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ON-LINE, LASER-BASED, DETECTION OF ETHENE IN EXHALED AIR AS INDICATOR FOR UV INDUCED SKIN DAMAGE

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1. Introduction

In photoacoustic spectroscopy, the fingerprint-like rovibrational absorption spectra of molecular gases is exploited in order to obtain highly sensitive trace gas detectors [1,2]. For several biologically and medically interesting molecular gases, the detection limits are orders of magnitude better than for commonly used detectors [3], opening new perspectives for on-line experiments under dynamically changing environmental conditions. In biology, the technique has already proven to be a powerful tool in investigations on dynamical changes in physiological processes [3]. Measurements on ethene emitted from single plants or plant tissue can be performed on-line due to the high sensitivity (6 ppt; i.e. 6 particles out of 10^{12}) of the intracavity CO₂ laser setup.

In medicine there is a large demand for techniques which make invasive treatments superfluous [4]. In some cases photoacoustics can fulfil this demand by monitoring trace gases e.g. in exhaled air or for gases emitted via the human skin.

In the present contribution the technique is used to investigate the effect of UV-radiation on the skin; 21 humans were exposed to UV-radiation for 15 minutes, under a commercially available solarium (Dr. Müller, Combi 12/12). During this treatment a part of the exhaled air was analyzed in a CO₂-laser driven photoacoustic detector [5] to monitor the exhaled ethene (C₂H₄) concentration.

Ethane and pentane are well known products of lipid peroxidation, i.e. cell membrane damage. This damage is mostly caused by free radicals, which can be formed under the direct influence of e.g. UV-radiation [6,7] but the tissue itself produces also free radicals, that play an important role in the immunity system. Because of the high sensitivity of the photoacoustic setup for ethene, another end product of lipid peroxidation, we used this gas as biomarker.

2. Experimental

Gas coming from a compressed air bottle is flown through a reduction valve into an aluminized huffer bag of 60 liters. The test persons are breathing air from this bag through a Hans-Rudolf valve. Most of the air is going to a Spirolog or an Oxicon to determine the pulmonary volume, needed to correct for the dilution rate of the measured gases. A flow of 3 liters per hour is flown through the photoacoustic setup to determine the ethene concentration. Water is removed from this flow by Nafion tubing to prevent condensation. Then, the air is compressed to an overpressure of one bar by a membrane pump. This overpressure causes the

flow of the gas through the scrubbers and the photoacoustic setup. Scrubbers are needed to get rid of some interfering gases; CO₂ is removed utilizing first a soda lime scrubber (bulk removal) followed by a KOH scrubber (final removal to concentrations below 1 ppm), CaCl grains are used to remove remaining water. Finally, a cooling trap at 125 K freezes out acetone and other spectroscopically interfering gases. With the help of a buffer volume and an electronic flow controller a stable flow of three liters per hour is led through the measuring cell.

In order to prevent large background signals from ethene emitted from the tubing, which is also partially exposed to the UV radiation, the tubing was covered with aluminum foil. To investigate the ethene coming directly out of the skin, a cylindrical, flat sample cell is constructed which can be placed on the skin. The diameter of this cell is 5 cm and it is closed with a quartz window. Air can be flown over the skin through a gas in and out let and analyzed in the photoacoustic setup.

The trace gas detector consists of a CO₂ laser driven photoacoustic setup, able to distinguish between different gases by making use of their wavelength dependent fingerprint absorption. Knowing the absorption coefficients of the gases at different laser lines (frequencies) we are able to determine the concentrations by measuring the photoacoustic signal in the absorption cell. This acoustic signal is produced via the absorption of photons by a specific gas. The absorbed photon energy is transformed into translation energy by collisions with neighboring molecules resulting in heating up of the gas molecules. This heating causes the pressure to rise. Switching the laser on and off at an acoustical frequency results in an acoustical wave in the detection cell, which can be monitored very accurately by a sensitive microphone.

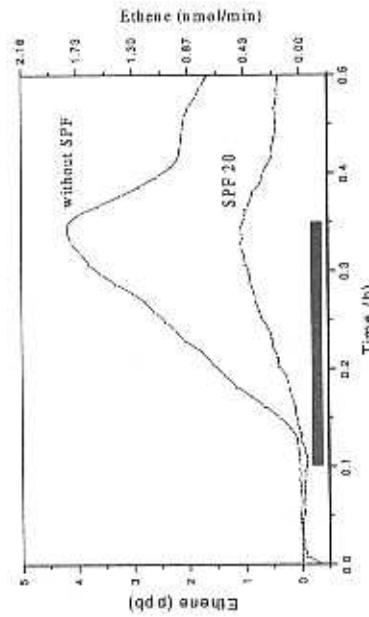


Fig. 1: The effect of UV-radiation on the human skin, monitored by ethene emission in exhaled air. Ethene is a gaseous product of lipid peroxidation induced by free radicals in the skin. The horizontal bar indicates the illumination period. The effect of suntan cream (Sun Protection Factor 20, SPF) is also shown.

3. Results

Fig. 1 shows the more than ten-fold ethene increase (1.7 nmol/min after 15 min) during treatment as compared to control emissions: 0.15 ± 0.05 nmol/min (average over 21 persons). Subjects protected from the solarium radiation by UV shielding (by lexane, blocking all radiation below 400 nm) showed no increase in ethene; suntan cream (sun protection factor 20) decreased the emission by 75%.

Oral ethene emissions are confirmed by skin emission experiments. A plot of the emitted ethene from the skin of the arm utilizing a cell with a diameter of 5 cm is given in Fig. 2. The shape of the signal is completely different from the shape of the ethene signals measured in exhaled air. After the UV source is switched on an almost immediate increase in ethene emission occurs. Within 4 till 5 minutes a steady state situation is reached. In contrast with the measurements in exhaled air, the decrease of ethene signal after switching off the UV source is only little slower as compared to the increase when the UV source is switched on. Here no transport through the body is required yielding much faster response times.

want to test sun creams, gases coming from the sun cream itself will also be taken through the photoacoustic setup and can interfere with the measurements. The measurement of ethene in exhaled air is not hampered by this problem. The disadvantage of this method is that we have to radiate the whole body. Repetition of experiments on the same test subject can only take place after a certain time (i.e. more than a week) because of adaptation of the skin to UV radiation.

A second disadvantage of this method is that we do not reach steady state conditions after permitted radiation periods. After 15 minutes of radiation (the longest exposure time permitted according to the factory) the signal is still linearly rising. This effect is caused by diffusion delay through the different tissues of the body. Calculations are underway to fit the measured curves and to determine the various diffusion coefficients. Using these results it is possible to determine the exact amount of lipid peroxidation in the skin, taking place due to UV radiation during 15 minutes exposure time. Although there are still several problems to overcome, we can conclude that ethene is a good biomarker for lipid peroxidation and the photoacoustic setup has the sensitivity required to perform on-line measurements to determine the effects of UV radiation on the skin.

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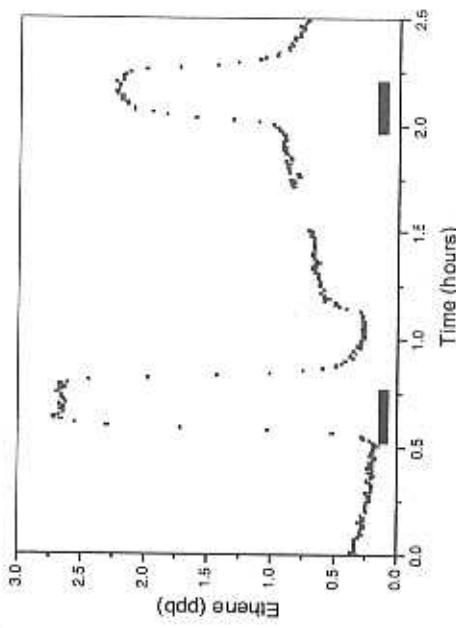


Fig. 2: The effect of UV-radiation on the human skin, monitored by ethene emission direct from the skin. The horizontal bars indicate the illumination periods.

4. Discussion

In this paper we discussed two methods to determine the degree of lipid peroxidation due to UV radiation by measuring products of lipid peroxidation in exhaled air or directly released by the skin. Both methods have their own advantages and disadvantages. Measurements directly on the skin give steady state values within several minutes making the measurements fast and calculations easy. Because of the limited surface needed for these measurements it is possible to perform several measurements on one test subject at the same day. However, if we