A HIGHLY SENSITIVE IR-OPTICAL SENSOR FOR ETHYLENE-MONITORING

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ABSTRACT

Precise and continuous ethylene detection is needed in various fruit storage applications. The aim of this work is the development of a miniaturised mid-infrared filter spectrometer for ethylene detection at 10.6 µm wavelength. For this reason optical components and signal processing electronics need to be developed, tested and integrated in a compact measurement system. The present article describes the proposed system set-up, the status of the development of component prototypes and results of gas measurements performed using a first system set-up.

Next to a microstructured IR-emitter, a miniaturised multi-reflection cell and a thermopile-array with integrated optical filters and microstructured Fresnel lenses for the measurement of ethylene, two interfering gases and one reference channel are proposed. Recently a miniaturised White cell as absorption path is tested with various commercial and a self-developed thermal emitter. First ethylene measurements have been performed with commercial twofold thermopile detectors and a Lock-in-amplifier. These showed significant absorption at an ethylene concentration of 100ppm. For the detection module different types of thermopiles were tested, first prototypes of Fresnel lenses have been fabricated and characterised and the parameters of the optical filters were specified. Furthermore a compact system electronics for signal processing containing a preamplification stage and Lock-in-technique is in development.

Keywords: IR-spectroscopy, fruit storage, ethylene, multiple reflection cell, White-cell, Fresnel lens

1. INTRODUCTION

In today's store-houses the ripening of fruits is controlled by the ethylene concentration in the ambient atmosphere. For long-term storage an ultra low oxygen atmosphere is used and low levels of ethylene have to be early detected since they are indicative of fruit ripening. Conversely, ethylene is actively added when the ripeness of the fruit in storage is to be promoted. In any case, precise and continuous ethylene detection would be very advantageous in such an application. However, up to now no suitable and compact ethylene-monitoring systems are available on the market.

For this reason a miniaturised filter spectrometer for ethylene monitoring in fruit applications has been developed. The aim is a small and comparably low cost optical system for the ethylene detection in the mid-infrared at the wavelength 10.6 µm. In fruit storage applications other gases appear and can disturb the optical measurement of ethylene. Numerous hydrocarbons in concentrations of ppb are negligible for the optical measurement, but ammonia, ethanol and acetaldehyde can occur in concentration ranges of several ppm, and thus have to be considered for cross sensitivity of the IR-measurement of ethylene. Whereas ethanol and acetaldehyde are the result of fruit stress, ammonia contamination may be caused by leakage of the cooling system. Therefore the absorption not only at the spectral range of 10.6µm but also other wavelengths have to be determined, i.e. a multi-spectral measurement has to be performed. For this application, a sensitivity of 20 ppm ethylene is needed. The principle set up of the measurement system is shown in Figure 1. The modulated radiation of a thermal emitter is coupled into a long-path gas cell and is detected by a multisensor array, preamplified and processed by Lock-in-technique. To reach the required selectivity and sensitivity of 20ppm for ethylene next to an IR-emitter, a compact long path absorption cell, a detection module and system electronics are currently in development and have to be integrated in a compact optical system. In the subsequent sections the stage of development of the component prototypes and gas measurements with a first system set up are presented.

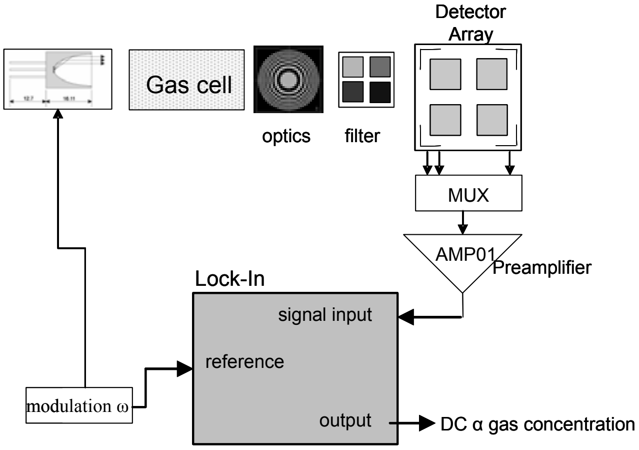

Figure 1: Schematic set up of the measurement system, which consists of a microstructured IR-emitter, a miniaturised multi-reflection cell, a thermopile-array with integrated optical filters and microstructured Fresnel lenses and signal processing electronics.

2. OPTICAL COMPONENTS, SYSTEM INTEGRATION

2.1. Micromachined IR-emitter

There are several micro sized thermal emitters commercially available, but compared with an ideal black body radiator, their emissivity and thus the emitted radiation power is moderate. This was the motivation to develop a novel type of micromachined thermal IR-emitter. The main difference compared with common thermal micro emitters is the use of 2D structured bulk silicon. The regular ordered macropores of the emitters are obtained by electrochemical etching of prepatterend silicon substrates [1]. Typical pore diameters of the fabricated photonic-crystal-like structures are in the range of 2.5 µm to 30 µm. The macroporous silicon shows a black-body-like emission profile for a wide wavelength range [2]. The device is heated using a thin film Pt-heater structured onto the backside of the substrate.

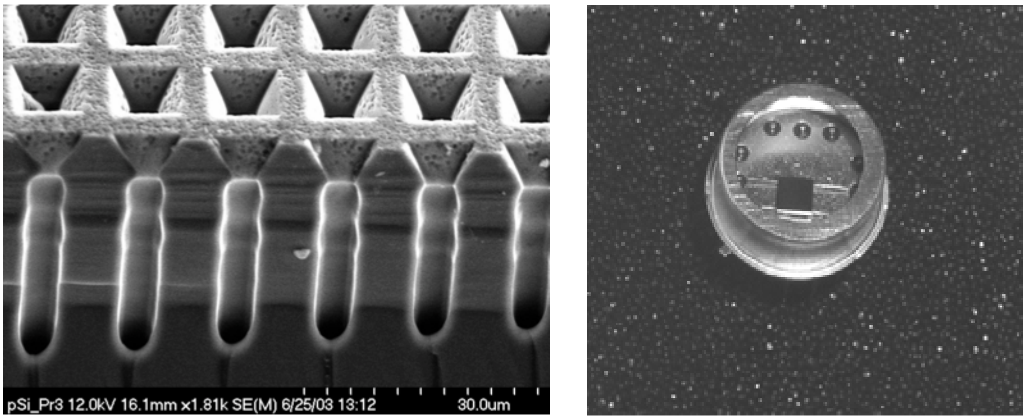

Figure 2: SEM-picture of the IR-emitter structure based on regular ordered macropore arrays (left). Emitter mounted by Pt-micro-welding in a TO8-housing (right).

2.2. Miniaturised White cell

Since there is a minimum required optical path length for the detection of ethylene in appearing concentrations in fruit applications a long optical path has to be incorporated in a small measurement system. To reach this goal a miniaturised White cell has been developed. The principle of the White cell is based on multiple reflection between three spherical concave mirrors, which have all the same radius of curvature [3]. The optical set-up features a high light transmission where radiation losses are caused only by absorption and scattering on the reflecting surfaces. The optical path, i.e. the number of reflections is dependent on the adjustment of the mirrors, but limited by the diameter of the active area of the source. The simulation of the miniaturised White cell with adapters for different optical sources and detectors is shown in Figure 3. Here an optical path length of 1.6 m is implemented in a volume of 11 x 5 x 6 cm^3. The body of the cell is machined in aluminium. The mirrors, gold-coated convex glass lenses are glued into the White cell (see Figure 4). For cost reduction a plastic White cell is planned.

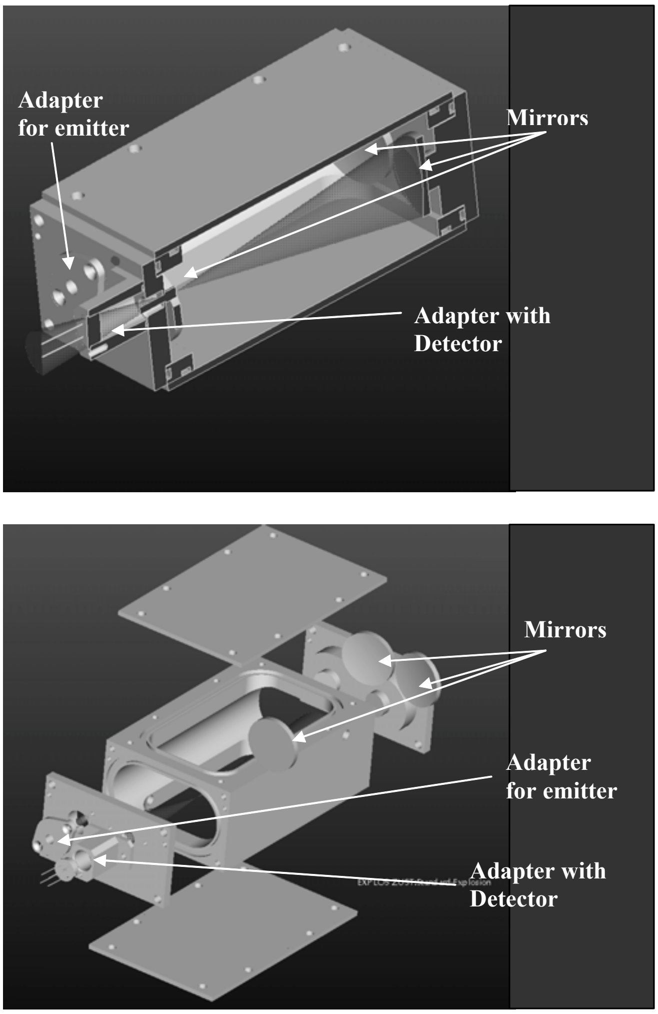

Figure 3: Schematic set up of a White cell with 1.6m optical path length cross sectional view (above) and exploded view(below).

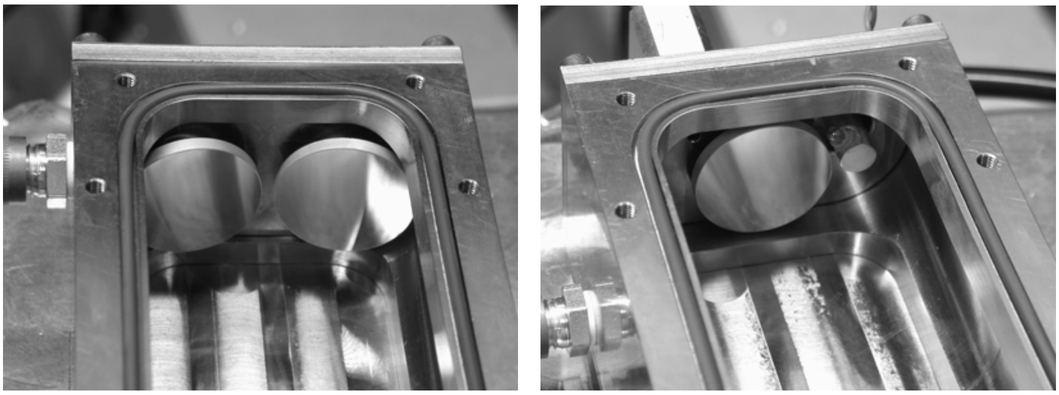

Figure 4: White cell with 1.6m optical path length using gold-coated lenses as mirrors.

2.3. Detector module

For multi-spectral measurements a thermopile-detector-array with integrated optical filters and microstructured Si-Fresnel lenses are currently under development. The general architecture of the detection module will be that shown in Figure 5. It consists of a substrate chip with a four-element thermopile-array. Optical filters will be flip-chipped on each thermopile. Attached on the top of the package will be a Fresnel multilens, intended to divide the total IR radiation reaching the detection module into four parts and focus each one of the parts into the corresponding absorber zone of each thermopile.

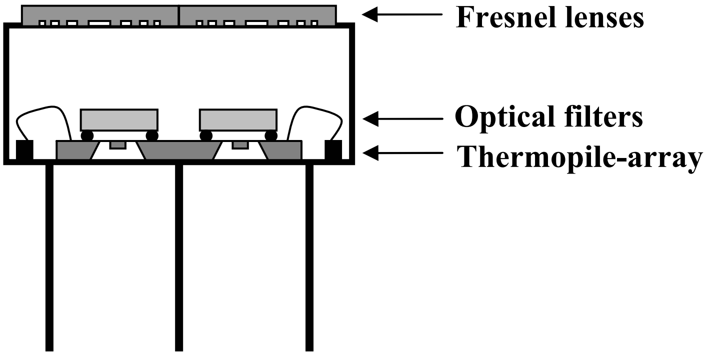

Figure 5: Schematic view of the proposed infrared detector module consisting of an array of 2x2 bulk micromachined thermopiles with different commercial infrared filters attached onto it by flip-chip techniques, wirebonded to a TO5 housing in whose lid a sectorized Fresnel lens will be physically attached.

2.4. Thermopile-array

For the detector module a bulk micromachined fourfold thermopile-array is proposed. A detailed description of the processing of the thermopiles can be found in [4,5]. First single thermopiles were fabricated for test purposes. Three types of thermopiles (see Table 1) were mounted in front of a cavity blackbody radiator with a temperature of 973.15K and an aperture of d_{Ap} = 1.02 cm /0.4". The distance d between blackbody radiator and detector was always greater than $10 \cdot d_{Ap}$, in this case the blackbody radiator can be approximated as a point source. All measurements were performed under ambient air at environmental temperature.

For the determination of the sensitivity S the distance dependent voltages U(r) were measured and fitted using the function $U(r)=C \cdot (r-r_0)^{-2}$ (C=const., r_o=distance offset). Since the sensitivity is defined as the ratio of the measured signal voltage and the incoming power P(r), S=U(r)/P(r), the sensitivity can be determined using the equation $U(r-r_0)=S \cdot P(r-r_0)=C \cdot (r-r_0)^{-2}$. The atmospheric absorption of the infrared radiation between blackbody radiator and the thermopile detector was smaller than 3% for blackbody temperatures ranging from 750 K to 1000 K and distances d in the range of 10 cm to 50 cm. Therefore the influence of atmospheric absorption on P(r) was neglected. The blackbody radiation was modulated by a mechanical chopper. The signal voltages of the thermopile elements were measured with Lock-in-amplifier. The three detector types were measured for distances to the BB radiator of 10 to 50 cm with a modulation frequency of 1.24Hz. The distance dependent signal voltages as a function of the r^{-2} are given in Figure 6 left. Furthermore measurements at different modulation frequencies have been performed. The normalized frequency-responses of the three types of thermopiles are given in Figure 6 right. The detectivity was calculated from the sensitivity and the thermal noise voltage U_R determined by the equation $U_R=(4k_B \cdot T_A \cdot R \cdot \Delta f)^2$, where k_B is the Stefan-Boltzmann-constant, T_A the ambient temperature, R the resistance of the thermopile and Δf =1Hz the bandwidth. In order to evaluate the performance of the whole detector, i.e. thermocouples and absorption layer, the sensitivities and detectivities were calculated with the assumption that the emissivity of the absorber layer is 100%. The determined values are given in Table 1 and the characterised thermopiles show good detectivities of about 10^8 cm·(Hz)$^{0.5}$/ W, which are comparable with the state of the art available silicon thermopile-detectors.

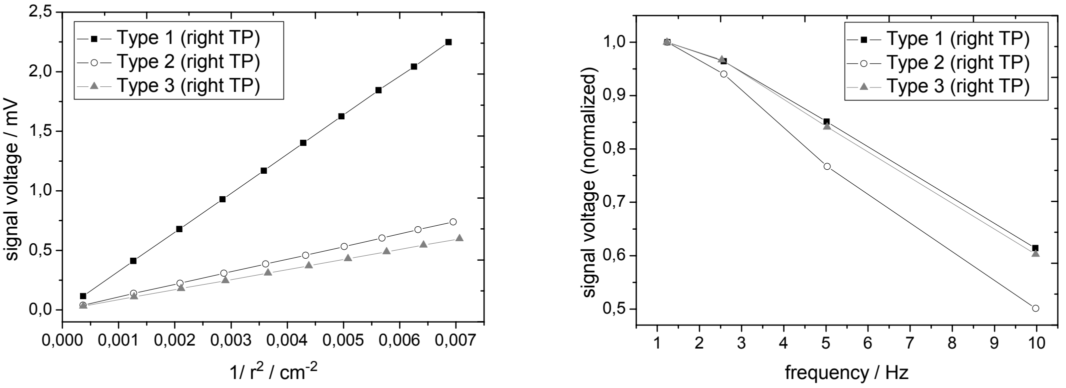

Figure 6: The distance dependent signal voltages as a function of the r^{-2} at the modulation frequency of 1.24Hz (left) and the normalized frequency responses (right) for 973.15K temperature of BB radiator for the three types of thermopiles.

Thermopile parameters	**Type 1**	**Type 2**	**Type 3**
Absorber area / µm^2	200x1100	350x1100	350x350
Number of thermocouples	130	40	40
Resistance / kOhm	156.4	14.5	20.5
Sensitivity / V/W	114.5	21.1	52.9
Detectivity/ cm·(Hz)$^{0.5}$/ W	$1.07 \cdot 10^8$	$8.56 \cdot 10^7$	$1.02 \cdot 10^8$

Table 1: Sensitivities and detectivities at a modulation frequency of 1.24 Hz for the different types of thermopiles.

2.5. Optical filters

The parameters of the optical filters were estimated from the absorption spectra of the relevant gases, i.e. ethylene, ammonia, ethanol and acetaldehyde [6]. The spectra of ethylene and the appropriate filter transmissions are given in Figure 7. The gases show interfering absorptions at 10.6 µm, i.e. they can cause cross sensitivities during the IR-measurement of ethylene. For the first investigations optical filters for ethylene, ethanol, ammonia and a reference channel have been chosen for a 4-element thermopile-array. The parameters of the filters are summarised in Table 2. Since the different detector-elements will react on several gases with different absorption effects the measurement data has to be assessed by means of multivariate data analysis to determine the ethylene level.

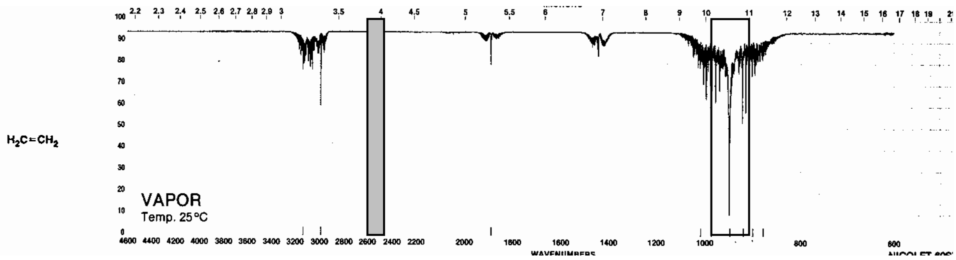

Figure 7: Spectra of ethylene and filter transmission for reference channel (grey) and ethylene (transparent) [6].

Parameters of the filter	Central wavelength / µm	Full width at half maximum / %	Transmission range/ µm
Reference	3.95	2	4.0 – 3.9
Ethylene	10.6	4	11.0 – 10.2
Ammonia	9.7	4	10.1 – 9.3
Ethanol	3.46	4	3.6 – 3.3
Acetaldehyde	3.64	4	3.8 – 3.5

Table 2: Parameters of optical filters for measurement of ethylene and interfering gases.

2.6. Fresnel lenses

In order to increase the irradiance on the thermopile elements diffractive lenses, so called Fresnel lenses, are used. In a conventional lens the curvature defines its focal, but the bulk material has no effect to the focusing properties. In a diffractive lens the bulk material is removed, and the surface is a set of grooves with curved surfaces that correspond to the original surface. The advantages of diffractive lenses are less absorption and the possibility to fabricate micro lenses with microelectronic technology. Silicon is suitable for micro-structuring and it is quite transparent in the infrared and therefore has been chosen as material.

Fresnel lenses of different size (1cm, 0.5cm diameter) and focal lengths (0.4, 1, 2, 5, 10cm) have been designed for 10µm wavelength and fabricated. In this first trial the surface of the lens has been structured approximating the theoretical groove shapes with single flat steps. This is usually called a binary Fresnel lens whose transmission is limited to approximately 40%.

Figure 8: SEM-picture of a micromachined silicon Fresnel lens.

Focal lengths and transmissions of the Fresnel lenses were determined. The schematic measurement set-up is shown in Figure 9. Since the first lenses were calculated and structured for 10µm wavelength a quantum cascade laser with emission at 10,3µm has been used as infrared source. The laser has been driven in pulsed operation with a repetition rate of 2000Hz and a pulse length of 100ns. The parallel laser beam was focused by the Fresnel lens into a pinhole with 100µm diameter. The radiation after the pinhole was detected by a pyrodetector with a large sensitive area of approx. 2mm x 2mm. The detector signal was measured by a commercial Lock-in-amplifier. Since the detection set-up with pyrodetector and Lock-in-amplifier was calibrated for the applied parameters of the laser pulse (2000Hz, 100ns) the detected radiation intensities could be calculated from the Lock-In output voltage. The focal lengths were measured by variation of the distance between Fresnel lens and pinhole as well as the vertical and horizontal positions of the Fresnel lens to the maximum intensity at the pyrodetector, i.e. the pinhole had the position of the beam focus.

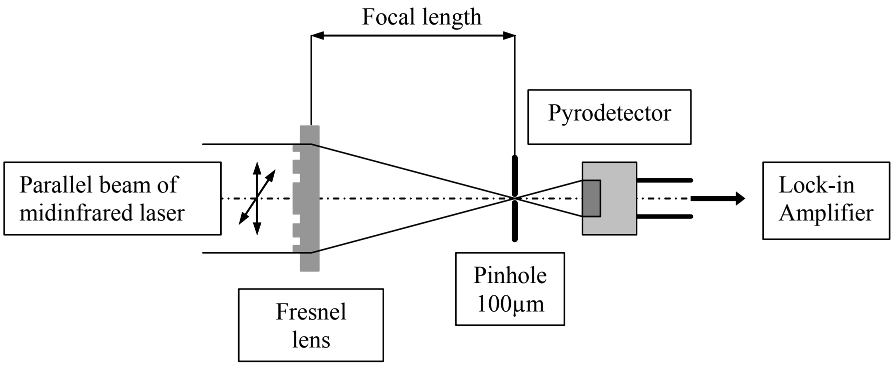

Figure 9: Principle optical set-up for characterisation of the Fresnel lenses.

The designed and measured focal lengths as well as the transmission of the lenses are summarised in Table 3. The measured focal lengths fit well to the designed values. The transmissions of the lenses have been calculated from the ratio of the detector signals with Fresnel lens and with a spherical mirror as focusing unit. Since the mirror had a larger diameter than the Fresnel lenses, an iris aperture with the same diameter as the Fresnel lens has been used to restrict the parallel laser beam. The measured transmissions range from 12 % to 25 %, which is less than the theoretical value. Assuming a refractive index of a planar silicon layer of approx. 3.4 and reflection losses at two surfaces the transmission should be approx. 50%. The transmission of a binary Fresnel lens is limited to approximately 40%. In the next steps a spatial scan of the imaging characteristics will be performed for an improved design of the Fresnel lenses to determine the exact diameter of the focus. This improved design will consist of a multilevel structured surface covered with the proper anti-reflection coating in order to increase the transmission up to 90%.

Type	**F_{DES} / mm**	**F_{MEAS} / mm**	**Transmission / %**
Type 1, diameter of lens 10mm	4	4.4	22.1
	10	9.6	17.1
	20	19.8	20.0
	50	49.5	15.6
	100	97.5	13.0
Type 2, diameter of lens 5mm	4	3.9	24.5
	10	10.1	15.9
	20	20.0	18.2
	50	48.5	12.7
	100	99.5	21.8

Table 3: Designed and measured focal lengths and transmission of the Fresnel lenses.

2.7. System electronics

A first signal processing electronics for the IR ethylene monitoring system has been developed. The schematic set-up is shown in Figure 1. A synchronous detection (Lock-In-amplifier) is used in order to increase the signal to noise ratio.

The emitter is modulated at a certain frequency. After passing the focusing Fresnel lenses and the optical filters the radiation falls on the thermopiles of the 2x2 array. The signals of the thermopile-detector array are multiplexed and processed by a preamplifier and a Lock-In-amplifier. The modulation signal of the infrared source is also used as reference signal for the Lock-In-amplifier.
The signal processing requires a low-noise preamplification of the thermopile signals. In the shown setup a voltage gain of about 7800 was chosen. For the filtering a second order low pass filter is used. From our experience the main disturbance in processing of thermopile signals is the net frequency (50Hz). However, in the first filter setup a low pass cutoff frequency of 5Hz was chosen, which is enough to eliminate the most important part of the noise. It is important to notice that we have an additional signal gain caused by the filtering stage. If the modulation frequency is 1Hz, this gain is about 2. The fourfold thermopile array provides three information channels and one reference channel. To acquire the information from the three channels, a multiplexer is used. Finally, the output is connected to a commercial Lock-In-amplifier (Thorlabs). The acquisition is managed by a PC with an acquisition card (Data Translation). The next step in the signal processing development will be the replacement of the commercial Lock-In-amplifier with specific low cost electronics.

3. MEASUREMENTS

First ethylene measurements have been carried out with the 1.6m-White cell, commercial detector and Lock-In-amplifier. As thermal emitter a Globar (as used in commercial FTIR-spectrometers) and the self-developed micromachined IR-emitter have been used. The Globar is based on Silicon carbide and was driven with an electrical heating power of 24W at a temperature of 1500K, the micromachined IR-emitter is heated with 2.3W to an operation temperature of about 1123K. Since the modulation at 10µm wavelength is critical, for first tests the radiation was modulated with a chopper and a frequency of 12Hz. Commercial thermopile detectors with two filters, a reference-channel at 3.95µm and an ethylene-channel at 10.6 µm have been used. Measurements are shown in Figure 10 and Figure 11. The time constant of the Lock-in-amplifier was 2s. Using the IPM-emitter a signal drift was observed which is caused by heating up of the emitter housing. There is a significant change in signal for 100 ppm ethylene with both emitters. The achieved sensitivities of the measurements are 60ppm with the Globar and 88ppm with the micromachined IR-emitter. To reach the required sensitivity of 20 ppm an improvement of the electronics is necessary. Also critical is the modulation of the source that has to be developed with more extent.

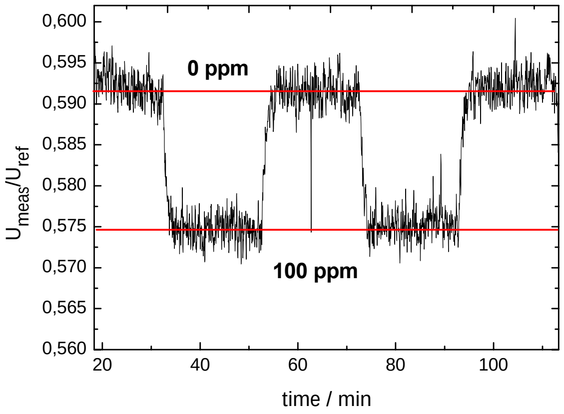

Figure 10: Ethylene measurement with 1.6m-White-cell using a Globar as infrared source and commercial thermopile detector (reference at 3.95 µm, ethylene at 10.6µm).

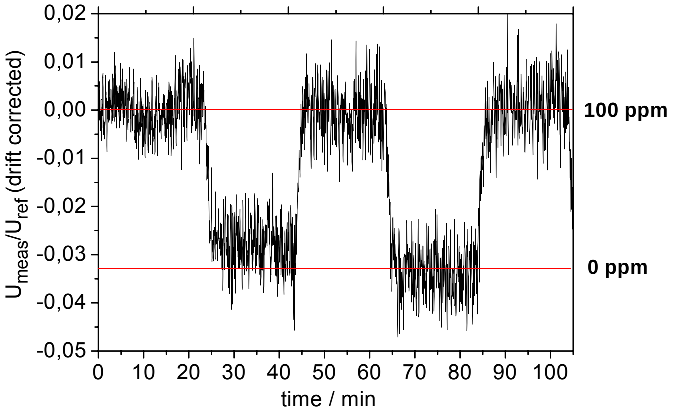

Figure 11: Ethylene measurement using the 1,6m-pathlength White-cell, the micromachined IR-emitter as infrared source and a commercial thermopile detector (reference at 3.95 µm, ethylene at 10.6µm).

4. CONCLUSION AND OUTLOOK

First prototypes of optical components have been fabricated and their functionality has been shown in characterisation measurements. The measurements using the miniaturised White-cell and commercial detector showed the proof of principle for ethylene measurement with this set-up, 100ppm ethylene could be detected significant, but to reach the required sensitivity of 20ppm the Signal-to-noise-ratio has to be increased by improved detection and signal processing. In the next steps we shall focus on the optimisation of the components, but also the system integration. Different relay optics at the White cell for IR-emitter and detection module will be investigated to optimise radiation intensity and absorption effect. Ethylene measurements with integrated components and the electronics will be performed including test of the cross sensitivities to ethanol, ammonia and acetaldehyde. The complete measurement system shall be tested in field tests for instance in fruit storage depots.

ACKNOWLEDGEMENTS

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