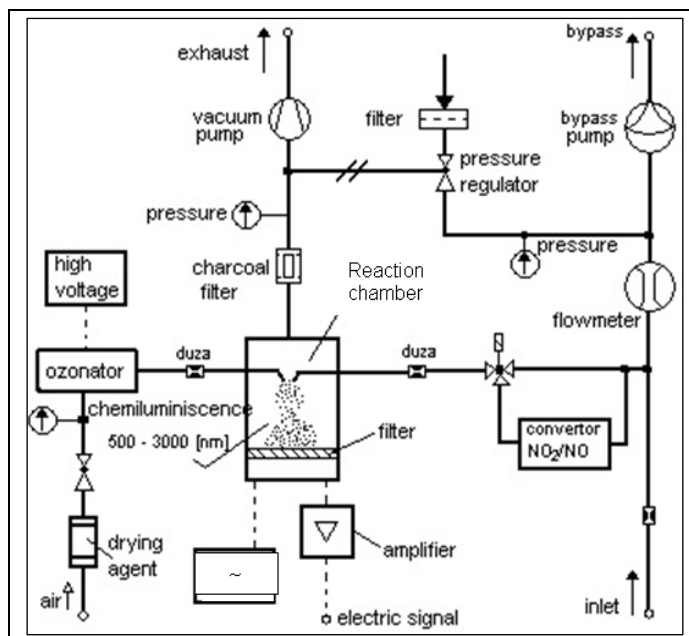


Fig. 8. NO_x monitoring device schematic (HORIBA AP370 User manuals).

3.4 Flame Photometry and Ionization

In flame-photometry atoms are excited in a flame and made to luminescence. The spectral line of the atom of interest is filtered out from the radiation of the flame via an interference filter and measured with a photomultiplier. In gas analyses this process is used mainly for sulfur measurements, but it is also suitable for measuring phosphorous compounds. In sulfur measurement, however, the flame-photometric effect is not based on an atom emission but on a recombining of sulfur atoms whereby excited S^*_2 molecules are formed which pass into their basic state under a light emission of approx. 320 nm - 460 nm. With an optical filter a wave length of 394 nm is chosen for sulfur detection (Birkle, 1979).

The total sulfur content of the air, mainly H_2S and SO_2 , is primarily measured. If individual compounds are to be identified, then single gases must be removed by absorption and adsorption filters prior to measuring. This process is distinguished by a high sensitivity (low detection limit!) and by a very brief response time. Therefore measuring devices working on this principle are used, e.g., for air quality measurements with aircraft (Paffrath, 1985). Owing to the fact that hydrogen is required as an auxiliary gas for generating the flame inside the device the flame photometer is used less frequently in stationary air quality measuring stations. It is not common practice to use it for emission measurements as the concentrations to be measured are too high and there are too many interfering components (quenching).

Gases can be ionized more or less easily by the addition of energy. For gas analyses the ionization of organic molecules in flames (flame ionization) has gained the greatest significance. Ionization by radiation of radioactive substances in detectors, e.g., in gas chromatography, is also applied (Kaiser, 1965).

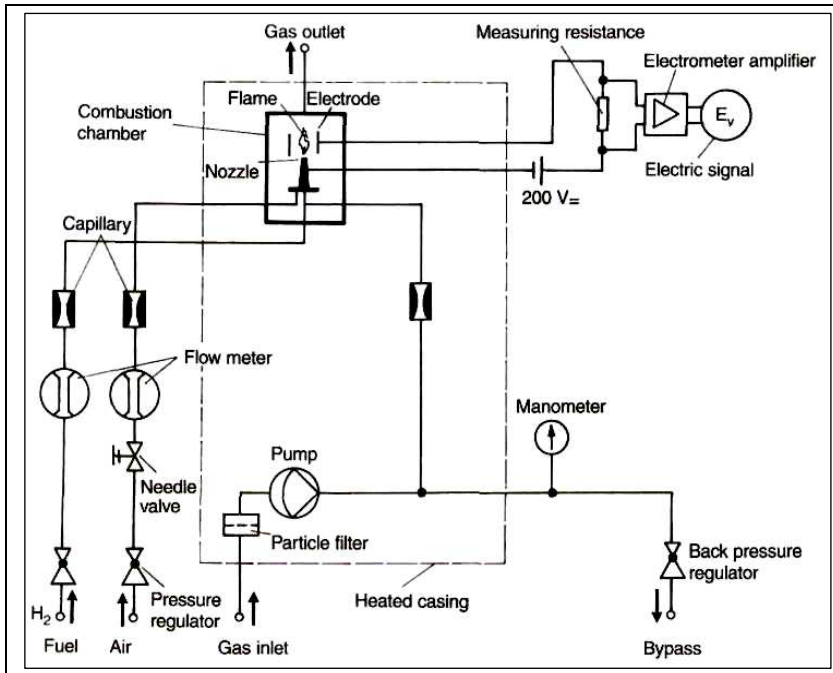


Fig. 9. Diagram of a flame ionization detector (FID) (Kaiser, 1965).

The so-called flame-ionization detector (FID) was originally developed for gas chromatography. Nowadays, it is also used as the most important measuring device for the continuous recording of organic substances in exhaust gases or in ambient air.

The measuring principle of the FID is classic and will be summarized here with the help of Fig 9.

The hydrogen flame burns out of a metal nozzle which simultaneously represents the negative electrode of an ionization chamber. The positive counter-electrode is fixed above the flame, e.g., as a ring. Between the two electrodes direct voltage is applied. The ion current is measured as a voltage drop above the resistor W . The measuring gas is added to the burning gas shortly before entering the burner nozzle. The air required for combustion flows in through a ring slot around the burner nozzle.

For stable measuring conditions it is essential that all gases - combustion gas, combustion air and measuring gas - are conducted into the flame in constant volume flows. For this, all gas flows are conducted via capillaries. Constant pressures before the capillaries ensure a constant flow. Sensitive pressure regulators for combustion gas and combustion air are used to achieve this fine-tuning. The measuring gas is pumped past the capillary in the bypass in a great volume flow. Pressure is kept constant by the back pressure regulator, so that a constant partial flow reaches the flame via the capillary. Most FID's operate with overpressure, i.e., the measuring gas pump is located before the capillary. To avoid condensation of the hydrocarbons to be measured almost all instruments can be heated to 150-200 °C. Heating includes the particle filter and the measuring gas pump; in most cases,

particularly with warm exhaust gases, a heated sampling line is also used from measuring gas sampling to the measuring instrument.

Hydrocarbon compounds are oxidized in the flame with ions being formed as an intermediate product. In a certain range of the accelerating voltage the strength of the ionization current is in first approximation directly proportional to the amount of C atoms of the burned substance. Thus, an FID basically responds to all hydrocarbons and measures their total sum. Corresponding to the number of carbon atoms, larger molecules with many C atoms produce a higher signal than smaller molecules with a small number of C atoms. Ionization energy does not only stem from the flame's energy, but mainly from the oxidation energy of the carbon. Accordingly partially oxidized hydrocarbons provide a weak detector signal, completely oxidized hydrocarbons no signal at all; HCHO, CO and CO₂, e.g., are not detected. If exhaust gases predominantly consist of mixtures of pure, i.e., non-oxidized or halogenated hydrocarbons, the FID provides a signal nearly proportional to the carbon mass content of the exhaust gas.

The reference method for HC (hydrocarbons) measurements (including CH₄ methane and NMHC - non-methane hydrocarbon) is the flame ionization method (FID). The principle of this method is represented in figure 10.

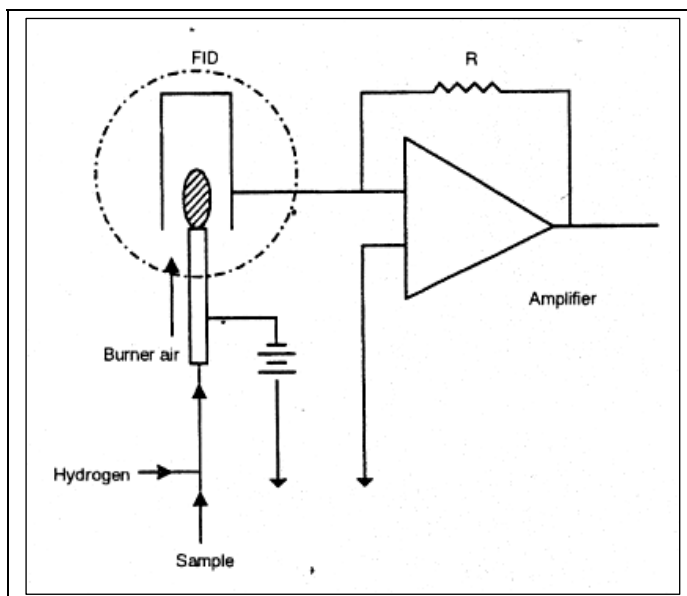


Fig. 10. FID monitoring device schematic for (Horiba, User manual)

When hydrocarbon is introduced to hydrogen flame, the high-temperature energy at the jet nozzle tip ionizes the hydrocarbon molecules. In this time, applying a direct-current voltage between two electrodes that face each other across the flame generates a minute ion current, proportional to the carbon number of the ionized hydrocarbon. The total hydrocarbon can be measured by passing this ion current through a high resistance to convert it to voltage. The sampled gas is divided in two flows: one is used for CH₄ concentration measurement by removing HC other than CH₄. The other is used for THC concentration measurement

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