IMPROVEMENT OF A LASER PHOTOACOUSTIC INSTRUMENT FOR TRACE GAS DETECTION

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In această lucrare sunt prezentate rezultatele obținute la detecția unor concentrații foarte mici de gaz folosind un instrument fotoacustic cu laser. Acest instrument este format dintr-un laser cu CO_2 stabilizat în frecvență și folosit ca sursa de radiații, cu ajutorul caruia am obtinut coeficienții de absorbție ai etilenei în peste 57 linii de vibrație-rotație în ramurile P si R ale laserului, la lungimi de unda cuprinse între 9.4 si 10.4 µm. Datorită sensibilității mari, în cazul detectării urmelor de gaz, nu este nevoie de acumulari mari ca în cazul altor tehnici, putând fi astfel monitorizată în timp real emisia de etilenă rezultată în urma coacerii fructelor și legumelor de la pară și roșie, precum și etilena rezultată în urma peroxidării lipidice din aerul uman exalat.

The paper presents the latest results obtained with a perfected system for trace gas detection based on laser photoacoustic spectroscopy. Tehnical details of the setup together with the performance parameters are presented. The laser source of the system is a CO_2 laser highly stabilized in frequency so we have obtained the today most accurate absorption coefficients for ethylene at 57 rotation-vibration lines in the branches P and R, at 9.4 and 10.4µm bands. The high sensitivity of the sistem is proved by real-time monitoring of ethylene emission as plant hormone from tomatoes and pears, and as result of lipid peroxidation from human breath.

Keywords: CO_2 tunable laser, photoacoustic spectroscopy, spectrophone, traces gas detection, ethylene absorption coefficients, plant physiology, lipid peroxidation, breath test.

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1. Introduction

The photoacoustic (PA) spectroscopy is based on the effect discovered by Graham Bell in 1880 and consists of the energy conversion of modulated light radiation to sound energy. A part of the energy absorbed by the sample under study is transformed into thermal energy due to the nonradiative transitions. The temperature variations determine the formations of acoustic waves that can be detected directly by appropriate sensors (sensitive microphones). High sensitivities were achieved by PA systems using midinfrared gas lasers such as CO and CO_2 lasers. Owing to their high output power in the watt range and their line tunability to strong fundamental vibrational transitions, these lasers turned out to be ideal sources to push the sensitivity of PA gas detection into the ppbV concentration range (parts per billion volume) and even sub-ppb concentration levels, necessary in the case of certains biological samples [1].

Gas sensing is of great interest in numerous areas. These include atmospheric studies (air pollutants, ozone detection, explosives), volcanic activity, agriculture (measurements of gaseous plant hormones), photochemistry (chemical processes monitoring, such as reaction rates, equilibrium constants, enthalpies or identification of different compounds, even isotopes, isomers and radicals), industrial process and workplace surveillance, gas certification, medical diagnosis, etc.

Trace gas sensing systems have to meet several requirements such as high detection sensitivity and selectivity, multicomponent capability, field suitability, etc. In this respect, devices based on tunable lasers combined with appropriate detection schemes are very attractive today.

There are three basic techniques of linear laser spectroscopy:

- the absorption method (intensity);

- the radiative method (fluorescence);

- the calorimetric method (pressure, temperature).

PA method is a calorimetric technique, which measures the precise number of absorbant molecules by simply measuring the amplitude of an acoustic signal.

A coincise comparison of linear laser spectroscopy methods is presented in Table 1.

Comparison of linear laser spectroscopy methods

Characteristics \ Method	Absorption	Fluorescence	PA
Sensitivity (cm^{-1})	$10^{-5} \div 10^{-7}$	Up to single atoms	$10^{-7} \div 10^{-10}$
Time resolution (s)	1	$1 \div 10^{-12}$	$1 \div 10^{-3}$
Necessary conditions	-	Radiative channels of relaxation	Nonradiative channels of relaxation

2. Measurements and photoacoustic signal analysis

To increase the sensitivity of the method and to measure trace gases at concentrations of sub-ppb (1 ppb = 10^{-9} atm) level, we have designed, constructed and optimized a new experimental set-up presently operating in our laboratory "Optics and lasers in life sciences, environment and manufacturing". With this experimental set-up, we investigated ethylene-releasing processes in fruits and lipid peroxidation effects were investigated, where the release of trace gases is very low (in the range of ppb), impossible to be measured by others means (mass spectrometry or gas chromatography).

Fig. 1 shows the line tunability of the frequency stabilized CO_2 laser in the 9 μm and 10 μm branches, as well the maximum power corresponding to each line, [2].
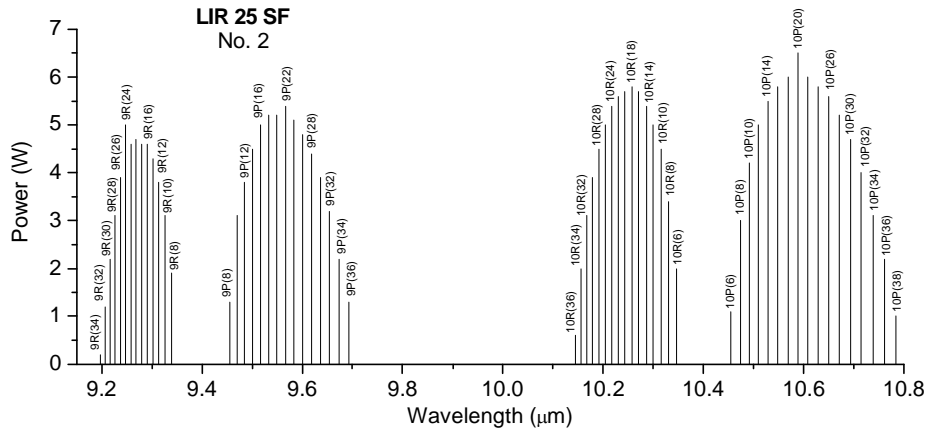
Fig. 1. Tunability of the frequency stabilized CO_2 laser

Based on a simple model for our system, one can obtain the following formula for the response of the PA system, [3]:

$$V = \alpha C P_L S_M c, \tag{1}$$

where: V [V] – photoacoustic signal (peak-to-peak value);

α [cm^{-1}atm^{-1}] - gas absorption coefficient at a given wavelength;

C [Pa cm W^{-1}] - cell constant;

P_L [W] - CW laser power before chopper;

S_M [V Pa^{-1}] - microphone responsivity;

c [atm] - concentration or partial pressure of the trace gas.

The product of the cell constant and microphone sensitivity gives the responsivity of the cell or the calibration constant (merit factor of the cell), R (V cm W^{-1}):

$$R = C S_M. \tag{2}$$

The photoacoustic cell is characterized by two important parameters: the quality factor Q it (defined as the ratio between the resonance frequency and the frequency bandwidth measured at $1/\sqrt{2}$ of the maximum of the resonance curve) and the responsivity R. The responsivity is defined as the ratio between the peak-to-peak microphone voltage ($2\sqrt{2} V_{\text{eff}}$, where V_{eff} is the effective voltage of the lock-in amplifier) and the product of absorption coefficient, trace gas concentration and the laser output power. Due to the chopper which modulates the power with a filling factor of 50%, the laser output power is given by the double average value measured by the powermeter.

$$Q = f_{rez} / \Delta f_{1/\sqrt{2}}, \tag{3}$$

$$R = \frac{2\sqrt{2}V_{eff}}{c\alpha P_L}. \tag{4}$$

The minimum detectable concentration is obtained when the PA signal equals the noise voltage (at a signal-to-noise ratio SNR = 1), that is $V = V_N$ (peak-to-peak noise voltage).

$$c_{\min} = \frac{V_N}{\alpha P_L R}. \tag{5}$$

Knowing the cell responsivity, we have the possibility to measure the absorption coefficient of a given absorption gas, α (cm^{-1}atm^{-1}):

$$\alpha = \frac{2\sqrt{2}V_{eff}}{cP_L R} \qquad\qquad (6)$$

Experimentally, using a calibrated gas mixture, one can determine the responsivity. For the calibration of the cell we used a certified mixture of 1 ppm ethylene in nitrogen. We used the 10P(14) line of the CO_2 laser for the ethylene which, has a known absorption coefficient of 30.4 cm^{-1} atm^{-1}.

To establish the quality factor (Eq. 3), we have measured the signal for frequencies between 500 and 670 Hz, obtaining the maximum at f_{res} = 564 Hz, and a $\Delta f_{1/\sqrt{2}}$ = 35 Hz (Fig. 2).
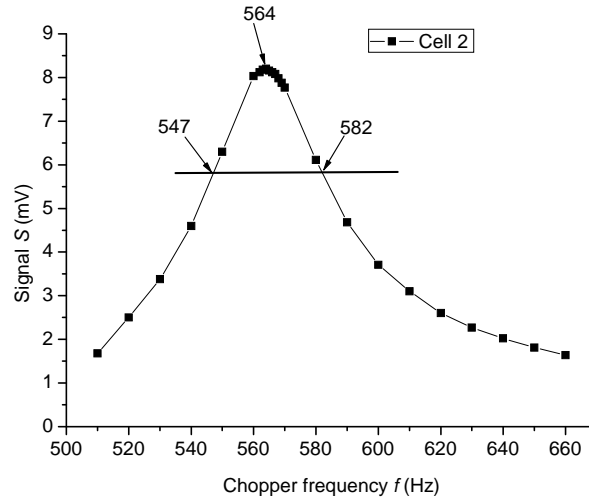

Fig. 2. Characteristics of the PA cell

We have determined a quality factor Q = 16.1 and a responsivity R = 173 $VcmW^{-1}$ of the cell, at a total microphone sensitivity of 80 $mVPa^{-1}$ (the individual sensitivity is 20 $mVPa^{-1}$). Therefore a cell constant of C = 2225 Pa cmW^{-1}. Because this quality factor is much lower than the one of a radial resonator, it renders our spectrophone into a less sensitive PA cell to environmental changes (especially temperature).

Further we have measured the absorption coefficient for ethylene at CO_2 laser wavelengths. The results are represented in Fig. 3.
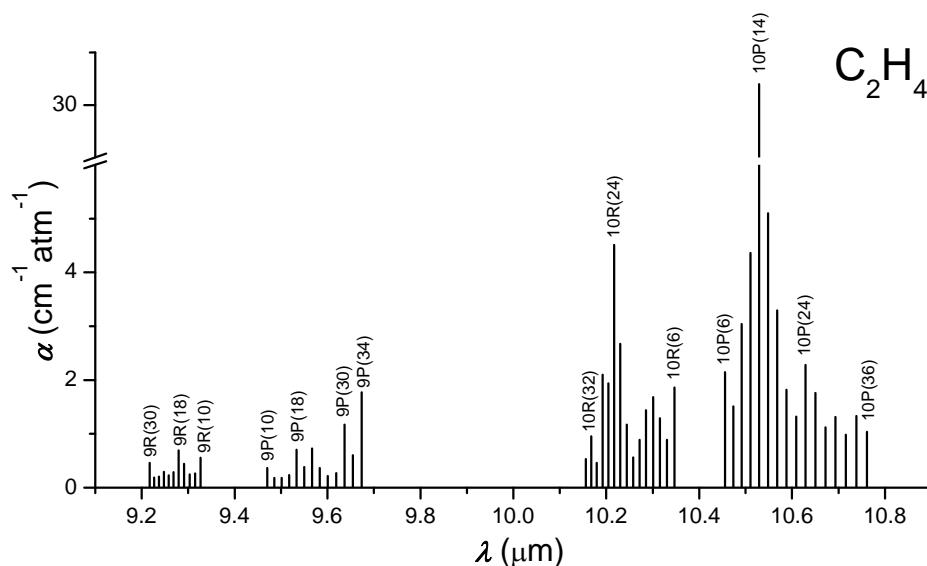
Fig. 3. Absorption coefficients of ethylene at CO_2 laser wavelengths

The strongest absorption of ethylene 10P(14) line of the CO_2 laser at $\lambda =$ 10,529 μm, where the ethylene has an absorption coefficient $\alpha = 30.4$ cm^{-1}atm^{-1}. The other absorption coefficients have values between 0.161 cm^{-1}atm^{-1} and 5.1 cm^{-1}atm^{-1}, covering the branches P and R, at 9.4 and 10.4μm bands, proving the wide band absorption character of ethylene.

3. Results

The high sensitivity of the method allowed us to investigate some basic processes in plant physiology, such as the release of the plant hormone ethylene during ripening of climacteric fruits and lipid peroxidation in humans induced by different stress factors.

A. Plant physiology

Ethylene (C_2H_4) acts as a vegetal hormone produced by all plant tissues. It is transported by diffusion through plant tissues and raises the plasmatic membrane permeability. It has multiple effects on the cell metabolism: it increases the oxidative processes, the transport inside the cells and biodegradation of the organic acids and chlorophyll. Ethylene plays a major role in many metabolic processes: seed and bud dormancy, seed germination, development of plant, flowering, fruit ripening (ethylene induces biochemical modifications responsible for the taste, aroma and texture of the fruit). Some fruits belong to the climacteric

type, showing a respiratory rise during ripening (tomato, pear, fig, mango, banana), while others belong to nonclimacteric family (cherry, strawberry, lemon).

The aim of our study was to monitor the ethylene emission by tomatos and pears. During ripening, the tomato and the pear show a strong increase in ethylene emission coinciding with the climacteric rise in respiration (CO_2 production). The probes were kept at 4^0 in a refrigerator for several hours and then introduced into a small glass cuvette (volume of 150 cm^3) at room temperature (22^oC). Before starting any C_2H_4 emission monitoring, the probes were allowed to acclimatize for two hours into the cuvette.

Usually, the respiration of the plants produces both CO_2 and C_2H_4, and that is why we need to identify the real level of the measured C_2H_4. In order to do this, one should change the detection line from 10P(14) to 10P(16). Decreasing the absorption coefficient with a factor of 6, from 30.4 cm^{-1}atm^{-1} to 5.1 cm^{-1}atm^{-1}, it helps us to check that we measure only C_2H_4. If the concentration level is not decreasing a factor of 6, it is very probably to have also other gases, mainly CO_2.
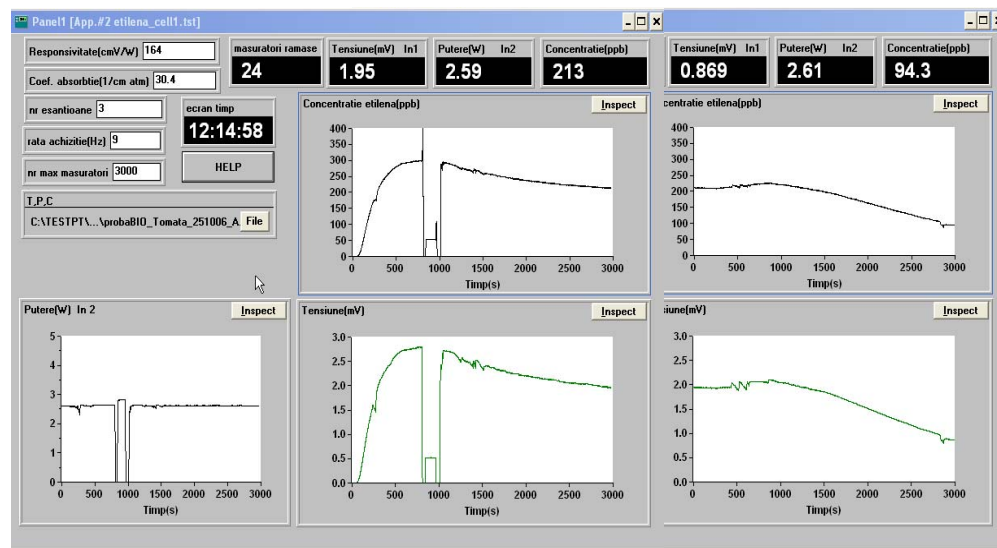

Fig. 4. C_2H_4 emission from tomato

In the case of tomato (Fig. 4), the ethylene emission starts from a level of 5 ppb and raise to 300 ppb. Changing the lines, we observe a decrease of the concentration from 300 ppb to 51.1 ppb, exactely the factor of 6 we looking for. During the whole measurement, the tomato was continuously flushed with synthetic air flow. The recording time was 100 minutes; after the complete re-aclimatization (tomato inner temperature reaches 22 ^oC), the C_2H_4 emission is stabilized around 100 ppb.

In the case of pear, for a comparable weight with the tomato, we have more than a double C_2H_4 emission, with a maximum at 750 ppb. When the laser line was changed from 10P(14) to 10P(16) the ethylene concentration decreased to 130 ppb. We know that the C_2H_4 emission is dependent not only temperature, but also of respiration conditions. Since C_2H_4 biosynthesis requires the presence of O_2, the replacement of the synthetic air flow with a N_2 flow will cause a decrease of C_2H_4 concentration. We switched several times between synthetic air and N_2. Every time that we have introduced N_2, we observed a severe decrease of the C_2H_4 level, which means that the C_2H_4 synthesis is an aerobic process.
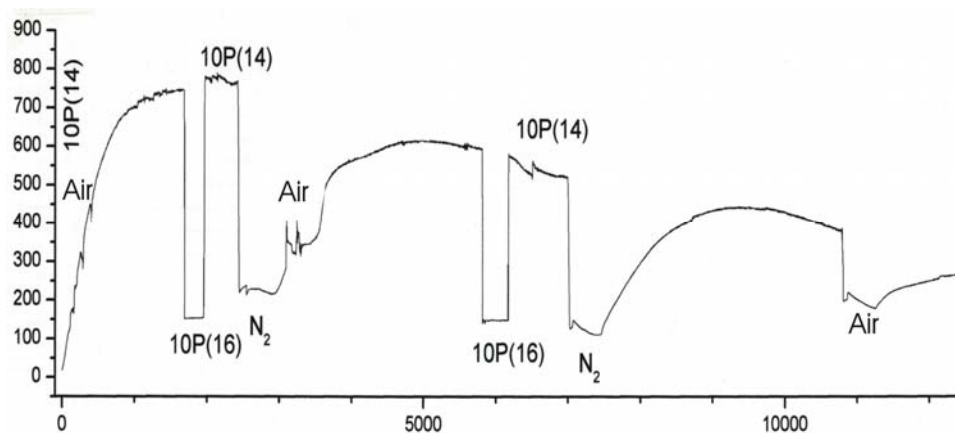

Fig.5. Ethylene emission from pear

Ethylene is involved in the post maturation processes, playing an important role in fruit ripening. During ripening, tomato and pear shows a strong increase in ethylene production coinciding with the climacteric rise in respiration (CO_2 production). Storage and shipping of fruits in terms of wounding effects, temperature, and composition of atmospheric gases or seal-packing conditions are important factors to establish the optimal environment necessary for their long term conservation.

B. Lipid peroxidation

The oxidative modification of biological molecules is an essential part of the normal biological activity in the human organism. An excess in some oxidant activities does cause injury to cells tissues. Particular attention is devoted to the oxidant activity of free radicals. An increased free radical formation in the organism is involved in the pathophysiology of several diseases. One of the events generated by free radicals interaction with biomolecules is the oxidative degradation of fatty acids. Biomembranes and cells are thereby disrupted, causing

cell damage and cell death. As a marker of free-radical-mediated damage in the human body, the measurement of the exhaled volatile hydrocarbons, such as ethylene (C_2H_4), is a good noninvasive method to monitor lipid peroxidation, [4].

The cigarette smoke contains many toxic components (heavy metals, free radicals, chemicals) that may induce ethylene formation by lipid peroxidation in the lung epithelium. Ethylene oxide is a chemical product that induces cancer in the lungs. In order to monitorize the damages caused by the inhaled smoke, we performed a breath test which gives us information about the volatile compounds under normal and stress circumstances. The exhaled air from the subject being tested is collected inside aluminized bags and then the sample gas is transfered into the measurement PA cell.

In the case of a non smoking person, the ethylene emission increases from a ground level of 8-10 ppb to a level of 80-90 ppb (Fig. 6).
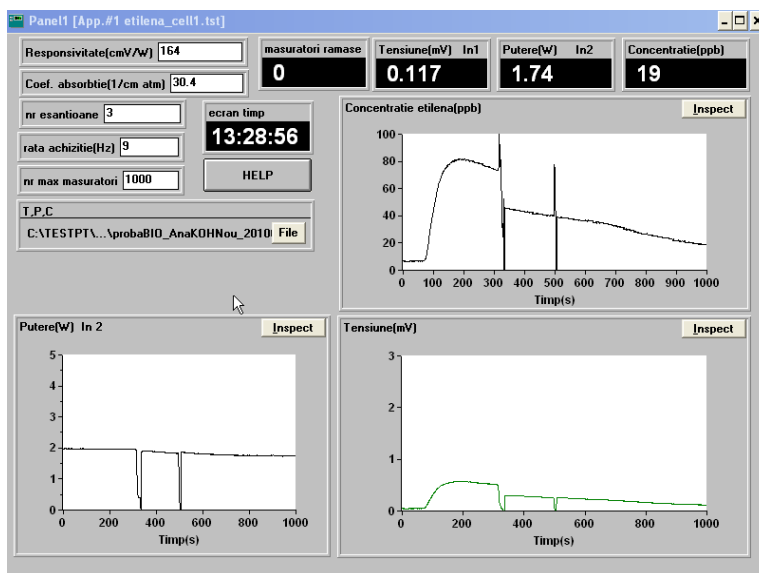

Fig. 6. Ethylene content of exhaled air from a non-smoker person

A potassium hydroxide (KOH) trap was inserted in the gas circuit to remove the high quantity of CO_2 from the human breath, though is not 100% efficient. Changing the laser line 10P(14) to 10P(16) we remarked the presence of CO_2, due to the fact that the decrease in C_2H_4 concentration was not scaled by the 6 factor.

The test for a heavy smoker person (Figure 7) shows a maximum emission after 15-16 minutes at 980-1260 ppb. This time we have changed to 10P(20) line, to check the presence of CO_2. Here the C_2H_4 absorbs almost 17 times less energy

($\alpha_{C2H4/10P(14)}$ = 30.4 cm^{-1}atm^{-1}; $\alpha_{C2H4/10P(20)}$ = 1.8 cm^{-1}atm^{-1}), as long the CO_2 absorption coefficient remains practically unchanged ($\alpha_{CO2/10P(14)}$ = 0.0021 cm^{-1}atm^{-1}; $\alpha_{CO2/10P(20)}$ = 0.0020 cm^{-1}atm^{-1}). The very low level of the concentration proves us that we have indeed only C_2H_4 emission. During the experiments a high value of ethylene concentration was found after smoking, followed generally by a slower decrease.
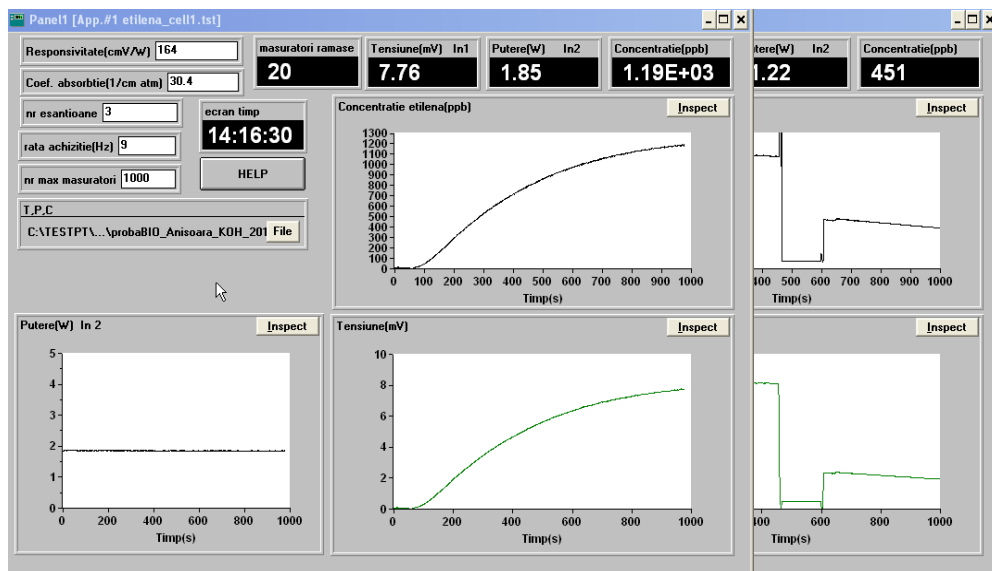

Fig. 7. Breath test registration from a smoker person

A common point for all the experiments is flushing the cell with N_2 flow for 5-10 minutes previously the detection to ensure a good cleaning of rezidual gases.

The breath test is a highly reliable noninvasive alternative to monitor various physiological and pathological processes in the human body. With photoacoustic spectroscopy different biological parameters can be measured and quantified: the presence of biological substances, specific enzymes or hormone concentrations. This serve to evaluate the indices for health: disease risk, metabolic processes, substance abuse, environmental exposure and its effects, epidemiologic studies. The presence of abnormal chemicals in the breath can aid in the early diagnosis of many diseases.

4. Conclusions

The results obtained in all these applications have demonstrated that photoacoustic spectroscopy technique presents flexibility, high stability, large

dynamic range to measure low concentrations, good time response and high sensitivity in detection.

We investigated basic processes in plant physiology and lipid peroxidation, where the release of trace gases (ethylene) is very low (several ppb to hundreds of ppb). We have exemplified the potential of laser photoacoustic spectroscopy to detect and measure quantitatively very low traces of ethylene, an important human biomarker. Measurement of human biomarkers in exhaled breath promise to revolutionize the manner in which diagnostics are carried out today and may soon lead to rapid diagnostics, improved results, decreased cost, improved quality of life.

Our method presents a large number of basic advantages like:
- a large number of gases and vapors are measurable with the same instrument;
- responsivity is independent of the wavelength of radiation;
- high immunity to surounding interference;
- high sensitivity, permitting the detection of ppb or even ppt concentrations;
- detection linearity and dynamic range over six orders of magnitude (100 ppm – 100 ppt);
- high selectivity, permitting clear differentiation between various compounds;
- real time analysis, permitting quasi continuous measurements;
- convenient data analysis;
- operational simplicity;
- relative low cost per unit.

Further the laser based instrument can also be used for detection of a wide variety of industrial gases, including benzene, hydrogen cyanide, acetylene, carbon monoxide and carbon dioxide, a broad range of chemical warfare agents including nerve gases (Sarin, Soman, Tabun), blistering agents (phosgene, mustard gas) and poisonous gases (hydrogen cyanide) or explosives such as TNT and PETN.

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