



THE DOAS METHODOLOGY FOR AIR POLLUTION STUDY AND INVESTIGATION IN INDUSTRIAL AND URBAN AREAS

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ABSTRACT

Object of this study is the versatility of a remote sensing measurement system through experimental survey of the levels of primary and secondary pollutants in urban and industrial Italian areas.

Data on NO₂, O₃, benzene and toluene are measured and discussed after intensive measurement campaign in different seasonal period by means of two Differential Optical Absorption Spectroscopy systems installed at ground level and on the roof of the ISPEL Mobile Laboratory, respectively.

Key Words: DOAS, Air Pollution, Secondary Pollution, Photochemical Smog

1. INTRODUCTION

In order to improve the air quality in Europe the European Commission issued some directive with regard to acceptable levels of a range of gaseous pollutants species as SO₂, NO, NO₂, O₃ and benzene (Commission European Communities, 1996). In particular, measurements of ozone and benzene represent nowadays a very important target in the atmospheric studies due to the different sources and health effects of both the gaseous species. Ozone has important adverse health and environmental effects such as respiratory irritation: chemically, it is the primary constituent of smog but it is not emitted directly into the air by specific sources but created by photochemical reactions involving sunlight, nitrogen oxides and volatile organic compounds (VOC) (Morales et al., 2004).

Among the different method used to analyze these compounds the technique involving open-path spectroscopy is ideal for monitoring pollutants for their advantages over classical methods and point-source analyzers (Avino et al., 2002).

The Differential Optical Absorption Spectroscopy (DOAS) is one of the most versatile optical techniques for the determination of air pollutants. DOAS is an useful measuring technique for routine work to control air quality and pollution emissions but also for applications in air pollution studies (Platt et al., 1979; Platt and Perner, 1980).

The DOAS is a remote-sensing analytical technique finding strong consents as demonstrated by numerous paper published during these last years. The DOAS analytical method is based on the UV and Vis light absorption (from 240 nm to 340 nm) of species with fine vibrational structures like SO₂, NO₂, ozone, nitrous acid,

formaldehyde, benzene and toluene; the Lambert-Beer's law regulates the relationship between the adsorbed light intensity and the concentration of each species.

The DOAS system is constituted from the following parts: a light source, a receiver, a spectrophotometer equipped with an optical fiber and a computer for the system management (data elaboration and data storage). The light source is a Xenon lamp (at high pressure and 150W): a transmitter sends the light to the receiver that transmits the beam through the optical fiber in the analyzer (Figure 1).

The absorption spectra of each monitored chemical species are acquired at their relative typical wavelength ranges; subsequently, the interferences are eliminated by comparison with the reference spectra.

This technique furnishes the concentrations related to a portion atmospheric environment varying also for some kilometers. In fact, these "integrated" concentrations represent the average area pollution level better than the measurements obtained by traditional analyzers which are considered "punctual".

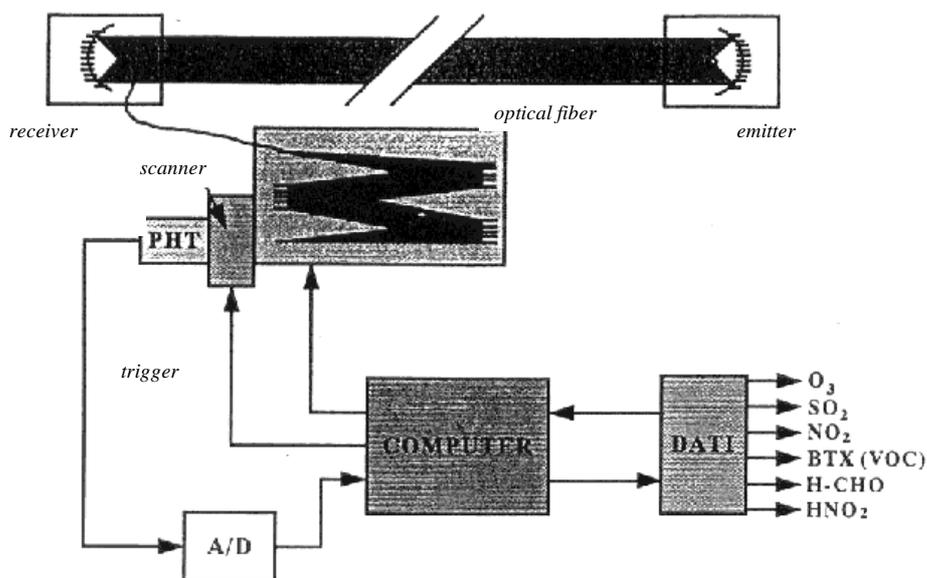


Figure 1. Flow-scheme of a DOAS system

The constituents investigated with DOAS technique include sulphur dioxide (SO₂), nitrogen dioxide (NO₂), nitrous acid (HNO₂), formaldehyde (HCHO), ozone (O₃), ammonia, mercury and aromatic hydrocarbons.

This paper reports measurements of NO₂, O₃, benzene and toluene carried out in downtown Rome during a springtime and in an industrial site during a wintertime by means of DOAS system installed at ground level and above a roof of the ISPESL Mobile Laboratory.

2. EXPERIMENTAL

The first DOAS system (mod. AR 500, Opsi, Sweden) has been installed at the

ISPESL monitoring station located in downtown Rome (near St. Maria Maggiore Cathedral) at about 10 m above ground level in an urban zone characterized by high density of autovehicular traffic. The second similar DOAS system was installed on the roof of the ISPESL Mobile Laboratory in an area at high density of industrial activity and the measurements can be considered at ground level: the site is close to a city at high density of anthropogenic activities (strong industrial emissions) and located in front of the sea.

For both instruments the analytical parameters are almost the same. The distance between emitter and receptor ranged between 200 and 250 m (this terms influences the sensitivity of the measures).

The absorbance of light from the emitter is continuously measured within the wavelength range 240-350 nm to determine several compounds (Table 1). The aromatic hydrocarbons are detected in the wavelength range between 250 and 290 nm where the major interfering gases are oxygen, ozone and sulphur dioxide; around 100 spectra per second are collected in this wavelength range and stored in a register with 1000 channels with a resolution of better than 0.05 nm. The concentrations of air pollutants are automatically calculated from the absorbance values in according with Lambert-Beer's law (Brocco et al., 1997).

Spectra are required on an average time of 7 min for the system located in downtown Rome, and 5 min for the system sited in the industrial site.

Table 1. Operative conditions of the DOAS system

Pollutant	λ (nm)	Time (min)	SD ($\mu\text{g}/\text{m}^3$)
SO ₂	270-380	1	0.5-2.0
NO ₂	398-450	1	1.5-2.0
O ₃	250-320	5	3.2-5.0
Benzene	240-310	1	3.5-6.0
Toluene	240-310	1	4.5-6.5
Nitrous acid	320-380	7	0.3-0.4
Formaldehyde	270-340	5	0.5-1.0

3. RESULTS

The data for nitrous acid, NO₂, O₃, benzene and toluene concentrations as measured by the two long-path DOAS systems during different seasonal periods in various areas are extensively discussed. All the data are hourly averaged from measures carried out every 5 min of sampling intervals.

In Figures 2 and 3 are provided spectra of the average hourly benzene and toluene concentrations in the two locations investigated.

The situation of the benzene pollutant, especially in urban areas, is really changed during this last decade. At the beginning of the years '90's, the benzene coming from autovehicular, industrial and anthropogenic emissions was present in atmosphere with concentrations among 40 and 80 $\mu\text{g}/\text{m}^3$. For both its toxicological characteristics (suspect carcinogenic for human) and chemical stability, such compound has constituted an element of constant hygienic-sanitary interest since many years.

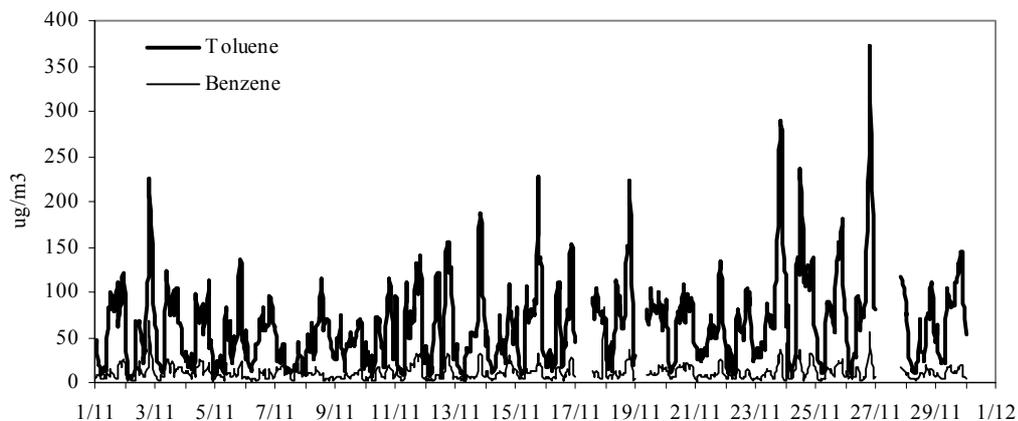


Figure 2. Hourly average concentrations of benzene and toluene measured in November 1999 in downtown Rome with the DOAS system.

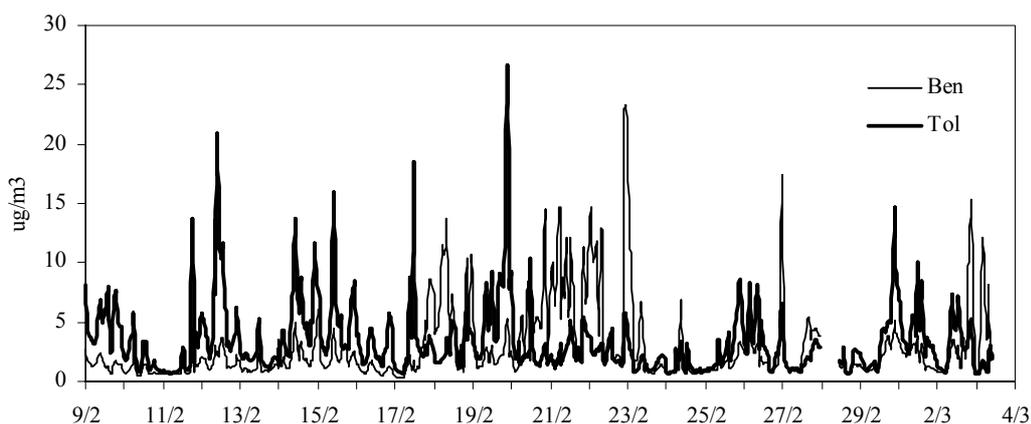


Figure 3. Hourly average concentrations of benzene and toluene measured in February 2000 in an industrial site with the DOAS system.

It is interesting to notice that during this decade there was a slight but clear decrease of benzene concentration in atmosphere also for the introduction in the Italian lifestyle of the use of the green fuel. And this reduction can be seen in the figure referring to the urban situation (Figure 2): benzene and toluene has the same trend and the ratio is almost constant around 3-5 time in according with those reported in literature.

In Figures 4 and 5 are reported the average hourly concentrations of nitrous acid measured in October 2002 and January 2003. During the month of October, because of the elevated solar irradiation the nitrous acid formed for heterogeneous reaction of NO_2 with H_2O , photo-dissociates itself producing OH radicals: consequently, the concentrations reach modest values ranging between some micrograms and $6\text{-}8 \mu\text{g}/\text{m}^3$. In the winter period the concentration levels of nitrous acid are notably more elevated up to $40 \mu\text{g}/\text{m}^3$. Also this compound has an important hygienic-sanitary interest being a gas phase mutagen and a precursor to nitrosoamines.

In Figure 6 are reported the average hourly concentrations of O₃ in winter period in an industrial site overlooking the sea. This characteristic results interesting when the histograms are examined: in fact, comparing the concentration values with those determined in other urban areas during the day, it can be evidenced nighttime ozone peaks of the same order of magnitude of those diurnal. This circumstance can be made possible by the presence of meteorological conditions related to phenomena proper of sea places such as the breezes.

In Figure 7 are reported the hourly average NO₂ concentrations measured in a winter month in the industrial area, where the production of nitrogen oxides is more massive. It can be noted how the concentration values trend respects the characteristics of NO₂ secondary pollutant: there are peaks in the warmest hours of the day (e.g., when the solar irradiation and the photochemical activity are greater) except in two cases (i.e., 5th and 6th of December) when a contribution of extraordinary emission intervenes underlined clearly by the histograms.

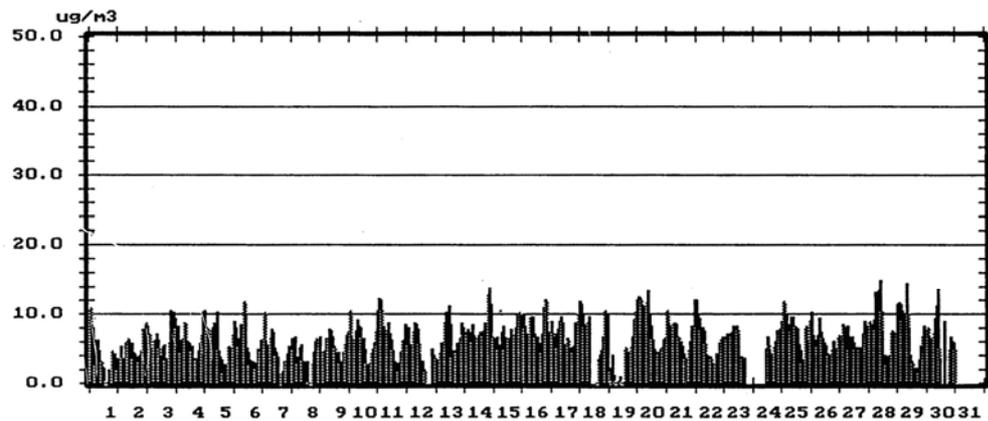


Figure 4. Hourly average concentrations of nitrous acid measured in October 2002 in downtown Rome with the DOAS system.

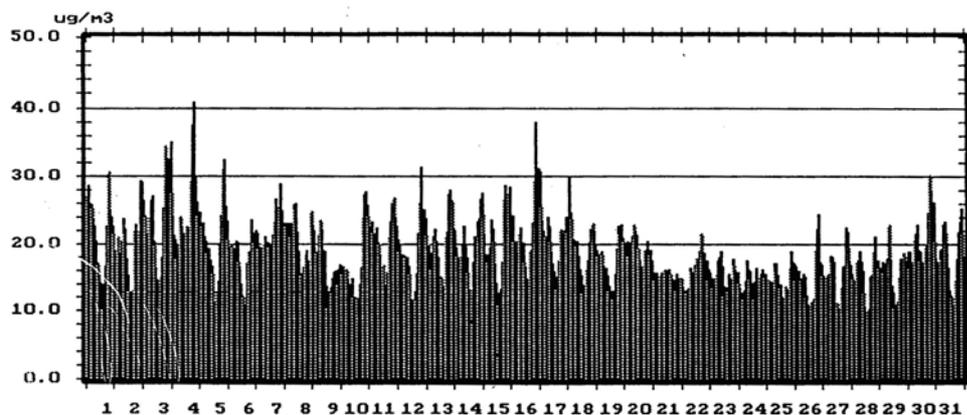


Figure 5. Hourly average concentrations of nitrous acid measured in January 2003 in downtown Rome with the DOAS system.

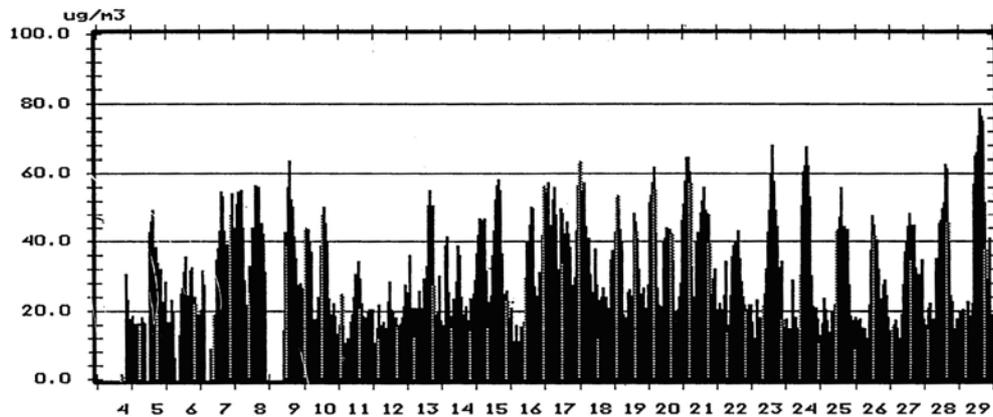


Figure 6. Hourly average concentrations of ozone measured in February 2000 in an industrial site with the DOAS system.

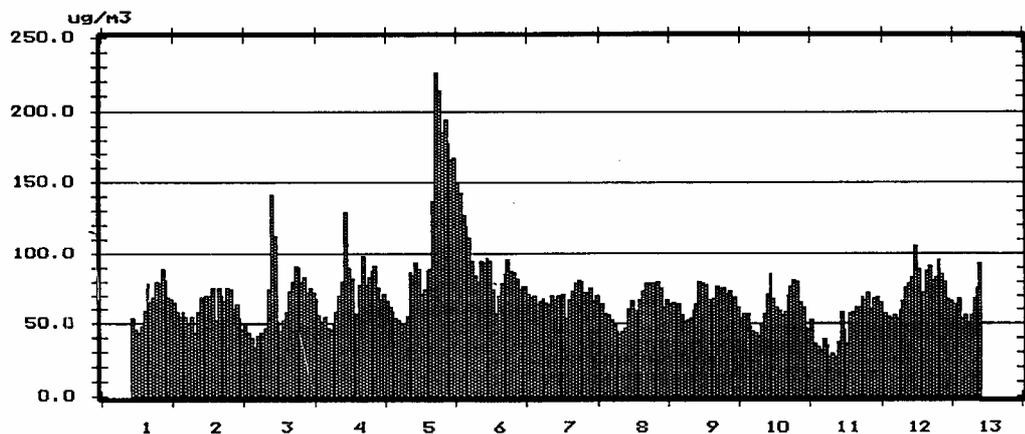


Figure 7. Hourly average concentrations of NO₂ measured in December 2002 in downtown Rome with the DOAS system.

It is evidenced that the secondary pollution, and in particular that derived from NO₂ and ozone, is not influenced by emission intensity and consequently assumes homogenous values in the entire urban area (Avino, 2004).

4. CONCLUSION

The DOAS technique is an advanced measurement system useful for integrating information coming from monitoring networks: furthermore, it allows to investigate and understand the complex mechanisms of formation and transformation of atmospheric pollutants through the contemporary measurements of gaseous primary and secondary species. In this way the representation of the air pollution is more correct than using automatic analyzers.

The results obtained take in account the spatial-temporal variations of the pollutant concentrations due to both the atmospheric dishomogeneity and the contributions of sources not directly present in the areas considered.

5. ACKNOWLEDGEMENTS

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