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Ozone measurement systems: associated instrumentation and calibration

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Abstract

The harmful effects produced by ozone have lead to a vast regulation to define and establish the quality goals of ambient air, based on common methods and criteria. The surveillance nets of atmospheric pollution are worldwide extended systems and the applied technology for the ozone measurement is nowadays quite standardized. The aim of this paper is to give a general view of the most common systems used in the ozone measurement in ambient air from a practical point of view. The used instrumentation and the usual calibration methods will be described.

1 Introduction

The ozone is an invisible and colourless gas with a high reactivity due to his third oxygen atom tendency to detach itself from the molecule.

Generally, two types of ozone are distinguished:

- Tropospheric ozone: located in the troposphere or first layer of the atmosphere, from 0-10 km. It is considered to be a pollutant for its adverse effects on the environment and people.
- Stratospheric ozone: included in the ozone layer or ozonesphere, above the troposphere which protects the Earth from ultraviolet radiations (UV).

We will focus on tropospheric ozone and the regular instrumentation used for its measurement.

The tropospheric ozone is a secondary pollutant formed from photochemical reactions. The precursors of this ozone are the nitrogen oxides and the Volatile Organic Compound (VOC) activated by solar radiation.

The basic chemistry of these reactions is explicigted on equation 1:

$$\begin{aligned}
&NO_2 + h\nu \rightarrow NO + O\\
&O + O_2 \rightarrow O_3\\
&COV + NO \rightarrow NO_2 + other\ products\\
&\Updownarrow\\
&O_3 + NO \rightarrow NO_2 + O_2
\end{aligned} \tag{1}$$

These chemical reactions are coherent with the verified fact that the major ozone values coincide with the hours of biggest solar radiation and usually later than the maximum nitrogen and VOC oxides obtained, primary pollutants generated, partially, as a result of wheeled traffic.

The State Rules which regulate the ozone presence in atmospheric air are found in the Real Decreto 1796/2003 where objective values of ozone concentrations are established to protect people's health as well as vegetation. This RD is the transposition to the Spanish legislation of the community guideline 2002/03/CE whose last purpose is that of avoiding, preventing and reducing the harmful effects of ozone on human health and the environment in general. In its articles, the parameters for the evaluation of the same are defined, among which we should underline the following:

- Objective value: ozone concentration to be reached in the year 2010 to avoid at long term the harmful effects on health and environment.
- Alert threshold of 240 μg m^{-3}
- Information threshold of 180 μg m^{-3}
- Evaluation of ozone concentrations and precursor substances.

A very important aspect included in these rules is the definition of the reference method for the ozone measurement. It involves the ultraviolet Photometry (UNE 77221:2000, equivalent to ISO 13964:1998).

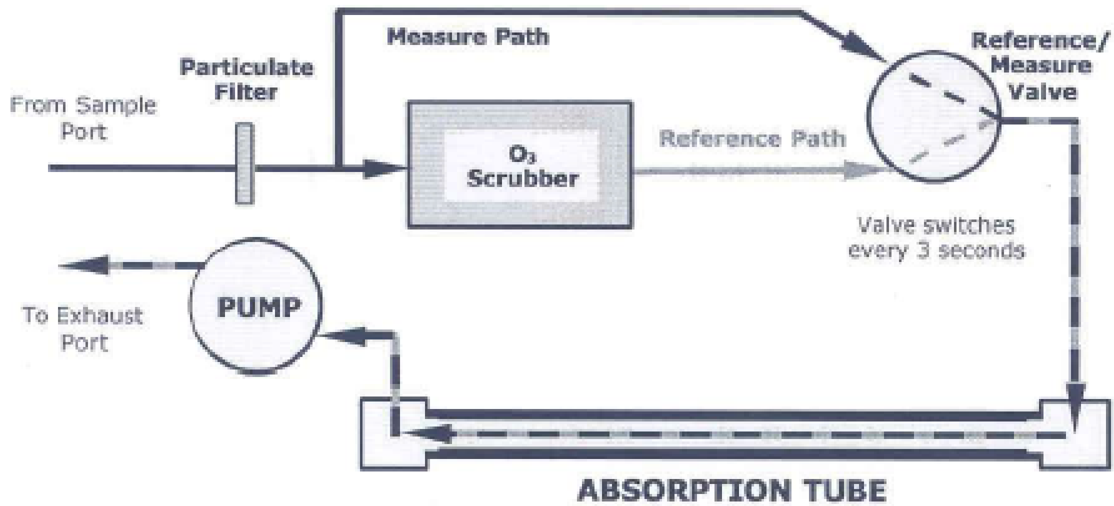

Figure 1. Reference cycle/Gas measurement.

2 Functioning Principle

The functioning principle of measurement for the continual determination of ozone as a pollutant of the lower atmosphere according to regulations is based on the characteristic absorption of the ozone molecule when being irradiated by ultraviolet radiation.

When a beam of ultraviolet light crosses a certain gas volume containing ozone molecules, they themselves absorb the UV radiation, which will be maximum for wavelengths of about 250 nm.

The physical principle is based on the Lambert-Beer Law, which is expressed in equation 2:

$$I = I_0 e^{-Kcl} \tag{2}$$

being: I, Intensity after the absorption; I_0, Intensity of the original source; K, Ozone absorption coefficient; c, Concentration in volume of the pollutant; l, Length of the optical path.

3 Functioning of the Analyzer

The air sample to analyze is filtered to avoid the entry of dust contained in the sample, reaching the electric valve that sorts out the passage of the air to be sampled through a catalyst that eliminates the ozone contained in the sample (figure 1).

The air without ozone is introduced in the optical cell and the radiation emitted by the UV lamp is measured through a photometer (I_o) within the reference cycle. Once the radiation is measured, the electric valve switches its position allowing the entry of the air to be sampled directly to the measurement cell. The emitted radiation by the UV lamp is again measured by the photometer (I) inside the measurement cycle (figure 2).

The absorption produced by ozone is calculated through the difference between the measured signals in the cell using the Lambert-Beer equation and therefore determining the ozone concentration in the analyzed air sample.

4 Elements of an ozone analyzer

4.1 Optical Bank

It is the part of the analyzer where the measured ozone absorbs the UV light, which is transformed into voltage. It is formed by:

- An UV mercury lamp.
- UV lamp feeder system.
  - Quartz absorption tube.
  - Ultraviolet detector/preamplifier. It transforms UV light into power, which is amplified and scaled by the preamplifier.
  - Measurement and temperature control elements.

4.2 Pneumatic system

It is responsible for supplying and measuring the air flow to be sampled, formed by:

- Vacuum bomb.
- Flow regulator which maintains the necessary flow in the measurement system.
- Flow sensor.
- Pressure sensor.

It also contains a filter which eliminates the dust particles contained in the sample to be analyzed.

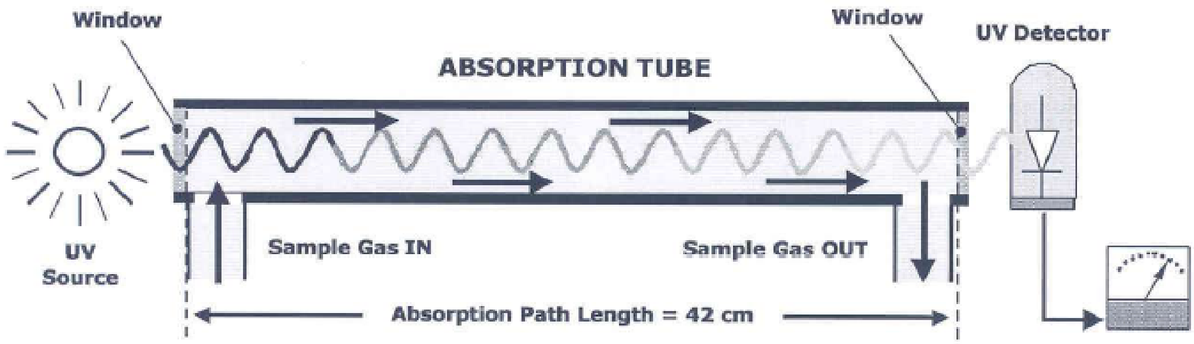

Figure 2. Detail of the 0_3 absorption.

4.3 Processing electronics

It carries out the detector signal process for each measurement providing the instantaneous ozone concentrations according to the Lambert-Beer Law. It also carries out a non-stop revision of the equipment operative parameters, it balances the pressure and temperature measurements, it stores data and establishes the data transmission protocol, etc.

5 Calibration

Calibration is the process of adjustment, control or determination of an instrument scale against a known standard. The reliability and utility of all the derived data from any gas analyzer depends mainly on its calibration status.

The dynamic calibration is used to express a multipoint verification against the known standards and it implies the introduction of span gas samples of known concentration in the instrument, to adjust it to a predetermined sensitivity and produce a survey of the calibration. This survey is the result of a answer of the instrument to consecutive samples of different known concentrations. We recommend a minimum of three reference dots and a zero dot to define this survey.

All the gas analyzers systems are subject to certain deviations and variations of internal parameters and we cannot expect them to maintain an exact calibration in long periods of time. Therefore, it is necessary to check the calibration according to a predetermined calendar, thus allowing its correct functioning.

5.1 Elements intervening in the calibration

Zero air source. It has to be free of ozone and any other substance which could react with ozone (i.e. NO, NO_2, hydrocarbons and particles). It can be obtained by means of atmospheric air through a zero air generator or using pure air bottles.

Calibration gas. Due to the ozone instability, the certificate of O_3 concentrations as reference materials is impossible. Therefore, when the O_3 concentration standards are required, they have to be generated and locally certified.

The calibration gas can be obtained by means of an ozone generator controlled by a primary UV photometer or a transfer pattern.

Data recording system. A data acquirement system has to be used for the control and recording of the analyzer concentrations.

5.2 Types of calibration

There are several types of calibration:

- Zero calibration and "span": it is a simplified two-dot calibration used when the instrument linearity does not need revising. It usually ha a weekly periodicity.
- Multipoint calibration: in addition to the previous process, several different concentrations are generated and uniformly distributed between the beginning and the bottom of the scale of the analyzer. It is usually carried out with a quarterly or half-yearly periodicity.

6 Other ozone measurement methods

6.1 Chemoluminiscence

The measurement principle is the same used for the determination of the NOx present in the atmosphere. It is based on the reaction of the nitrogen monoxide (NO), with the ozone (O_3), to form NO_2, by means of the equation 3:

$$\begin{aligned} NO + O_3 &\rightarrow O_2 + NO_2^* \\ NO_2^* &\rightarrow NO_2 + h\gamma \end{aligned} \qquad (3)$$

In this reaction, a chemoluminiscence, or generation of visible or infrared radiation, occurs when two species react to form an excited compound, which, when returning to its fundamental state, emits a characteristic radiation; the method is based on the measurement of the produced chemoluminiscence, which is proportional to the amount of ozone.

6.2 Method of the Passive Tubes

It involves inert cylindrical tubes with an open end to the atmosphere, and on the opposite end there is an absorber capable of retaining the gaseous pollutant whose concentration we wish to determine. They collect the ozone by molecular spread. In the open end, it has a mesh to avoid the entry of dust particles, where as in the opposite end there is an IK-NaOH drenched filter. The ozone concentration is determined by means of an analysis by ionic chromatography.

6.3 Other methods

The Systems without Sample Extraction, also called long optical way systems or remote sensors, are other methods fundamentally used with research purposes.

7 Conclusions

There are different methods to measure the ozone in the lower atmosphere, but the most used by the government authorities and private companies by far is the ultraviolet photometry. Among other technical and economic reasons, we have to attribute its large spread to the Legislation which defines it as a reference method.

The natural tendency in all the information systems is knowing beforehand what is going to happen; it is no longer enough to measure what is happening or maintaining a historical values record. This need explains the appearance of techniques to predict ozone with different complexity and accuracy levels, among which we could mention the statistic models, the climatological models, the neuronal nets, the 3D physical models, etc.