Optical soundings of cars’ exhaust and urban atmosphere with laser-plasma light and open-path spectrophotometry

Antonio Borghese and Luciano Speranza

Instituto Motori – Consiglio Nazionale delle Ricerche, Via Marconi 8, 80125 Napoli, Italy

E-mail: a.borghese@im.cnr.it

Abstract. Optical soundings of i.c. engines’ exhaust and urban atmosphere have been carried out, using an Open-Path UV Spectrophotometer, based on a Laser-Produced Plasma as the light source. The measured optical depths are numerically inverted in terms of known species, by means of the Non-negative Least-Squares (NLS) algorithm. Concentrations of major UV-absorbing species are evaluated at the tailpipe of in-use vehicles (NO, NO$_2$, EC) and in urban atmosphere over a 200m-long optical path (O$_2$, O$_3$, NO$_2$, EC, nitrates). Also, we report on the detection in both environments of an additional compound, the nanometric organic carbon (NOC), known to form in fuel-rich flames, which is not considered yet in ordinary emissions inventories. Also, the problem of dilution/dispersion of primary species is addressed, by tracking the combustion-formed CO$_2$ at the tailpipe and in urban atmosphere.

1. Introduction

Emission of combustion by-products (exhaust) from internal combustion (i.c.) engines into the atmosphere results in a) the dilution/dispersion of the burnt gases, b) the physical and chemical evolution of some primary species and c) the formation of new (secondary) compounds, their identities and amounts depending on complex reaction pathways. On one side, relevant primary species consist mainly of carbon, nitrogen and sulphur oxides, along with hydrocarbons (H/C) and elemental carbon (EC), the latter believed to derive mostly from diesel engines. On the other side, air quality standards consider primary NO$_2$ and SO$_2$, secondary O$_3$, and the overall PM$_x$ aerosols; the latter are known to be composed of internal/external mixtures of both inorganic (sulphates/nitrates) and carbonaceous matter. Albeit cars’ emissions and air pollution are clearly linked by a cause-to-effect relationship, yet the processes a-c) have only partially been understood and still deserve further investigations, particularly on the sources and the amounts of atmospheric OC [1].

Reported on here are optical soundings of engines’ exhaust and urban atmosphere, using an Open-Path UV Spectrophotometer, based on a Laser-Produced Plasma as the light source. We measure concentrations of exhaust emissions (NO, NO$_2$, EC and OC), at the tailpipe of in-use vehicles on a chassis-dynamometer, and of some relevant species (O$_2$, O$_3$, NO$_2$, OC, EC, nitrates) over a 200 m long optical path in urban atmosphere. Also, the problem of the dilution/dispersion of primary species from the emission sources to the urban atmosphere is addressed, by considering the combustion-formed

---

1 Now with ARPA Lombardia, Brescia, Italy.
CO₂ for internal calibration of the relative abundances of species at the tailpipe and in urban atmosphere.

2. Open-path Spectrophotometry

Most species of environmental concern, whether gases or particles, absorb and/or scatter light in the UV wavelength band (200-400 nm). The resulting attenuation – or extinction – of the travelling light is measured by the optical depth \( \tau = \log(I_0/I_T) \), where \( I_0 \) and \( I_T \) are the light intensities incident and transmitted, respectively, through the medium. The optical depth \( \tau \) is a function of the light wavelength \( \lambda \) and describes the medium in terms of the optical-path length \( L \), the number concentrations \( N_s \) and the extinction cross-sections \( \sigma_{ext,s}(\lambda) \) of the \( S \) species, according to the composition model:

\[
\tau(\lambda) = L \cdot \sum_s N_s \cdot \sigma_{ext,s}(\lambda) + \epsilon
\] (1)

In open atmosphere, the low values of the number concentrations of some relevant species and of their extinction cross-sections require optical paths \( L \) of the order of several hundreds meters, in order to provide detectable attenuation. On the other hand, the strong absorption of atmospheric oxygen and ozone at \( \lambda < 300 \text{ nm} \) sets a natural barrier for long-path spectroscopic measurements. The emission intensity of commercially available light sources (e.g. Xenon or D₂ lamps) either vanish below 250 nm or are too weak at all to work as required. Instead, Laser-Produced Plasmas (LPP’s) constitute a breakthrough, since they have an extremely high and broadband emission intensity [2], even extending into the Vacuum Ultra-Violet region [3].

An LPP-based UV Spectrophotometer has been developed for applications of Open-path Extinction Spectroscopy to track gases and aerosols from cars’ exhaust to the urban atmosphere. A typical lay-out is shown in Figure 1. The instrument comprises a Transmitter, where the UV emission from an LPP, fired by a Nd-YAG Q-switched laser, is collimated by a parabolic mirror, and a Receiver, which includes a collection optics, a spectrograph and an MCP-intensified CCD detector, all embedded in a compact case. Two retroreflectors \( RR_1 \) and \( RR_2 \), set at the distances \( L_1 \) and \( L_2 \) along the optical axis, reflect two fractions of the transmitted light back to the receiver.

![Figure 1. Optical lay-out of the Open-path Spectrophotometer.](image)

Using two retroreflectors adds key-features to the optical configuration: i) the transmitter and the receiver can be housed in the same compact case; ii) the incident light \( I_0 \) and the instrumental response \( \eta \), which are of difficult evaluation, are canceled out; iii) media at remote distances \( L_1 \) can be optically probed.

3. Numerical inversion of optical data

For each light pulse, two spectra \( I_1(\lambda) \) and \( I_2(\lambda) \), corresponding respectively to the light returns from \( RR_1 \) and \( RR_2 \), are acquired and processed to give the optical depth \( \tau \) due to \( G \) gaseous species and \( P \) size-distributions \( n_p(d) \) of particles:

\[
\tau(\lambda) = \log(I_1/I_2) = 2 \cdot \Delta L \cdot \sum_g N_g \cdot \sigma_{ext,g}(\lambda) + 2 \cdot \Delta L \cdot \sum_p \int n_p(d) \cdot \sigma_{ext,p}(\lambda,d) \cdot \partial d + \epsilon
\] (2)
The number concentrations \( N_g \) and \( n_p(d) \) of \( S = G + P \) species are retrieved by numerically inverting the optical data, using the NLS (Non-negative Least Squares) routine \[4\]; the algorithm is based on: 1) a composition model of \( S \) species with known cross-sections; 2) the non-negativity constraint of the solutions \( N_g, n_p(d) \geq 0 \); 3) recursive minimization of the error \( \varepsilon \).

4. Results at the cars’ exhaust and in the urban atmosphere

Figures 2A-B show two exemplary results of Open-path UV Spectrophotometry, obtained over a 5 m long round-trip optical path on the exhaust of vehicles – production year 2004 – equipped with spark-ignited (A) and diesel (B) engines. The vehicles are run at the chassis dynamometer over the New European Driving Cycle (NEDC), which accounts for both urban and highway driving. Air/exhaust dilution of 10:1 avoids condensation of the combustion-formed water vapor. Besides the known spectra of NO, NO\(_2\) and EC, the composition model requires for best fit a fourth component, shown as NOC in figures 2A-B, which will be discussed later on.

**Figure 2A.** Measured (dots) and modelled (thick line) optical depth in the full UV spectral band (200-400 nm) of air-diluted exhaust emitted from a car equipped with a spark-ignited engine. Also shown (thin lines) are the four contributions to the total extinction from NO, NO\(_2\), EC and NOC. Numerical inversion of the optical data has been carried out with the NLS algorithm (see text).

**Figure 2B.** Measured (dots) and modelled (thick line) optical depth in the full UV spectral band (200-400 nm) of air-diluted exhaust emitted from a car equipped with a diesel engine. The four contributions to the total extinction from NO, NO\(_2\), EC and NOC, shown with thin lines, have been obtained as those in figure 2A.

**Figure 3.** Measured (dots) and modelled (thick line) optical depth in the full UV spectral band (200-400 nm) of urban atmosphere over 2x100m-long optical path. The contribution to the total extinction from \( O_2 \), \( O_3 \), NO\(_2\), EC, NOC and nitrates, (thin lines) have been obtained using the NLS algorithm.
Figure 3 shows another exemplary result of Open-path UV Spectrophotometry, now obtained over a 100m-long round-trip optical path in urban atmosphere, at 2.00 p.m. on a summer day in 2005. In addition to the primary species shown in figures 2A-B, other (secondary) compounds: O$_3$, O$_2$, and nitrates, need to be included in the composition model. The resulting best fit predicts nitrate particles with mean size $d \approx 100$ nm and standard deviation $\sigma_d \approx 1.5$. Here again, the ‘excess’ optical extinction observed below $\lambda = 250 \text{nm}$ can only be fitted by considering the NOC contribution as with data of figures 2A-B.

5. Discussion and conclusions

Data in figures 2A-B show the amounts of known species (NO, NO$_2$, EC) emitted from i.c. engines, which are consistent with those obtained with standard analytical instrumentation. As expected, spark-ignited engines emit amounts of EC far smaller, yet measurable, than diesel engines. Data in figure 3 show a more complex composition, comprising both primary (NO$_2$, EC) and secondary (O$_3$, nitrates) species, reflecting the intervention of atmospheric photochemistry.

In all the cases examined, the experimental data could be fitted only by providing the composition models with the spectral contribution denoted as NOC in figures 2A-B and figure 3. NOC is an acronym for Nanometric Organic Carbon, a precursor of EC particles as well as a stable by-product of slightly fuel-rich combustion, which has been thoroughly described in previous studies on laboratory flames [5,6]. Compared to EC, NOC has much smaller particles size ($d < 5 \text{nm}$), as well as quite different chemical composition (organic) and optical properties (transparent below $\lambda \approx 250 \text{nm}$). Due to such properties and since substantial amounts are emitted from i.c. engines and practical combustors, NOC is currently considered by nano-toxicologists as a pollutant with potential health risk [7].

A further point refers to the quantitative relationship between the species concentrations measured at the exhaust and those resulting from dilution/dispersion in urban atmosphere. A viable approach to the problem considers primary and chemically stable species, e.g. EC, NOC and CO$_2$, which are expected to conserve their relative abundances from source to sink. At the air-diluted exhaust in figures 2A-B, the combustion-formed CO$_2$ concentration is nearly 1.3% and the evaluated abundances of EC and NOC, relative to CO$_2$, are $[\text{EC}]/[\text{CO}_2] \approx 1/20,000$ and $[\text{NOC}]/[\text{CO}_2] \approx 1/60,000$. On the other hand, in conditions of urban atmosphere (figure 3), the measured CO$_2$ concentration exceeds the background level ($\approx 390 \text{ppmv}$) by 80 ppmv ($\approx 150 \text{mg/m}^3$), an ‘excess’ CO$_2$ mostly due to traffic emissions. As a result, the relative abundances are estimated at $[\text{EC}]/[\text{CO}_2] \approx 1/2,000$ and $[\text{NOC}]/[\text{CO}_2] \approx 1/5,000$. Such values are at least ten times higher than those evaluated at the exhaust of new cars (figures 2A-B); however, the discrepancy is only apparent, since i) the circulating fleet is much older and more emissive than the new vehicles tested in this work, and ii) the drive style of most cars is more irregular, hence again more emissive, than the well-controlled conditions of a standard driving cycle at the chassis dynamometer.

References
[1] Bond T, Streets D G, Yarben K F, Nelson S M, Woo J-H and Klimont Z 2005 J. Geophys. Res. 109 D14203
[2] Borghese A and Merola S S 1998 Appl. Opt. 1998 37 1-7
[3] Borghese A and Di Palma T M 2007 Appl. Opt. 46 4948-53
[4] Paatero P 1997 Chem. Int. Lab. Syst. 37 23-35
[5] Sgro L A, Basile G, Barone A C, D’Anna A, Minutolo P, Borghese A and D’Alessio A 2003 Chemosphere 51 1079-90
[6] Sgro L A, Borghese A, Speranza L, Barone A C, Minutolo P, Bruno A, D’Anna A and D’Alessio A 2008 Environ. Sci. & Technol. 42 859-63
[7] Oberdörster G, Oberdörster E, Oberdörster J 2005 Environ. Health. Perspect. 113 823-39.