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Photoacoustic response of cherry tomatoes contaminated with car engines pollution and UV radiation

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The photoacoustic spectroscopy plays a very important role in the assessing of the photoacoustic response released by red fruits undergo external environmental factors (such as pollution and UV radiation) with valuable proven atributes: sensitivity, selectivity, versatility, reliability, robustness, ease of use and relatively low cost per unit. In this research, the measurements were concentrated on the potential of IR spectroscopy in the analysis of red fruits cherry tomatoes exposed to pollution from various car engines and UV radiation. The results were correlated with red fruits cherry tomatoes exposed to nitrogen air flow (anaerobic conditions) with red fruits cherry tomatoes exhibited normal aerobic conditions (synthetic airflow). With the advantages of laser photoacoustic spectroscopy technique, we showed that red fruits cherry tomatoes under pollution and UV radiation, emit more ethylene gas than those analyzed under normal conditions.

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1. Introduction

The history of the discovery of the ethylene biosynthetic pathway in higher plants represents a good example of advancement of science through the stepwise utilization of novel scientific concepts, plant models and methodologies [1, 2].

Ethylene gas is a natural senescence hormone which is produced by fruits and vegetables at varying rates. Generally, ethylene production rates increase with maturity at harvest, physical injuries, disease incidence, increased temperatures and water stress. On the other hand, ethylene production rates by fresh produce are reduced by storage at the lowest safe temperature and by low oxygen or elevated carbon dioxide levels [1].

Another source of ethylene production is from air pollution due to burning of coal, oil, or natural gas in industrial uses; refuse burning; operation of internal combustion engines (motor vehicles, for lifts, etc.); decomposing plant materials; cigarette smoke; fluorescent lamp ballasts; etc [1-3]. These metabolic disturbances (toxicity, temperature, engines pollution, UV irradiation, etc.) in fruit are followed by significant and rapid changes in the rate of ethylene response.

Engines pollution influences the activities of ethylene plant hormones and growth regulators, which affect developing tissues and normal organ development, without causing leaf-tissue damage. In high tunnels, which burn propane, kerosene or use motors that burn gasoline, that have poor or no ventilation, even minute amounts of this pollutant can cause severe damage to fruits or vegetables [3-5]. Since ethylene gas is also active within humans, it can lead to uncontrolled cell division or cancer. Cancer is primarily an environmental disease with 90-95% of cases due to lifestyle and environmental factors and 5-10% due to genetics. Common environmental factors leading to cancer death include: tobacco, diet and obesity (fruit quality), stress, physical activity, environmental pollutants. These environmental factors cause abnormalities in the genetic material of human cells [1-8].

For human health, studies [9-13] have shown that ethylene is metabolized to ethylene oxide, which has more adverse effects on human health.

The International Agency for Research on Cancer has designated ethylene oxide as a carcinogen [9-14].

There are a number of methods, which can be used to determine ethylene levels from plants and fruits.

The IR spectroscopy technique could be a solution for a proper monitoring of the ethylene concentration in red fruits cherry tomatoes, with valuable proven advantages: high accuracy and selectivity, near real time analysis, capability to measure gas concentrations at sub-ppbV levels (partial pressure of 10^{-10} atm), large dynamic range and minor sample preparation [15].

The success of the photoacoustic based trace gas sensing techniques crucially depends on the availability and the performance of the tunable laser source and of the detection scheme employed. Lasers offer the advantage of high spectral power density owing to their intrinsic narrow linewidth in the range of MHz. Since the laser linewidth is usually much smaller than the molecular absorption linewidth (GHz region at atmospheric pressure), it is not an important issue in most measurements [15-20].

The most widely used sources are CO and CO_2 lasers [17-21], lead salt diode lasers, quantum cascade lasers [22, 23], and nonlinear optical devices like optical parametric oscillators and difference frequency generation. Because the spectrum of CO_2 laser overlap, at room temperature and normal atmospheric pressure, for the absorption spectra of numerous gases, a good choice is to use a frequency-stabilized CO_2 laser and a photoacoustic cell (PA cell), in performing of the biological sample gas measurements [15, 21].

The kind and number of detectable substances is related to the spectral overlapping of the laser emission with the absorption bands of the trace gas molecules.

The number of detectable compounds is firstly limited by the laser wavelength range that should overlap the absorption spectrum of the each individual gaseous compound and secondly by the fact that the laser source (CO_2 laser) enable only discrete wavelength tuning. On the other hand, a partial overlapping of the individual absorption spectra of several compounds existing in the biological sample could happen, making difficult to distinguish between them. This issue could be overcome looking for a specific wavelengths placed at a reasonable distance in spectrum, at which one of compounds has a strong absorption while the other one is transparent and vice-versa [15-19].

According to these features, we used a state-of-the-art trace gas CO_2 laser photoacoustic spectroscopy technique to quantify and to compare the photoacoustic signal intensity from red fruits cherry tomatoes exposed to pollution from various car engines and UV radiation, in order to test and control the impact of these two environmental conditions (that may be a cause of fruit stress).

2. Experimental method

The emitted ethylene concentration measurement is analyzed by laser photoacoustic spectroscopy (LPAS) technique, as it offers a high sensitivity that makes possible to evaluate absorption coefficients on the order of 10^{-8} cm^{-1} [16, 20]. To test the cherry tomatoes exposed to engines pollution and UV radiation, we operate a sensitive instrument and we report, the ethylene vapors from exposed fruits, measured at the CO_2 laser wavelengths in precisely controlled experimental conditions that includes a detector running in a resonant regime, a certified calibrated mixture of ethylene and nitrogen, a cw-line-tunable CO_2 (with a discrete spectrum consisting in 60 distinct spectral lines as result of the vibrational-rotational transitions of the CO_2 within 9.2–10.8 μm region, grouped in 4 branches: 9R , 9P, 10R and 10P) frequency stabilized laser together with a fully Test Point data acquisition and real-time processing system.

The CO_2 laser is frequency stabilized to the centre of the curve representing its output power *versus* frequency [15]. The measurements were made with the laser operating in the TEM_{00} mode for all wavelengths.

The following important parameters were used throughout the experiments for the detection of ethylene gas at cherry tomatoes: biological sample cuvette pressure: ≈1024 mbar; responsitivity of the PA cell: 433 cmV/W; synthetic air: Linde Gaz Romania, 20% oxygen and 80% nitrogen (impurities: hydrocarbons max. 0.1 ppmV, nitrogen oxides max. 0.1 ppmV); working laser line: 10P(14), where we have a maximum absorption coefficient for ethylene: λ= 949.479 cm^{-1} , α= 30.4 $cm^{-1}atm^{-1}$; operating temperature: 23–25 ^oC; glass cuvette total volume: ≈150 mL; PA cell total volume: ≈1000 mL; biological samples analysis time: ≈3 minutes.

A full description of the entire IR spectroscopy installation together with the characteristics, measurement protocols and gas handling system have been previously described and published in [15-23].

In brief, the laser beam, tuned at a certain wavelength, is modulated in intensity by a mechanical chopper and then focused through a ZnSe lens into the detector filled with the gas sample (Fig. 1).

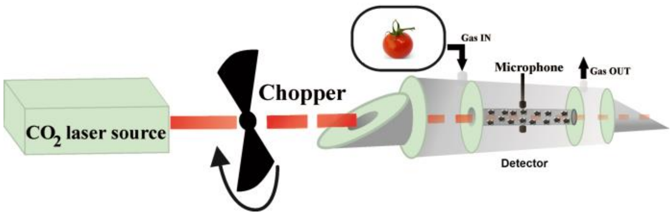

Fig. 1. Configuration of the IR spectroscopy system for red fruits cherry tomatoes sample testing

The cw, tunable CO_2-laser beam is chopped, focused by a ZnSe lens, and introduced in the cell. The light beam was modulated by a high quality, low vibration noise and variable speed (4–4000 Hz) mechanical chopper model DigiRad (30 aperture blade), operated at the appropriate resonant frequency of the cell. The laser beam diameter is typically 6.2 mm at the point of insertion of the chopper blade and is nearly equal to the width of the chopper aperture. An approximately square waveform was produced with a modulation depth of 100% and a duty cycle of 50% so that the average power measured by the power meter at the exit of the cell is half the cw value. By enclosing the chopper wheel in housing with a small hole (10 mm) for the laser beam to enter and exit, reduces chopper-induced sound vibrations in air that can be transmitted to the microphone (sensitivity 20 mV/Pa) detector as noise interference. A compatible phase reference signal is provided for use with a lock-in amplifier (time constant 1s sensitivity 1-100 mV).

The acoustic signal, produced as result of interaction between the laser radiation and the ethylene vapors, is detected using four sensitive microphones which generate a corresponding electrical signal [21]. This signal is fed into a lock-in amplifier, where it is analyzed and delivered as amplitude and phase of the detector signal synchronized to the chopper phase (the chopper was operated at the frequency of 564 Hz, near the resonance frequency for which the photoacoustic cell is excited at its first resonant longitudinal mode). The detection sensitivity is highly improved when the cell is built as an acoustic resonator working in a resonant regime which is achieved for a certain modulation frequency of the laser beam, known as the cell resonance frequency. This sensitivity brought by the resonant regime is described by a quality factor, *Q*, representing the amount of signal enhancement that occurs when the laser is modulated at the resonance frequency [15]. At resonance, the amplitude of the photoacoustic signal is *Q*, times larger than the amplitude far from the resonance frequency, i.e., the amplification is equal to the value of the *Q* factor. The quality factor of the system *Q* (experimentally determined value: 16.1) is the ratio between the energy stored in a specific mode and the energy losses per cycle of this acoustic wave [15].

At the exit of the detector (that is connected to a complex gas handling system built to ensure a proper manipulation of the gases along the delivery path) a power meter measures the laser beam. The useful data such as the laser beam power delivered by the powermeter and the signal from the lock-in amplifier are automatically recorded in real time under the computer control.

3. Results

The red fruits cherry tomatoes were obtained from local farmers and transported to the laboratory were we selected and evaluated the fruits only at harvesting stage/ red fruits (50 g).

The cultivation area for harvested cherry tomatoes fruits was treated only with compost of animal manure, the weeds were controlled with the help of hand weeding, crop rotation, mulching and tilling, while insects are controlled using only natural methods like birds or traps.

All fruits used in these measurements were stored at 4^0C for subsequent use.

Before starting the analysis of cherry tomatoes (expressed in grams), all fruits were acclimatized over 1 h at room temperature (23 - 25^0 C) and then introduced into a small glass cuvette (with volume of 150 cm^3) to be exposed for 25 min to pollution from various car engines and 25 min to UV radiation at 365 nm with the lamp power of 8W.

To measure the ethylene vapors from exposed fruits, the IR fingerprint of ethylene was also previously achieved [15-21] based on the values measured for 62 lines of the CO_2 laser with wavelengths between 9.4 - 10.8 µm.

The assessment of red fruits cherry tomatoes were performed for one specific CO_2 laser line (949.479 cm^{-1}) [15-20].

The IR spectroscopy instrument allows detection of gas emission in a continuous-flow system down to 1 ppb and the sensitivity of the technique is such that absorptions of $<10^{-7}$ cm^{-1} can be measured over path lengths of a few tens of centimeters.

The IR spectroscopy system was first used to quantify the level of ethylene that is normally produced by cherry tomatoes fruits in normal aerobic conditions (synthetic air flow) compared to anaerobic conditions (nitrogen air flow).

Fig. 2 presents the production of ethylene experimentally measured for 50g of red cherry tomatoes fruits.

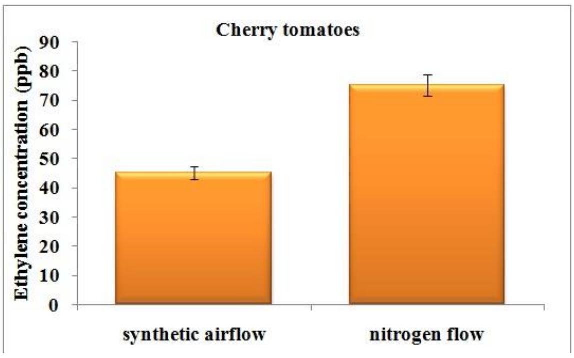

Fig. 2. Ethylene vapors at cherry tomatoes fruits produced in aerobic vs. anaerobic conditions

We observed the increased of ethylene concentration when we exposed the red fruits in anaerobic conditions compared to normal aerobic conditions.

In addition, Fig. 3 shows ethylene vapors from cherry tomatoes exposed 25 min to pollution from various car engines and 25 min to UV radiation.

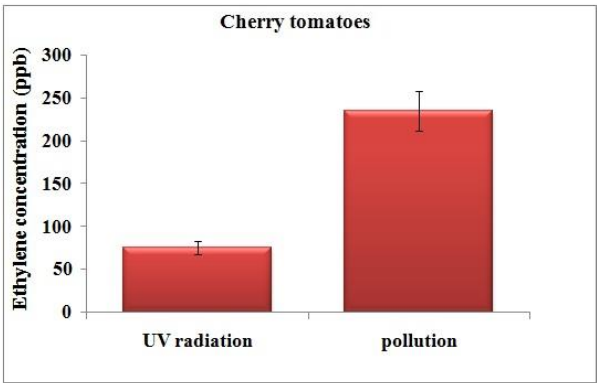

Fig. 3. Ethylene vapors at cherry tomatoes fruits produced after 25min exposure to UV radiation and after 25min exposure to pollution

We achieved also additional results (presented in Fig. 4) for real-time measurements of ethylene emission produced by cherry tomato flowers and by cherry tomato fruits (green and red) [20].

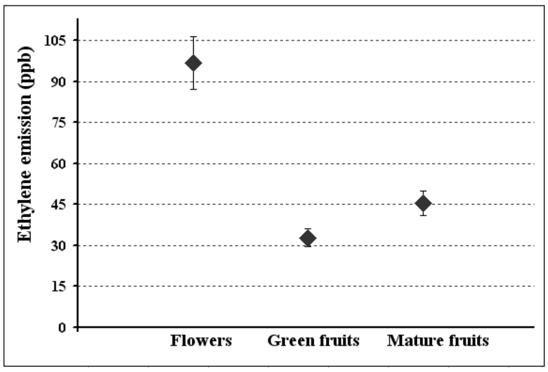

Fig. 4. Ethylene production in cherry tomatoes (from flowers to mature red fruits) [20]

The emission of ethylene in normal conditions for flowers was approximately 97 ppb, for green fruits about 33 ppb, while for red fruits about 46 ppb.

To assess the gas vapors from the glass cuvette contents, firstly we evacuated thoroughly the previous gas mixture from all the handling system, including the detector, traps, pipes etc., and then we cleaned the system for 20 minutes. After a second vacuum cleaning, the gas from the sample was transferred in the detector and analyzed.

We can observed from the determinations that cherry tomatoes under stress emit more ethylene gas (rises by more than 400% when are exposed to pollution) than those under normal conditions.

Such differences could originate from limitations to growth imposed by the stress in these two environmental conditions, prevailing in fruits exposed to pollution and UV radiation.

The higher level in ethylene response confirms that oxidative stress was higher in cherry tomatoes fruits exposed to UV radiation and pollution than in fruits exposed to aerobic conditions.

4. Conclusions

In the present research, tests were made to determine if the cherry tomatoes fruits exposed to UV radiation and pollution release more ethylene gas compared with normal ones.

Our determinations demonstrated that exposed red fruits at pollution, determine a greater increase of ethylene vapors in the respiration of cherry tomatoes after 25 min of exposure. The level of the ethylene was about 400% higher for red fruits in pollution conditions than for red fruits in normal conditions.

A common consequence of stress conditions (like environmental pollution and UV radiation) is that they result, in an increased production of reactive oxygen species/ROS. ROS may lead to the unspecific oxidation of proteins and membrane lipids or may cause DNA injury. As a consequence, tissues injured by oxidative stress generally contain increased concentrations of carbonylated proteins and malondialdehyde and the effects of stress conditions are shown also in the ethylene concentrations.

The higher level in ethylene vapors confirms that stress, was higher in exposed fruits at anaerobic conditions (e.g. UV radiation and pollution) compared to fruits in normal conditions, which could induce the degradation of RNA in cherry tomatoes fruits.

Several other studies [24-26] have demonstrated that ROS production and oxidative stress play a key role in plant tissue and carcinogenicity of environmental pollution.

The tests demonstrates that IR spectroscopy is an important tool for sensitive and selective detection of ethylene molecules at cherry tomatoes fruits and can play an important role in testing the contaminated vegetation in particular fruit quality.

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