Photoacoustic Detection and Monitoring of Pollutant Gases from Urban Public Transport

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Abstract. Nowadays, air pollution is presented as a serious threat to the planet. The concentration of gases from anthropogenic activities, such as transport, cause consequences ranging from local to global scale, affecting the climate, the environment and the human health. It is necessary to detect and monitor of a large number of gas species emitted by these sources of pollutants. The photothermal techniques, specially photoacoustic spectroscopy, allow the detection of many gaseous species. In this work, it is presented a new detection limit for a photoacoustic spectrometer composed of a CO₂ Laser and a Photoacoustic Resonant Cell. Analyses of many gas samples collected in the exhaust of urban buses in the city were performed. Ethylene was detected with the help of the CO₂ Laser photoacoustic spectroscopy and concentrations of CO, CO₂ and NO were obtained through a commercial infrared photoacoustic analyzer called URAS.

1. Introduction
One of the most concerning problems faced by the modern society is the atmospheric pollution, which can cause dangerous environmental consequences, such as the degeneration of air quality, acid rain, photochemical smog, ozone layer depletion, health diseases and the global warming.

The transport is liable for a great part of the damaging pollutant emitted by anthropogenic sources. The municipality of Campos dos Goytacazes located in the northern state of Rio de Janeiro has 431,839 inhabitants, being the largest inland city of Rio de Janeiro. Having a great fleet of old buses, it is summarily important to evaluate bus emissions of gases harmful to planet and human health.

In this context, photoacoustic represents an excellent technique to track environmental gases for supplying many requirements to gas detection, such as high sensibility, spectral selectivity, multicomponent detection and good temporal resolution. [1-4]

In this work, we used a Photoacoustic Spectrometer composed by a CO₂ Laser and a Resonant Cell to detect ethylene (C₂H₄), which is a primary pollutant gas which produces the tropospheric ozone (O₃), an important greenhouse gas. In addition to this technique, we used the Infrared Analyzer URAS, which permitted the monitoring of Carbon Monoxide (CO), which can occasion serious health problems, Carbon Dioxide (CO₂), the most effective greenhouse gas and Nitric Oxide (NO), that besides being harmful to human health, also contributes to the production of tropospheric ozone, associated with hydrocarbons, as ethylene. [5]
2. Methodology

In Photoacoustic technique, a modulated radiation is absorbed by the sample molecules, which are excited in their rovibrational levels and suffer a non-radioactive decayment, generating a periodic heating. Once the heating occurs in a constant volume, a pressure wave will be generated, being detected by microphones in a photoacoustic cell and converted into electrical signal.

In our Photoacoustic Spectrometer (Fig. 1), a CW infrared CO2 laser Synrad J48G-2W-039, tunable over about 80 different lines between 9-11 μm, was employed as the excitation source. These lines can be swept by a step motor controlled by the microcomputer. The Photoacoustic signal is detected and filtered by a Lock-In amplifier (Stanford Sr 850) at the resonance frequency of about 2400 Hz of our resonant cell. Our photoacoustic cell is composed by a resonant cavity of 68 mm of length and 18 mm of diameter, and its optical windows are disposed in Brewster angles.

Figure 1. Photoacoustic Spectrometer Composed by a CO2 Laser and a Resonant Cell.

The Photoacoustic Signal of multicomponent gas samples can be obtained by:

\[ S(\lambda_i) = S_i = C.P_i.N_{tot}\sum_{j=1}^{\lambda_c}\sigma_{ij} \]

with \( i = 1, 2, \ldots, m \); \( j = 1, 2, \ldots, n \); and \( m > n \). Here, \( P_i = P(\lambda_i) \) represents the laser power at wavelength \( \lambda_i \) and \( c_j \) is the concentration of the component \( j \) with absorption cross section \( \sigma_j \) at \( \lambda_i \). \( N_{tot} \) is the total number density of molecules in the mixture. The value of the constant \( C \) was determined through a calibration proceeding \( (C = 40.2 \text{ V.cm/W}) \) [6]. This expression allows the calculation of the concentration of the analyzed gas as well as the lowest detection bound.

Besides this technique, we have worked with the Infrared Analyzer URAS to monitor CO, CO2 and NO. The URAS gas analyzer of Hartmann & Braun uses a photoacoustic detection scheme (Figure 2) which is able to detect a specific gas out of a multicomponent gas mixture without cross interferences.

Figure 2. Detection Scheme of Infrared Analyzer URAS.
An infrared radiation, modulated by a “chopper”, crosses two different cells. The first one contains an inert gas, nitrogen and the other one contains the sample that will be analyzed. The radiation that emerges from the two cells has different intensities due to differential absorption. The detection system consists of two sealed chambers filled with pure gas (certificate) of chemical species under investigation (absorber) interconnected with a membrane connected to a capacitor. The different intensities of the radiation that enter the two chambers produce pressure waves with different intensities between the cells, which are capacitively detected by the membrane. The signal generated in the capacitive membrane permit us to obtain the concentration of the analyzed gas. [7]

3. Results and Discussion
In order to monitor ethylene in our samples, we performed the calibration of the photoacoustic spectrometer composed by a CO2 Laser and a Resonant Cell. We diluted a standard sample of Ethylene (5 ppmV) with gaseous Nitrogen and it was possible to determinate the linearity of the photoacoustic signal with the gas concentration (Figure 3) as well as the lowest detection limit of the Photoacoustic Spectrometer (10 ppbV).

![Graph](https://example.com/graph1.png)

**Figure 3.** Linearity of Photoacoustic Signal with Ethylene Concentration.

The gas samples were collected in the exhaust of eight buses from four different bus companies using a pre-evacuated recipient called canister. The measures were made in two operation modes: accelerated (engine rotation of about 3000 rpm) and not accelerated (engine rotation of about 1000 rpm). The Infrared Analyser URAS allowed to detect CO, CO2 and NO and the CO2 Laser Photoacoustic Spectrometer was used to monitor C2H4. The results are shown in the graphs below.

![Graph](https://example.com/graph2.png)

**Figure 4.** (a) Graph showing the CO bus emissions. (b) Graph showing the CO2 bus emissions.
The companies A and B have older fleet, from 1995 and 1996, while the companies C and D have modern buses from 2006 and 2007. The emission of Carbon monoxide is a result of incomplete combustion and it is greater in the oldest vehicles. In the not accelerated mode we can also notice that the vehicles emit more CO than in accelerated mode. The Carbon Dioxide is emitted in all buses analyzed as a result of complete combustion of diesel fuel.

![Graph showing the NO bus emissions.](image)

The gaseous nitrogen oxides are produced whenever a fuel is burned in the presence of air at high temperatures, where nitrogen and oxygen combine to form nitric oxide [5]. Therefore, the higher the temperature of the flame, the greater the amount of NO. The behavior of the NO concentration in our samples is probably related to temperature of the engine, since the collection of the samples B1, B2 and C1 were performed in garages without bus services on the day of collection, where we could detect the lowest values of NO.

Ethylene emission, as well as CO emission, is much greater in the oldest buses than in the newest ones. The samples from the A buses presented ethylene concentrations of 10.4 and 7.13 ppmV in the non-accelerated mode and 35.2 and 46.6 ppmV in the accelerated mode, whereas the samples from the D buses presented ethylene concentrations of 2.1 and 1.77 ppmV in the non-accelerated mode and 2.3 and 2.53 ppmV in the accelerated mode.

All evaluated gases are typically provenient from diesel combustion. CO and C2H4 are produced during the incomplete burning of the fuel whereas CO2 is generated during the complete one. NO emission, however, is directly related to the engine temperature. In conclusion, we can observe that diesel powered vehicles emit considerable amounts of pollutant gases, such as CO, CO2, NO and C2H4 in ppmV range. Since these gases cause damages to the environment and to the human health, it is extremely important to monitor them. The photoacoustic spectroscopy proved to be a selective and sensitive technique to detect pollutant gases.

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