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Optimal characterization of a commercial ozone analyzer in ambient air for purposes of Air Pollution Control

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Abstract **–** The main purpose of this paper is to characterize an analyzer of ground level ozone based on the photometric UV method. Particular attention is devoted to the sampling phase with the aim of investigating the main variables influencing the measurement process. In this way it is possible to identify the best sampling configuration able to minimize the measurement uncertainty.

Keywords: ozone analyzer, calibation, sampling phase.

I. Introduction

Ozone in the smog is a secondary pollutant produced by photochemical processes that involve nitrogen oxides (NOX) and volatile organic compounds (COV). Power plants, motor vehicle exhaust, industrial facilities, gasoline vapors and chemical solvents are the major human-made sources of ozone emissions.
Ozone concentrations are sensitive to a variety of meteorological variables such as wind direction and speed, temperature and intensity of solar radiation. Seasonal variations in meteorological conditions, particularly solar intensity and temperature, impose systematic ozone seasonal variations in ozone concentration. For this reason ozone level tends to increase during the summer because it is characterized by stagnant meteorological conditions, high insulation and high temperatures [1].
International directives and prescriptions require many monitoring and controlling systems to asses the air quality and to identify the impact of anthropic activities on ambient and human health. In Particular, Europe directive 2002/3/CE [2] provides long term objectives, target values, an alert threshold and an information threshold for concentrations of ozone in ambient air.
In this context, it is very important to have reliable and comparable data measured with suitable instrumentations that must be periodically verified by means of calibration procedures.
The main difficulty in calibration of ozone analyzer is to produce gaseous mixtures with known ozone concentration. In fact, the very reactive nature of ozone molecule precludes its storage in cylinders. As a consequence, ozone has to be produced dynamically *in situ* and verified with a suitable reference instrument.

II. Measurement method

ISO standard 13964 [3] specifies an ultraviolet (UV) method for the determination of ozone concentration in ambient air. For the calibration phase, this international standard specifies the ultraviolet photometry as the primary reference procedure because of its proven accuracy and specificity to ozone.
The measurement principle is based on adsorption of UV light at 253.7 nm by ozone molecule. Sample air is draw continuously through an optical absorption cell where monochromatic radiation centered on 253.7 nm is irradiate by means of a stabilized low pressure mercury discharge lamp. A photodetector locate at the opposite end of sample cell measures the reduction in UV radiation caused by the presence of ozone. The Lambert-Beer law is used to relate the measured UV transmittance to the path length of absorption cell and the ozone concentration.

$$\frac{I_t}{I_0} = e^{-\alpha CL} \tag{1}$$

where:
I_t/I_0, the transmittance of the ozone sample, is the ratio of the UV radiation intensity I_t measured by detector when the absorption cell contains sample air, to the UV radiation intensity I_0 measured when the cell contains ozone scrubbed air;

$\alpha = N_A\sigma$ is the ozone absorption coefficient: N_A is the Avogadro constant, σ is the ozone absorption coefficient;

C is the ozone concentration in the sample air at the sample temperature and pressure in the absorption cell,

L is the optical path length.

Most modern commercial ozone analyzers measure the temperature and pressure of the sample air in the absorption cell. Using these data and the ideal gas law, equation (1) can be rewritten to express the measurement results in function of mole fraction (x) of ozone in the air.

$$C = \frac{xp}{RT} \quad \rightarrow \quad x = \left(-\frac{RT}{N_A \sigma L p}\right) \ln\left(\frac{I_t}{I_0}\right) \tag{2}$$

where x is the ozone-in-air mole fraction, p and T are the sampled air pressure and temperature respectively and R is the molar gas constant.

The ozone analyzer used in our study has a double-cell configuration (Fig. 1) consisting of two absorption cells constructed of material inert to ozone, two solar blind photodiodes and a single lamp. The lamp is equipped with a quartz plate in order to filter out the radiation at 185 nm which would produce ozone for photolysis.

This instrument measures reference and sample air simultaneously. By using the double-cell configuration it is possible to compensate the influence of UV radiation intensity variations on ozone measurements. Concentration measurement is obtained in two steps [4]. The time of each step is 10 s. In the first part of measurement cycle the sample air is passed both in the first absorption cell (cell A) and in the scrubber that removes ozone. Then, scrubbed sample air enters the second cell (cell B) to establish a reference light intensity at zero ozone concentration. The scrubber removes ozone, nitric oxide, nitrogen dioxide, sulphur dioxide and hydrocarbons that represent interfering substances that can cause an undesired measurable positive or negative response in UV photometer.

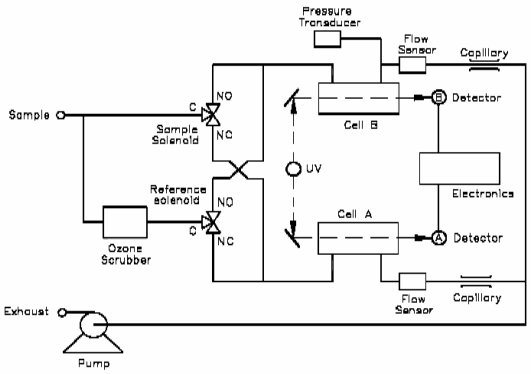

Fig.1 - Scheme of double cell ozone photometer.

After 7 s of flushing, in the last 3 s the detectors measure the light intensity transmitted through each cell ($I_{t_{A1}}$ and $I_{o_{B1}}$) respectively. In the second 10 s–step, the role of the two cells is interchanged by appropriate switching of the solenoid valves, and the measurement of $I_{o_{A2}}$ and $I_{t_{B2}}$ is carried out. At the end of measurement cycle the ozone concentration values (x_A and x_B) are measured by means of eq.(2). Then, the instrument calculates the average of the two concentration values, under the hypothesis that the optical lengths in cells A and B are equal:

$$x_{Ml} = \frac{x_A + x_B}{2} = -\frac{1}{2} K \ln\left(\frac{I_{t_{A1}}}{I_{0_{A2}}} \frac{I_{t_{B2}}}{I_{0_{B2}}}\right) + x_{losses} \tag{3}$$

where K is constant value depending on the optical path length and on the values of temperature and pressure, and x_{losses} takes into account the presence of ozone losses inside the photometer.

III.Characterization of commercial ozone photometer

In a first step of the proposed study we carried out the characterization of a commercial photometer for ozone measurement *Thermo Environmental 49C* (shown in Fig 2) with the aim of identifying the main uncertainty contributions. In this phase the analysis of the instrument performances was carried out without to consider the influence of sampling system. For calibration procedures we used the regional reference instrument of Lombardy (Thermo Environmental 49CS) that was tested and certified in Metrological Institute "Gustavo Colonnetti (IMGC) in Milan (Italy). The calibration tests were carried out in Regional Agency for the Protection of the Ambient (ARPA) of Lombardy with the effort of

Fig. 2 - Photo of the ozone Analyzer TE49C

technicians and researchers working in the calibration department.
The calibration cycle consisted of producing ozonized air whit six different mole fractions. These concentration values ranging 0-500 nmol/mol and they were measured by reference instrument and analyzer under test simultaneously. Each concentration value was obtained by averaging 10 points per measurement.
We carried out three calibration cycles. The selected sampling frequency was a sample per minute. To evaluate the instrument linearity the least square linear regression was applied. Then, three couples of values for slope (m) and intercept (q) were calculated. To account the accuracy of the linear regression, the values of the standard deviation (σ_m and σ_q) of the two coefficients m and q have been calculated [6]
Standard EPA (U.S. Environmental Protection Agency) tests for the calibration [8] were applied to evaluate the variability of regression parameters m and q. The EPA standard specifies that the results of calibrations are acceptable if the following criteria are met:

- the slopes are whiting ± 0,5% of the average slope;
- the standard deviation of the slopes is < 3.7% of the average slope;
- the standard deviation of the intercepts is < 1.5% of the average intercept.

The results of three calibration cycles found that the EPA requirements were respected. Fig 3 shows the linear regression fit of the measurement points.
Once the calculation of regression parameters, it is possible to write the following relationships:

$$O_{3c} = mO_{3m} + q \tag{4}$$

where m and q are the average of slopes and intercepts obtained in the three calibration cycles respectively, while O_{3m} and O_{3c} represent the ozone value measured by the commercial photometer and the value corrected by means of the linear regression, respectively.
There are two uncertainty contributors: the uncertainty on the reference photometer, and the uncertainty due to the linear regression of the calibration. These contributions, being composed by two terms referring to error probability density functions (pdf's) that are supposed uniform, have a resulting trapezoidal pdf, evaluated by means of the convolution of the two original pdf's.
For each measured value (O_{3_m}), the total uncertainty value U is calculated according to the "Guide to the Expression of Uncertainty in Measurement" [7]. The extended combined uncertainty (at k=2) turns out to be the sum of the two above-mentioned components:

$$U_{k=2} = 2\sqrt{\left(A_c^2 + B_c^2 O_{3m}^2\right) + \left(\sigma_q^2 + \sigma_m^2 O_{3m}^2\right)} \tag{5}$$

where A_C and B_C are the uncertainty components of the reference photometer [4].
The experimental data obtained in the calibration cycles show that the absolute uncertainty is approximately U=2 nmol/mol in the range 0-100 nmol/mol, and the relative uncertainty is u = 2 % in the range 100-500 nmol/mol (as shown in Fig. 4).

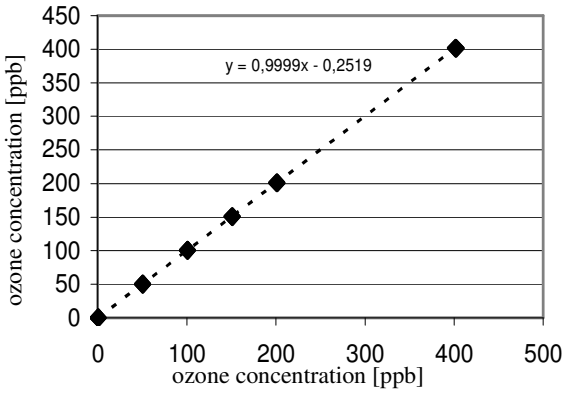

Fig. 3 - Results of liner regression fit of the measurement points

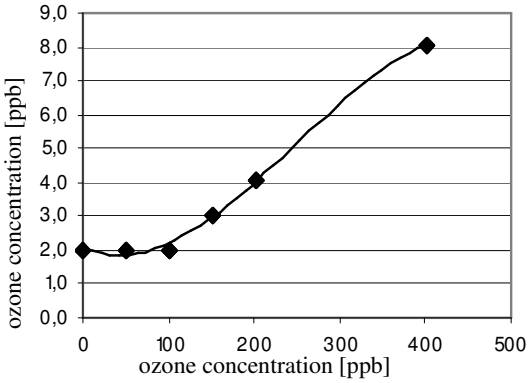

Fig. 4 Uncertainty of calibration cycle

IV. Sampling phase

The most critical phase of measurement process of ozone is the sampling of ambient air. International Standard EPA [9] describes the attributes of the sampling system that will ensure the collection of data of a quality acceptable for the ambient air quality monitoring.
According to the data quality objectives expressed in annex VII of the directive 2002/3/EC of the European Parliament [2] the allowed percent uncertainty for individual measurements is 15%.
Starting from the point that the uncertainty evaluated in the calibration procedure does not exceed 5%, the uncertainty due to the sampling phase should be included in the 10% of the measurement value.
The sampling equipment is constituted of the following four fundamental components shown in Fig. 5:

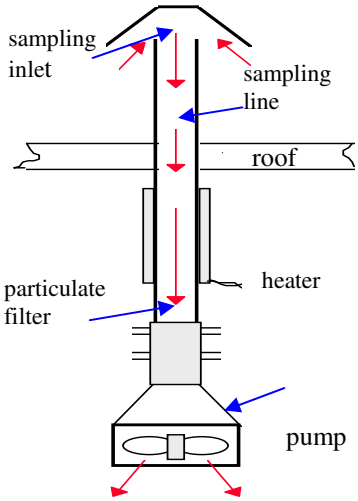

Fig. 5 - Scheme of the sampling system

I. *Sampling inlet*: constructed in such a way that ingress of rainwater into the sampling line (or system) is prevented. It shall be done with materials which do not react with ozone;
II. *Sampling line*: it shall be as short as practicable to minimise the residence time. The sample line may be moderately heated to avoid any condensation that can occur when there are high ambient temperature and/or humidity.
III. *Particulate filter*: made of material inert to ozone. It must be able to remove all particles that alter the performance of analyser. The filter shall be changed on a regular basis depending on the site-specific conditions.
IV. *Sampling pump*: it is located at the end of the sampling system. The sampling pump shall have sufficient rating to ensure that all analysers connected to the manifold are supplied with the required amount of air and to ensure that the residence time of a sample from inlet until entering the analyser is less than 5 s.

Our aim is the estimation of the uncertainty contributors due to the sampling phase on the total measurement uncertainty [10]. For this purpose, we want measure ozone concentrations with the same analyzer's models, in the same place, with different sampling conditions and configurations.
The main variables influencing the sampling phase are: the *height of the sample inlet* (in general, the inlet sampling points should be between 1,5 m, the breathing zone, and 4 m above the ground higher positions; up to 8 m, may be necessary in some circumstances), the *geometry of the sampling* inlet and of the *rain shield*, the *manifold*, the *length of the sampling line*, the *temperature* of sampling line, the *filters* and the *materials* used for all the sampling equipment [5].
By changing and combining all these variables it will be possible to obtain different sampling configurations that produce different uncertainty contributions. Condition and layout of the sampling equipment contribute to the combined expanded uncertainty of the measurement.
To account the contributions of the different influencing quantities on the whole measurement uncertainty, the Authors carried out many experimental tests performed by changing some sampling parameters. All experiments were carried out in the Air Quality Metrological Laboratory of ARPA Lombardy in Milan.
A first series of tests were performed by using a very long sampling tube to maximize the effect of the residence time in the sampling line. To evaluate the measurement uncertainty, we applied the same procedure described in the previous chapter. Fig. 6 show the behaviour of the uncertainty related to the variation in length of the sampling line. The results

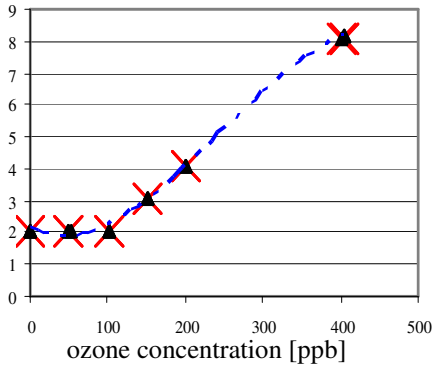

Fig. 6 - Uncertainty of test with short sampling line (red cross markers) and long sampling line (black triangle markers). Blue line is the tendency curve.

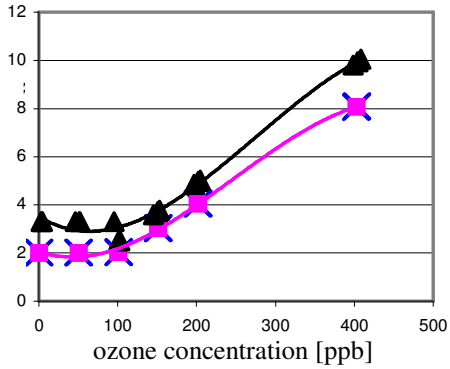

Fig. 7 - Uncertainty of test without filter (blue cross markers) with cleaned filter (magenta quadrate markers) and with dirty filter (black triangle markers.

highlight that even if the line length determinates the residence time, its influence on the total measurement uncertainty is negligible.
A second series of tests carried out by interposing a cleaned and dirty filter between the analyzer and its sampling inlet. Fig. 7 compares the experimental results in terms of measurement uncertainty. It is possible to note that the effect of insertion of a cleaned filter is negligible. Instead the degree of filter dirtiness has an important weight on uncertainty. Then, the filter is a crucial component of the sampling system.

V. Conclusions

In the paper the characterization of a commercial ozone analyzer was proposed. An accurate analysis was allowed to study separately the uncertainty contribution due to the performance of both the instrument and the sampling system.
In this way it will be possible to identify the critical phases of the sampling system, studying and improving them for the purpose of choosing the sampling configuration that minimizes the uncertainty contribution.
With all these prescriptions it will be possible to fulfil the data quality objectives of the directive 2002/3/EC.
A next step will be to create a mathematical model starting from this experimental data from which the uncertainty parameters can be obtained changing the input quantities relating to the different sampling configurations.

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