Romanian Reports in Physics, Vol. 67, No. 4, P. 1558–1564, 2015

Dedicated to
International Year of Light 2015

MULTICOMPONENT DETECTION IN PHOTOACOUSTIC SPECTROSCOPY APPLIED TO POLLUTANTS IN THE ENVIRONMENTAL AIR

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Received October 12, 2015

Abstract. The present paper deals with the detection of pollutant trace gases in the environmental air from enclosed spaces. The targeted spaces were subway network of Bucharest, representative for urban agglomeration, and some technologized greenhouse as characteristics feature of the modern rural area. The pollutant detection was performed by laser based photoacoustic spectroscopy where a CO_2 laser was employed as radiation source. Our study investigated the concentration levels of various air pollutants: carbon dioxide, methanol, ethanol, ammonia, ethylene and water, within metro cars at rush hours and in intensive greenhouse agriculture for a complete cycle of a plant growth.

Key words: photoacoustic spectroscopy, CO_2 laser, infrared, absorption, air pollutants.

1. INTRODUCTION

In the last decades, due to a great development of the industry and economy, the urban area also developed, concentrating a large number of people living and working here. In order to respond to the new requirements of the urban agglomeration, the city's infrastructure increased correspondingly by construction of new buildings, roads and enlargement of the public transport network. Followed by an increase in car traffic and waste, resulted from industrial and people activity, all this expansion became an important source of pollution with a potential negative impact on the air quality. In the same time, the agriculture performed in the rural area has to satisfy the increasing demand of the urban market for various and high quality vegetables in any season. From this perspective, the intensive greenhouse agriculture represents a great solution for large and continuous production of herbs, vegetables and fruits all-round-year. The greenhouses beneficiate by an artificial environment specially designed for an optimal growing of plants. In order to improve the productivity, various chemicals like fertilizers, pesticides and insecticides are used for treatments during the plant growing cycle, so that high levels of pollutant concentrations could be accumulated in the air inside these spaces, especially due to limited air ventilation.

Considering the above reasons, the air quality should be careful monitored in such sites susceptible to pollution, in order to keep a healthy environment on long term, and to be able to immediately detect any increase over the admitted levels of pollutants in the air. In the present paper we have investigated the air quality from two categories of enclosed spaced: firstly, the air quality inside the public underground transport network (subway network), with specific application to the underground network of Bucharest, and secondly, the air quality from greenhouses where an intensive agriculture is performed.

The underground network of Bucharest is managed by Metrorex company, which performs activities of public and strategic interest. In Bucharest, over 170 million of passengers annual use the underground network due to its comfort, regularity and safety traffic conditions. This traffic figure corresponds to an average of 600.000 passengers/business day or 15 million passengers/month and represents about 20% of the total passengers using the Bucharest urban public transportation. The underground network of Bucharest is currently integrating 69.20 km double tracks, structured on 4 metro lines, 51 metro stations and 4 depots placed exclusively underground. There is a controlled air climate, but during the time considerable amounts of various pollutants could be accumulated inside due to a variety of pollution sources such as high level of passenger traffic, failure of the air ventilation system, cleaning detergents, chemical/hydrocarbons residues from cars or rail maintenance, etc. The fleet in use includes: 84 cars of type IVA (old) metro cars, manufactured by Astra Arad, Romania and 228 cars of type Bombardier BM 2 and BM 21 new generation metro trains (Metrorex Activity Report-2013 [1]). Our study address comparative measurements of the air quality inside of these two type of cars at rush hours of the working time.

Regarding the air quality from greenhouses, the presented measurement campaign was concerned with the concentration level of pollutants for a culture of peppers at key moments of the plant growing cycle from the plant time to the harvest time. The greenhouses in study are owned by the HORTINVEST centre of the University of Agronomic Sciences and Veterinary Medicine of Bucharest, and have modern technological characteristics: automated ventilation system, drop-by-drop watering, and sensor controlled environment.

All measurements were performed by laser based photoacoustic spectroscopy, one of the most sensitive techniques in the world, being able to detect trace gas concentrations down to ppb level (10^{-10} atm partial pressure [2]). This technique has proved multiple advantages: high accuracy and selectivity, non invasive determination, locally sampling, large dynamic range and multicomponent capability. The targeted pollutants were: carbon dioxide, methanol, ethanol, ammonia, ethylene and water.

2. EXPERIMENTAL SETUP AND MEASUREMENT PROCEDURE

A schematic of the photoacoustic setup involved in measurements is presented in Fig. 1. The entire installation was fully detailed in previous papers [2, 3], so in this paper we shall give only a briefly description. The multicomponent detection was mainly possible due to the frequency stabilized CO_2 laser employed as radiation source, of which spectrum between 9.2–10.8 µm overlaps with the absorption spectra of the targeted pollutants. The radiation delivered by the CO_2 laser is collimated by a ZnSe lens, modulated in intensity by a mechanical chopper and then is introduced into a photoacoustic cell (PA cell) which contains the air sample. The acoustic wave generated from the selective interaction of the laser radiation with the absorbing molecules is detected by four in series connected sensitive microphones embedded in the cell resonator tube. Finally, the microphones convert the acoustic signal into an electrical one, feeding a lock-in amplifier with double role: it sets the chopper frequency and delivers the PA signal as amplitude and phase locked to this frequency. The amplitude of the PA signal is proportional with the concentration of the absorbing molecules. A powermeter measures the laser beam power at the exit from the PA cell. All useful data were recorded by a computer controlled interface, using a LabView program which gathers the signals from a National Instruments acquisition card (NI cDAQ-9174).

The air samples were collected in aluminum coated bags (supplied by QuinTron), and the PA cell was usually filled with the air sample up to the atmospheric pressure. In some cases, due to the variation of the air sample volumes, a pressure below 1 atm was attained in the PA cell. By consequence, the system responsivity was adjusted applying a correction factor estimated from the calibration curve (responsivity *versus* pressure inside the cell) previously recorded [3].

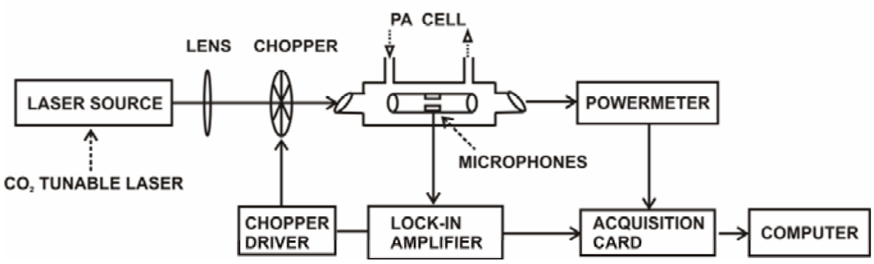


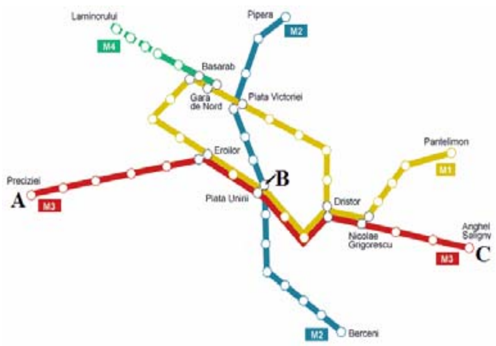
Fig. 1 – Schematic of the CO_2 laser based PA set-up.

The multicomponent detection was performed corresponding to the following algorithm: firstly we estimated the concentrations of water and of CO_2 by measuring the PA signal at the 10R(20) line where water has maximum of absorption [4], then at the 10P(26) line where the absorption of CO_2 has a significant level [5]. For these two considered lines, the absorption levels of the other pollutants are low so that their contribution at the generated PA signal is negligible. Secondly, for detection of the rest of pollutants we selected the CO_2 laser lines at which the targeted pollutants present a maximum of absorption: 9R(22) line for ethanol [6], 9P(14) line for methanol, 9R(30) for ammonia [7, 8], 10P(14) for ethylene [3]. From the signals measured at these lines we always subtracted the contribution of water and carbon dioxide. The 10P(16) line was used for verification of the estimated concentrations.

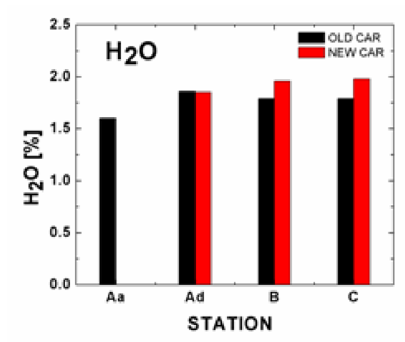
3. RESULTS

3.1. UNDERGROUND NETWORK

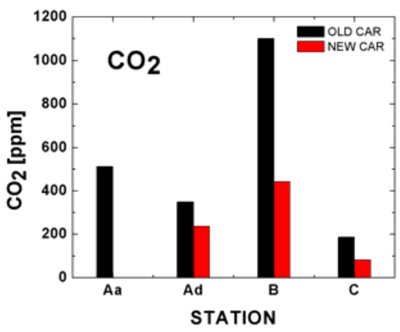
The measurement results regarding the air quality from the two types of the metro cars (old and new) are illustrated in Fig. 2 for each considered pollutant. The samples were collected at rush hours in the morning when the passenger traffic is from periphery to the city centre, for several stations of the M3 line.



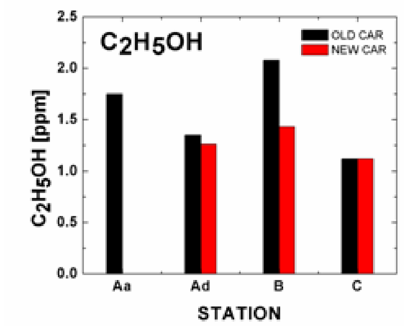
a.



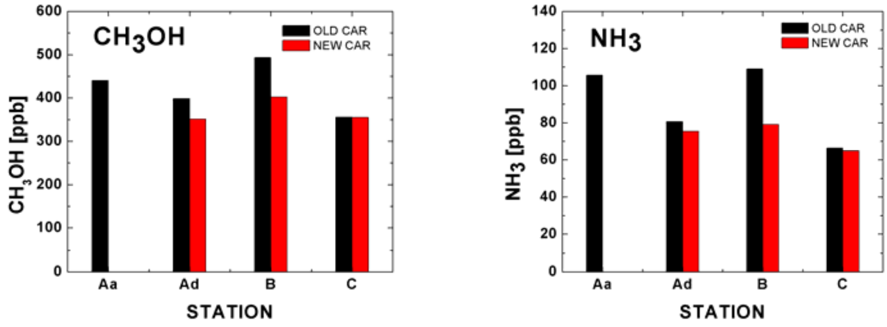
b.



c.



d.



e. f.

Fig. 2 – a) Map of the Bucharest's underground with the collecting points of the air sample; b)–f) concentration levels of pollutants measured inside the two types of metro cars: water (b), carbon dioxide (c), ethanol (d), methanol (e), ammonia (f).

The Fig. 2a presents the important collecting points of the air sample, namely A, B and C stations on the Bucharest's underground network map. The A point represents the start station (Preciziei), where the metro leaves the depot starting its trip to the city center, the B point is the biggest node of the network (Unirii Square station) and C point is the end station (Anghel Saligny).

From Fig. 2b–f it can be observed that the concentration level of considered pollutants in the air inside the metro cars increases with the people agglomeration for both types of cars, recording a maximum level arriving in the point B, a representative station for down town city and office centers where the majority of passengers are getting out. After this station, the number of passengers in the metro cars is significantly decreased, leading to a lower level of the air pollutant concentrations for the next part of the trip, until the end station C. It is also observed that the accumulation of pollutants is significantly higher in the case of old metro cars (without ventilation system) with respect to the pollutant levels measured in the air from the new metro cars designed with air conditioning system. Thanks to the proper ventilation system, the pollutant levels in the new metro cars do not change significantly with the number of passengers, and could be considered approximately constant for a complete trip.

For station A, which is placed close to office buildings so that the passenger traffic is also considerable at the arrival in this station, we investigated the influence of ventilation in the old cars for the time spent in the depot, sampling twice the air: at the arrival moment – Aa, and at the time of the next departure from the station – Ad. The conclusion was that all the pollutant levels are decreasing, excepting the water, a behavior generated by the fact that old cars are simply refreshed by the mean of opened windows. As the depot Preciziei is a half-open space enclosure, the quality of air exchange is strongly dependent on the weather conditions.

It should be also noticed that we do not detect the presence of ethylene. The main source of ethylene is the passenger's breaths, in which we could find only few ppb for a healthy person. Thus, such very low concentrations, diluted in the large air volume of a metro car, will fail to be detected being under the detection limit of our system.

3.2. GREENHOUSE – INTENSIVE AGRICULTURE

The measurement results obtained for the concentration levels of targeted pollutants for a culture of pepper at key moments of the plant growth are presented in Table 1. It is observed that starting with the moment when the seedlings are transplanted, the level of carbon dioxide decreases being consumed by the plants, while the levels of ammonia increases as consequence of using ammonium based nutritive substances. The level of methanol also rises as consequence of the fact that the plants emit methanol during the growing cycle. The ammonia level remains aproximatively constant during the plant maturity process. Significant increases are observed for the concentration levels of carbon dioxide, ethanol and methanol at the harvest time, most possible explained by some fermentation processes occurred in some overripe fruits.

Table 1

Concentration levels of targeted pollutants at key moments of the plant growth (pepper culture)

PERIOD	H_2O [%]	CO_2 [ppm]	C_2H_5OH [ppm]	CH_3OH [ppb]	NH_3 [ppb]
ground (only substrate)	0.53	351	0.37	13.7	29
young plant (seedling)	0.53	100	1.45	299	116
flowers and small fruits	0.72	131	1.28	305	100
fruits and harvest	0.81	402	1.87	523	94

Regarding the ethylene concentration, once again we are below the detection limit of our system. This can be explained by the very low emission rate for ethylene in the case of peppers [9], combined with the huge volume of the greenhouse.

4. CONCLUSIONS

All the measured values, both for underground network and greenhouse, are within the safety levels regarding pollutant exposure. For the underground network, the concentration variations for the monitored pollutants closely followed the passenger flux, and they clearly reflected the importance of the ventilation system.

Also, corroborating our results with those recorded by the greenhouse sensors, generally a good agreement for the levels of CO_2 and H_2O was observed. The values for the other investigated pollutants fit into the general biological behavior of the growing cycle: permanent increased values of ammonia starting with the onset of fertilizers and high levels of methanol corresponding to the plant growth. In the same time, the levels of carbon dioxide are low as long the developing plants are consuming it, and increases back once the fermentation processes are initiated.

Gladly, in both cases, the pollutant concentrations remained bellow attention levels, but the PA technique proved the suitability for the detection of small changes of very low concentrations, down to ppb level. The conclusion of our study is that the PA method is very versatile for multicomponent detection, being a very good candidate for an optimization which shall embedded an automated scanning of the laser lines and a mathematical reconstruction apparatus, in order to increase the abilities over a larger number of pollutants.

Acknowledgements. This work was supported by a grant of the Romanian Ministry of Education, CNCS – UEFISCDI, project number PN-II-RU-PD-2012-3-0207.

The authors would like to thank HORTINVEST Centre of the University of Agronomic Sciences and Veterinary Medicine of Bucharest for help.

REFERENCES

1. www.metrorex.ro/despre_metrorex_p774-1.
2. D. C. Dumitras, S. Banita, A. M. Bratu, R. Cernat, D. C. A. Dutu, C. Matei, M. Patachia, M. Petrus, C. Popa., Infrared Phys. Technol. **53**, 308 (2010).
3. D. C. Dumitras, D. C. Dutu, C. Matei, A. M. Magureanu, M. Petrus, C. Popa, J. Optoelectron. Adv. Mater. **9**, 3655 (2007).
4. M. S. Shumate, R. T. Menzies, J. S. Margolis, and L.-G. Rosengren, Appl. Opt. **15**, 2480 (1976).
5. I. R. Ivascu, C. E. Matei, M. Patachia, A. M. Bratu, D. C. Dumitras, Rom. J. Phys. **60**, 1121 (2015).
6. I. Doroshenko, V. Pogorelov, V. Sablinskas, *Infrared absorption spectra of monohydric alcohols*, Dataset Papers in Chemistry, 2013, 329406 (2013).
7. D.C. Dumitras, D. C. Dutu, C. Matei, R. Cernat, S. Banita, M. Patachia, A. M. Bratu, M. Petrus, C. Popa, Laser Phys. **21**, 796 (2011).
8. R.J. Brewer, C.W. Bruce, Appl. Opt. **17**, 3746 (1978).
9. V.M. Russo, *Peppers: Botany, Production and Uses*, CAB International, 2012.