

# Approaches to Increase the Sensitivity of Miniaturized Ethylene Concentration Measurement Systems in the Fresh Fruit Chain

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**Abstract:** *This paper presents two approaches for realization of measurement systems for low level ethylene concentration measurement in the ppbv region. One approach is based on combination of NDIR-detectors and preconcentrator devices. The second approach is based on miniaturized gas chromatographic devices. For both cases system realization, measurement procedures and results are described.*

## 1. Introduction

Equipment for measurement of trace concentrations of ethylene gas in ambience is of high interest for the fruit logistic industry. Especially mobile systems are needed which can operate autonomously in transport environment. These systems have to fulfill the requirements concerning small size, robustness, autonomy and low costs. Additionally the equipment has to be able to detect ethylene concentrations within the ppbv region to apply monitoring of the overall ripeness of fruits during transport.

Different approaches have been examined for this task. For example, a wide range of electronic noses was tested in fruit quality control applications. Simion, Llobet and Di Natale, Brezmes et al used varieties such systems to measure the ripeness state of different fruits in post-harvest applications [1-4]. But poor selectivity and sensitivity of electronic noses allow just a rough classification of the ripeness state of fruits. An overall online monitoring of ripeness and a ripeness prediction are not possible. A simplified electronic nose approach was used by Sayhan, Llobet et al in handheld RFID-Reader [5, 6]. The application of such combined equipment makes no sense in autonomous transport scenarios, because measurements can just be done before closing or after opening the doors of containers. During the transport itself measurements are not possible.

Other mobile systems for ethylene concentration measurement were developed based on the non-dispersive infrared (NDIR) spectroscopy [7, 8]. The main advantage of those systems is their robustness and selectivity due to a target gas. Their disadvantage is low sensitivity against ethylene. Here the question arises, whether an indirect sensitivity increase is possible using combinations of preconcentrator (pc)-devices and NDIR-detectors. In this paper such an experimental combination and related experimental results are presented.

Additionally a new developed system based on traditional gas-chromatographic (GC)-techniques using miniaturized silicon-based devices is described in this paper. The choice of this approach seems to be promising because it guarantees good selectivity due to other gases in ambience. The usage of a miniaturized PC-device in the system providing increased sensitivity on one hand and a well controlled sample injection into the system on the other hand.

## 2. NDIR-detector System and Preconcentrator combination

### 2.1 NDIR-detector System

Gas measurement systems based on the NDIR-spectroscopy use the nature of some gases to absorb infrared (IR) light. This adsorption can be observed in gas specific wavelength of radiation. It causes an attenuation of IR-light emitted by a source, if the target gas molecules are present in a volume

between the source and an IR-detector. This relation between radiation, gas and geometry is described by the well known Lambert-Beer's law

$$\frac{I_{Trans}}{I_{Source}} = \exp(-\varepsilon \cdot C \cdot l) \quad (1)$$

with the initial IR-radiation intensity  $I_{Source}$ , the transmitted light intensity  $I_{Trans}$ , the gas specific adsorption coefficient  $\varepsilon$ , the gas concentration  $C$  and the optical path length  $l$ . Equation (1) is related to a specific adsorption wavelength  $\lambda$ . It shows the physical limitation of NDIR-measurement systems. A sensitivity increase can be just achieved when  $I_{Source}$  and/or  $l$  are increased. Because of the exponential behavior of the equation, the effect of  $l$  is limited for higher path lengths. Additionally, the direct relation between the optical pathway and the system size leads to a compromise between the system size and the selectivity. An increase of  $l$  makes just sense, when the sensitivity rises in relation more than the system size. Increasing  $I_{Source}$  is just possible, when the radiation intensity of the used IR-Source is increased. This is just possible by using bigger sources and thus, bigger system sizes and more energy consumption is the result.

The IR-adsorption spectrum of ethylene is shown in figure 1. The main wavelengths where ethylene absorbs IR-light are located at about 3.25  $\mu\text{m}$  and about 10.5  $\mu\text{m}$ . The usage of the 3.25  $\mu\text{m}$  is not suitable for selective ethylene concentration measurement because this absorption band interferes with absorption bands of gases which are similar to ethylene like Ethane and Propane. A better solution is the usage of the 10.5  $\mu\text{m}$  radiation, because here nearly no interferences are observed.

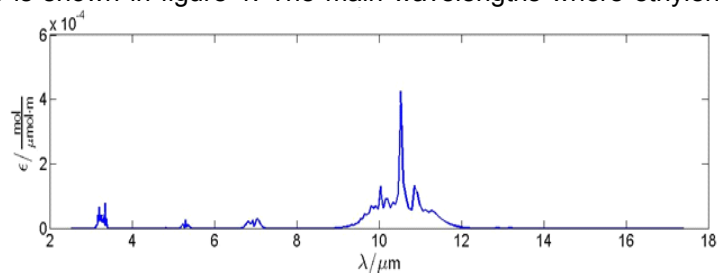


Figure 1: IR-Adsorption spectrum for ethylene. Data based on [9]

Using this wavelength leads to two other disadvantages. First, special IR-sources have to be used which have a brought blackbody radiation behavior. Simple IR-bulbs are not suitable because they don't emit light for wavelengths over 5  $\mu\text{m}$ . Second, the IR-light emission intensity at about 4  $\mu\text{m}$  is about four times the emission intensity at 10.5  $\mu\text{m}$  for blackbody temperatures of miniaturized IR-sources (e.g. 450°C). Thus, the system design must be efficient related to utilization of the available radiation.

Taking these limitations into account, an NDIR-measurement system based on the above considerations was developed. It consists of a measurement cell equipped with an IR-blackbody source. The measurement cell size is 215 mm x 25 mm x 40 mm. The measurement active volume is about 40 ml. Two thermopile detectors with optical wavelength filters were applied to detect the IR-absorption; one for the ethylene specific wavelength and one as reference in a neutral wavelength. To provide an efficient use of radiation, the measurement chamber has a conical form. To avoid losses caused by the detector housings and inactive detector areas, two IR-lenses were applied in front of the detectors to focus the radiation on the detector's active area. The developed NDIR-detector showed sensitivities of about 10 ppmv within  $\pm 2\sigma$  in laboratory test measurements. Additional information about the system design can be found in [8].

## 2.2 Preconcentrator for NDIR-detector System

PC-devices are usually used in gas chromatographic systems, where they are used for gas sampling and preconcentration of gas mixtures out of the ambient. It uses the adsorption of gas molecules on the surface of special materials, so called adsorbents. This process is strongly temperature dependant. The strength of the adsorption is inversely proportional to the temperature. The preconcentrator temperature should be room temperature or below during the sampling procedure. After the gas molecules were accumulated for a certain time, the temperature of the preconcentrator is increased to values above 200 °C. The exact temperature depends on the adsorbents used. Applying the temperature disturbs the adsorption equilibrium. The accumulated molecules are desorbed. When flushing the channels of the preconcentrator with a carrier gas, the desorbed gas molecules are transported to the preconcentrator fluidic output.

For examination of the ability of combining NDIR-detectors with PC-devices for an indirect increase of the detector's sensitivity, such a device was realized in aluminum. To integrate the adsorption material into the aluminum, four parallel fluidic channels were cut into the material. Each channel has a length of 20 mm, a height of 2 mm and a width of 3 mm. It has a total edge length of 5 cm x 5 cm. A heater pad was integrated at the bottom side of the preconcentrator. The channels were filled with about 280 mg of the commercially available adsorption material Carbosieve S-II which needs lower desorption temperatures compared to Carbosieve S-III

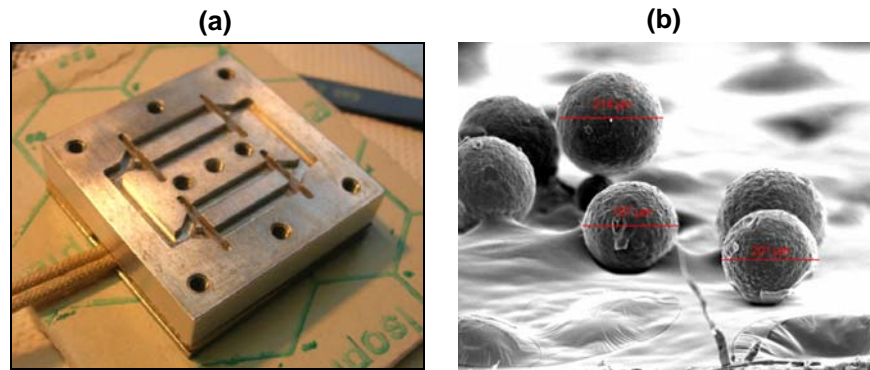


Figure 3 (a): PC-device combined with the NDIR-measurement system. SEM-picture Carbosieve S-II

(220 °C to 320 °C). At the beginning and at the end of the channels a grid was integrated to avoid loss of adsorption material into the air stream. At the bottom of the preconcentrator a heater pad was integrated to heat the PC-device electrically. Figure 3 (a) shows the used PC-device and its channels. Figure 3 (b) shows a SEM-picture of the used adsorption material.

### 2.3 Combination of NDIR-Detector with Preconcentrator and Results

The combination of the PC-device and the NDIR-ethylene detector results in the experimental setup pictured in figure 2. The PC-device was connected pneumatically between two valves to control the way of the applied gas stream. For applying different ethylene concentrations to the system, two mass flow controllers (MFC) were used with a gas bottle containing synthetic air and a bottle with 100 ppmv ethylene concentration in synthetic air. By mixing synthetic air and the ethylene, different ethylene concentration could be applied by dilution. The NDIR-detector input was connected with the pneumatic output of the PC-device. The acquisition of the measurement results was realized using an ADC card connected to a laptop.

Before measurements were started, the adsorption material in the PC-device had to be preconditioned in a thermal process to remove all impurities adsorbed during the integration of the material into the channels. During the cleanup phase the PC-device was heated up to 250°C and was flushed with nitrogen for 15 min. The experimental measurement procedure applied after cleanup phase is divided into three process steps. The first step is the adjustment of the input ethylene concentration using MFC 1 and MFC 2. During this step the flow is led around the Preconcentrator device until a constant concentration is adjusted. This takes a few minutes and can be checked using a reference detector instead of the NDIR-detector.

The second step is the *adsorption process* or *sampling process*. In this phase the valves  $V_1$  and  $V_2$  are set to the PC-device, so that the gas stream containing the constant ethylene concentration is led through the adsorbents material. The flow rate is limited in this process to values between 12 ml/min and 120 ml/min [10]. As flow rate a moderate value of 50 sccm was chosen for all measurements. The temperature of the PC-device was held at room temperature. The duration of application of the ethylene to the adsorption material was varied between different measurement runs. Adsorption times up to 16

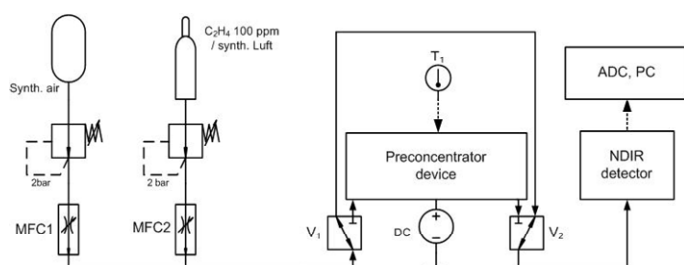
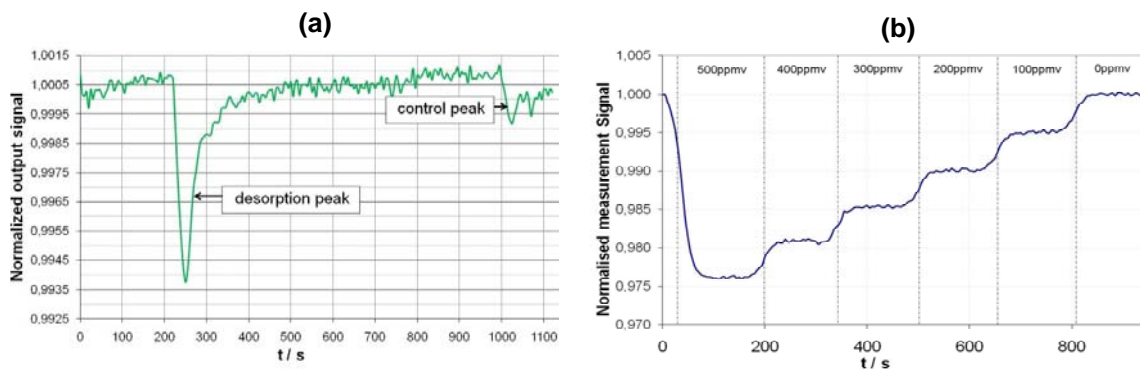


Figure 4: Schematically pictured setup for combination experiments

minutes were used. Finally the ethylene supply was turned off and pure synthetic air flushed the adsorption channels and the setup. This is necessary to remove all ethylene residues out of the fluidic channels to avoid systematic measurement errors. After no ethylene is left in the channels, the valves  $V_1$  and  $V_2$  are adjusted to bypass. The third step is the *desorption step*. Here the preconcentrator

device is heated up to 220 °C by applying a DC-Voltage to the heater pad of the PC-device. This causes desorption of the accumulated gas molecules into the space between the adsorbents particle. The PC-device is still bypassed. During this step the output signal of the NDIR-detector is already logged by the laptop. 260 s after beginning of the desorption step, the *transfer and measurement process* starts. The valves  $V_1$  and  $V_2$  are switched and the synthetic air flow is flushing to the channels of the PC-device, transporting the desorbed molecules to the detector. The heater is turned off after 30 s and the valves are switched again to bypass.

The response of the NDIR-sensor to this measurement process is shown in figure 5 (a). For this measurement a constant ethylene concentration of 12.5 ppmv was applied to the adsorption channels for 16 minutes. The signal height of the first peak is related to the desorbed ethylene into the NDIR-detector volume. The peak height corresponds to a static concentration of more than 100 ppmv concentration, referred to the calibration curve in figure 5 (b). The second peak in figure 5 (a) is the control peak which is used for checking whether all ethylene was desorbed during the measurement. The height of the control peak is negligible compared to the main desorption peak. The time independent preconcentration factor resulting from this measurement and from measurements with other ethylene input concentrations is  $0.5 \text{ min}^{-1}$ . This value leads to a theoretical minimal detectable ethylene concentration of about 800 ppb at least, but even lower values are expected when increasing the adsorption time.

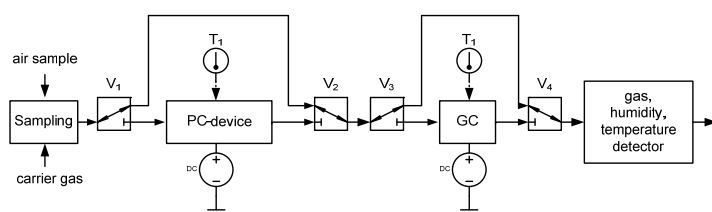


**Figure 5 (a):** Reactions of NDIR-detector to ethylene desorption and control peak. **(b):** Reaction of the NDIR-detector to static ethylene concentrations from 500 ppbv to 0 ppbv

### 3. Miniaturized Gas Chromatographic System

#### 3.1 Assembly

The second approach for low level ethylene detection was the miniaturization and application of traditional gas chromatographic devices known from laboratory equipment. The main components used here were a miniaturized gas chromatographic column, a miniaturized PC-device and a non selective ethylene detector. The diagram of connection of the three components is shown in figure 5. Additionally a sampling block is shown in the schematic which is used for gas transport in the system. The miniaturized gas chromatographic column and the miniaturized PC-device are based on silicon technologies.



**Figure 6: Schematic of miniaturized GC-system**

3.5 cm x 3.5 cm. The column is closed using Pyrex. On the backside of the silicon a 10 Ω platinum heater is integrated. As stationary phase the commercially available material Carboxen 1000 was used which is suitable for ethylene separation [12].

The GC-column is needed for separation of a gas mixture into its single gases. This separation is needed to apply a selective measurement of a target gas or to analyze an entire gas mixture with a non selective gas detector. The GC-column used in the system was developed in a former project [11]. It has a length of 75 cm and is 1 mm wide and 820 μm high. It has a chip size of

The principle of the PC-device used here was already described in section 2.2. The PC-device used in the GC-system works in the same way. The difference between the above described device and the miniaturized device for the GC-system is the material used for fabrication, the fabrication process, the size of the device. The PC-device used in the GC-system was fabricated in silicon technology and bases on previous works [13, 14]. It consists of 16 parallel channels in silicon (length of 4 mm, width of 260  $\mu\text{m}$  and high of 570  $\mu\text{m}$ ). At the backside of the silicon a platinum heater is integrated for the desorption process. The channels were filled with 10 mg Carbosieve S-III as adsorption material. The gas detector used in the system was developed using a commercially available low cost catalytic metal oxide methane sensor integrated into a low volume measurement chamber and applied with heater control and measurement electronics. The components were applied into aluminum chambers for fluidic housing (figure 7). The signal processing and the data acquisition were realized using an ADC card and a laptop.

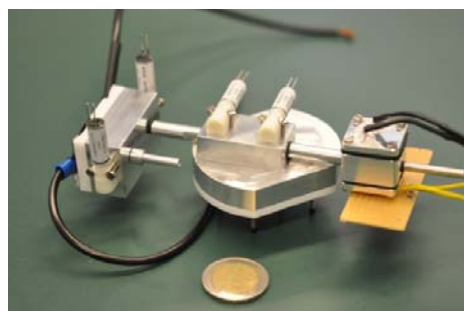


Figure 7: Schematic of miniaturized GC-system

### 3.2 Measurement results

Two aspects of the GC based ethylene measurement system were tested. The first question was whether a gas separation is achieved using the GC-column. Therefore a septum was integrated into the fluidic channels in front of the CG-column. The column was heated to about 60°C. After a constant flow of a carrier gas (synthetic air) was applied to the GC-system and the ethylene detector showed a stable baseline, a standard gas mixture was injected manually into the GC-column. This mixture was a standard product for analytical calibration containing CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> each 1% in nitrogen. These gases are similar to ethylene and thus it is a challenge to get a good separation without peak overlapping. In this measurement the carrier gas flow was adjusted to 10 sccm. The measurement duration was about 100 min. The response of the ethylene detector to the gas injection is shown in figure 8 (a). The plot shows a typical chromatograph with five peaks. The first two peaks are CO and CH<sub>4</sub>. After that C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> (ethylene) and C<sub>2</sub>H<sub>6</sub> are following. As expected, the smaller molecules show a weaker affinity to the stationary phase resulting in a smaller retention time than the bigger molecules. The retention time for ethylene is about 45 minutes. For CO<sub>2</sub> and N<sub>2</sub> no peaks are seen because the used detector is not sensitive to these gases.

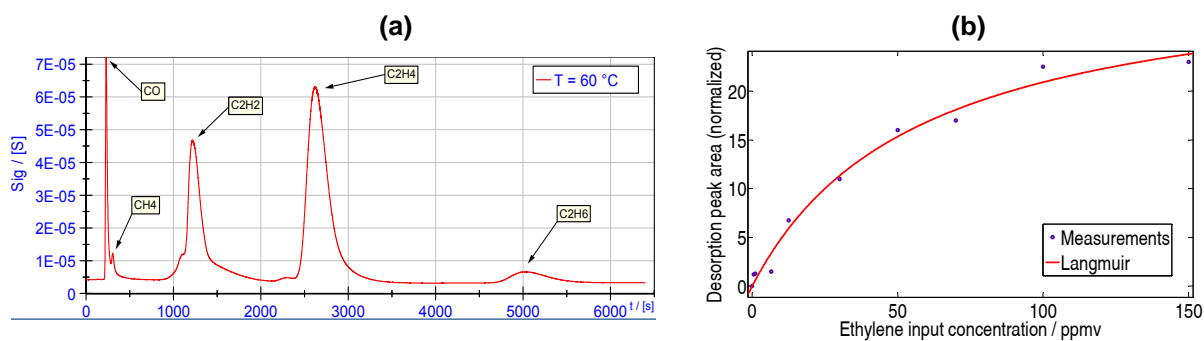


Figure 8 (a): System response to manual injected gas mixture. (x-axis: time in [s], y-axis: detector response signal)  
(b): Ethylene peak area versus PC-device input concentration

After the functionality of the GC-column was evaluated, the miniaturized PC-device was tested. This was made by application of different ethylene concentrations in synthetic air on the PC-device. After the sampling process the device was bypassed and heated up to about 250 °C by using connecting a voltage of 25 V to its platinum heater. After one minute the carrier gas was adjusted to the PC-device and the desorbed ethylene was transported to the GC-column and to the detector. No peaks were seen expect one peak with the retention time of 45 minutes corresponding to ethylene. The peak area was calculated for every input concentration. The resulting relation between the input concentration and the ethylene peak area is plotted in figure 8 (a). The achieved data can be fitted by the well known Langmuir isotherms which describe monolayer adsorption on surfaces. The lowest concentration detected was 500 ppbv. This result shows the functionality of the measurement system and one hand and that low ethylene concentrations can be measured using the described approach.

#### 4. Conclusion & Outlook

Two measurement systems for low level ethylene measurement in fruit logistics were presented. The first system is based on NDIR-spectroscopy. The detector is able to detect ethylene in concentrations of about 10 ppmv selectively. Although this is a good value compared with similar systems [7], but this sensitivity is not suitable for ethylene monitoring in the logistic fruit chain. To increase the selectivity, the system was merged with an ethylene PC-device. This device increased the sensitivity indirectly. The theoretical detection limit is about 0.7 ppb for adsorption times at about 20 minutes. Next steps in the developing process of these NDIR-systems will be the entire integration of the NDIR-detector with embedded signal processing into one system to avoid the usage of laptops and to achieve a autonomous operation. Because the described PC-device is just an evaluation setup, it is necessary to implement a PC-device for the NDIR-detector which is proper for in field applications. Additionally the existing setup will be used for further examination of the adsorption effects and the limitations of this approach.

The second system presented was a miniaturized gas chromatograph consisting of miniaturized devices. An evaluation of the functionality of the GC-column was made. The GC column is suitable for separation of a gas mixture consisting of different gases which are similar to ethylene at temperatures of about 60°C. In future works it has to be examined which retention times appear for bigger gas molecules (over C<sub>2</sub>). Probably these molecules will show much bigger retention times. In such a case it may be necessary to apply a temperature programming to the GC-column to shorten the measurement time. The test of the sample injection using the miniaturized PC-device results in a Langmuir behavior between the PC-device input concentrations and the area of the measured ethylene peaks after desorption. The concentration which could be measured was about 500 ppbv. A redesign of the PC-device is currently made. The device will be able to contain about 100 mg of adsorption material. It is expected to achieve better resolution using this device. Moreover, it is also expected to be able to measure lower concentrations of ethylene when the PC-device used in this paper can be cooled down to Temperatures under 10 °C because of the relation between adsorption and temperature. This question will be answered in future works.

#### 5. Acknowledgements

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