ETHYLENE MEASUREMENT FOR FRUIT LOGISTIC PROCESSES IN A RANGE OF 400 PPBV

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ABSTRACT

The small gas chromatograph presented in this paper was for the first time able to detect an ethylene concentration of 400 pp**b**v. Deduced from this measurement a detection limit below 50 pp**b**v can be reached which is absolutely mandatory for the shelf life prediction of climacteric fruits. To achieve the necessary sensitivity a complete new large-capacity-on-chip preconcentrator device was realized. New stationary phases were tested. The used packed gas chromatography column is now capable to separate vaporized water and ethylene gas from each other which was a yield breakthrough in the analysis of ethylene concentrations in ambient air. It can be predicted that the system will be available at a price under 1000€.

KEYWORDS

Ethylene measurement, post-harvest, preconcentrator, stationary phase, gas chromatography column, stationary phase, intelligent container, intelligent logistic, FEFO

INTRODUCTION

The research project 'The Intelligent Container' started in 2010 and is founded by the federal ministry of education and research. In this project new approaches in sensor technologies, sensor networks and logistic processes were developed. Especially the prediction of the shelf life of climacteric fruits like bananas was fundamental. [5;6] In figure 1the principle of 'The Intelligent Container' is shown.

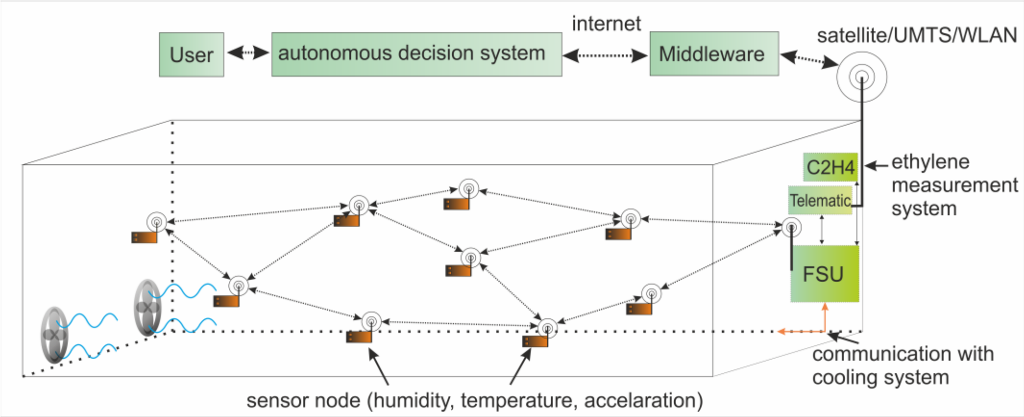

Figure 1: Principle of the "Intelligent Container". A sensor network in the container sending their data to the FSU (mainframe of the container), an ethylene measurement unit is near the FSU. With a telematics the container communicates via WLAN, GPRS or satellite with a middleware.

The shelf life of perishable goods is not a static parameter. Besides the fact that every fruit is different, the shelf life depends on transportation temperature, humidity and air composition. A change of only one of these parameters could already reduce the shelf life significantly. Early knowledge of a container with spoiled food during the logistic process leads to several benefits. On the one hand issues with the plantation can be revealed and unnecessary transports can be avoided. On the other hand compensation delivery can be in time. Decision support tools can predict the shelf life with the sensor data of the transported product at any time. With this dynamic shelf life prediction the logistic concept FEFO (First Expire First Out) can replace the custom FIFO-concept (First In First Out). Even more the logistic process can decide which destination is best for each container individually. The reduction of unnecessary transport is the result.

Especially to predict the ripeness of climacteric fruits like bananas at any time during transportation, an ethylene measurement system with detection limit of about 50 parts per billion by volume (pp**b**v) is absolutely mandatory (e.g. fig. 2) [1].

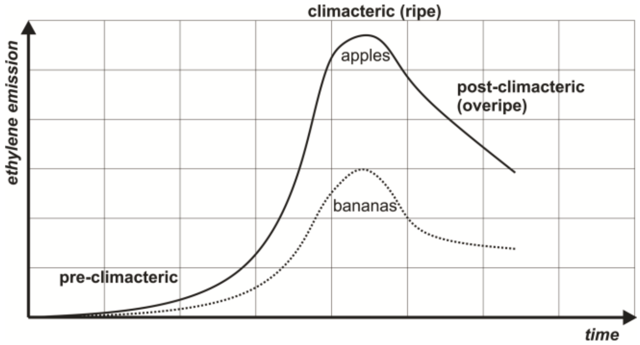

Figure 2: Ethylene emission of bananas during their different states of ripeness. (a): bananas are green (pre climacteric state); (b) Bananas are yellow (ripe, climacteric state); (c) brown sugar spots(post climacteric state); the measurement is in (a) where the logistic process takes place, the ethylene concentration in a container is here in a range of ppbv

Latest work on the subject of the coupling of a packed µ-gas chromatography column (µGC) and a µ-preconcentrator device was presented by us in 2012 [2]. The detection limit of this system was at 6 parts per million by volume (pp**m**v). Gas chromatography systems are common for the analysis of specific gas compounds. These systems normally have two main disadvantages. Usually they are big and therefore not suitable for mobile use. The injection process of sample gas compounds is complicated. By using a µ-preconcentrator, besides the indirect increase of the sensitivity, the process of the injection gets easier and more reliable. In the following, new solutions to overcome the latest detection limit are presented. The focus was set on the development of a complete new large-capacity-on-chip preconcentrator device and to overcome fatal influence of vaporized water on the non-selective sensor.

GAS CHROMATOGRAPHY

The main parts of a gas chromatograph are an injection unit, a gas chromatography column and a non-selective gas sensor.

A carrier gas–the mobile phase–flows with a specific flow rate through the system. The sample gas compound is injected in the system ahead of the GC which is filled with the stationary phase. Different stationary phases depending on the GC-design–packed of capillary column–are applied. In our case of a packed GC carbon as adsorbents is common. The carbon comes in several particle sizes, pore sizes and forms which are fundamental for the adsorption and separation behavior.

The different parts of the gas compound have different pass-through times–retention times–through the GC. Due to these different retention times the parts of the gas compound are separated from each other, and therefore they arrive at the sensor at different times. With the knowledge of the specific retention time every peak in the output signal can be assigned to a specific gas component.

In the system described in this paper the injection and the sampling is replaced by a preconcentrator which is also needed to increase the sensitivity of the system. The first generation of our preconcentrator device is shown in figure 3. It was filled with 8 mg Carbosieve®-SII and was a simple two layer glass silicon compound with a 50 Ω platinum heater on the bottom. Eight channels where filled with the Carbosieve®-SII. Each channel is 5000 µm x 500 µm x 250 µm.

Figure 3: First generation of our PC-device. It is filled with 8 mg CSII as the adsorption material.

The used packed GC is shown in figure 4. It has a platinum heater at the bottom and is 0.9 mm high and 1 mm wide. As the stationary phase Carbosieve®-SII (CSII) and Carboxen® 1000 (C1000) were used.

As mentioned before, these are adsorbent materials based on carbon. CSII have a particle size of 60 to 80 mesh, a pore size of 6 to 15 Å and a surface area of about 1200 m^2/g. C1000 have a particle size of 80 to 100 mesh, a pore size of 10 to 12 Å and a surface area of about 1200 m^2/g. In order to get the same retention time for ethylene a 50 cm long GC with CSII and a 75 cm long GC with C1000 were used.

(a) (b) (c)

Figure 4: (a): 75 cm packed gas chromatographic column with Carboxen 1000 (Chip size 40 mm x 40 mm); (b): platinum-spiral heater. The filling is simply done by using vacuum to suck in the stationary phase; (c) REM-picture of the stationary phase.

PRECONCETRATOR DEVICE

In order to overcome the limits in the sensitivity a complete new large-capacity-on-chip preconcentrator device was realized. The new PC is shown in figures 5 and 6. It consists of a three layer system of glass, silicon and glass in a triple stack bonding.

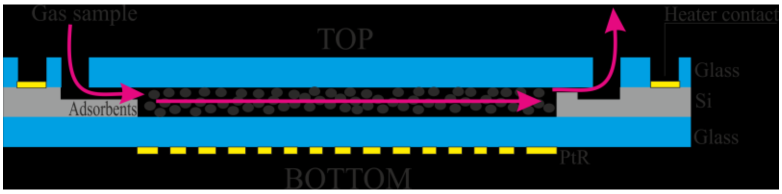

Figure 5: Cross section of the large-capacity-on-chip preconcentrator device with Carbosieve® SII as adsorbents; Silicon walls between channels used as heater; Platinum thin film resistor PtR for temperature measurement on the bottom of the device.

The silicon walls between the channels are used as the heater for the desorption process. The silicon is etched in a two-step DRIE–process. In the first step the front is etched with the structures that are not going through the whole wafer. In the second step the channels were etched open from the back. For temperature measurement and regulation a platinum thin film resistor with a resistivity of about 1000 Ω is used (PtR). Ultrasonically drilled holes in the top glass wafer are used for contacting the silicon-heater and for pneumatic coupling. The adsorption material is CSII. With the dimensions of 40.0 mm x 2.0 mm x 0.9 mm for each of the eight channels the PC contains 290 mg of CSII [3]. In comparison to our first generation PC-devices this is 36 times more. Due to the PC design the filling of the adsorption material is very simple. It is simply done by using vacuum to suck in the stationary phase. Silicon pillars at the end of each channel are used as a sieve to hold the CSII in the PC. The housing is made of three parts; a Teflon plate and two aluminum parts. The aluminum parts are structured with drilling and CNC technology. With two valves the air flow is led through the PC or a bypass.

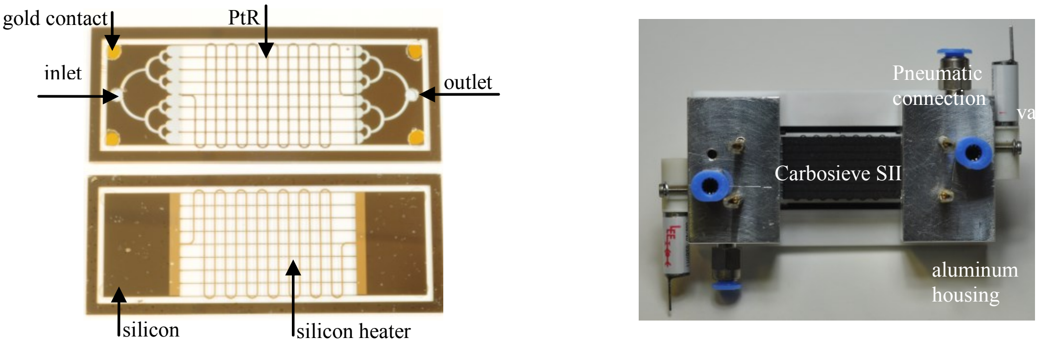

Figure 6: (a): Top- and bottom view of the PC device; (b): topview with Carbosieve SII as filling material and housing

A thermographic measurement was used to test the temperature behavior with and without filling material in order to have a controlled desorption process. The temperature spreading due to the voltage on the silicon heater is shown in figure 7. During the measurement the PC was in its housing to take into account the influence of temperature behavior of the housing as well. Because of the superposition of the heat produced by every heating structure the heat in the middle is higher than the outer regions of the device.

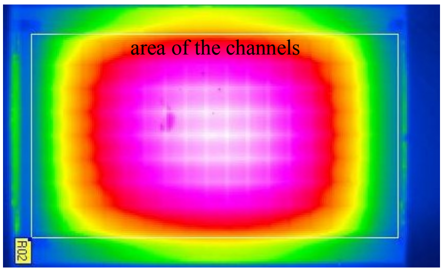

Figure 7: Temperature over the PC-Device with CSII as filling material; the interesting area is marked by a white rectangle (voltage: 30 V; mean value ~292°C)

The measurements were performed with different voltages. The result is shown in figure 8. A Voltage of about 23 V is needed to get the necessary average temperature of 200°C for the desorption process.

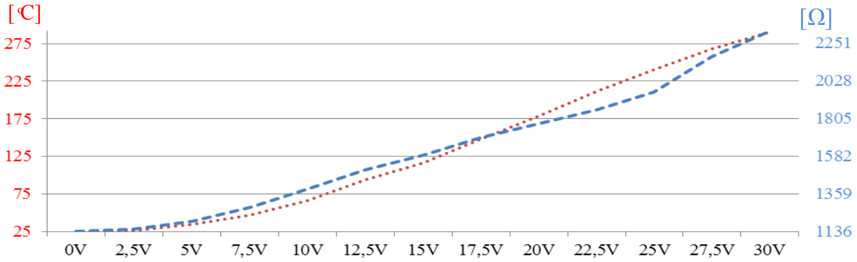

Figure 8: Red dotted line:Heating behavior of the filled PC-device in its housing over the voltage (mean value over the channel area of the PC) [V]; Blue dashed line: The reading of the PtR in [Ω]

MEASUREMENT SETUP

The measurement procedure is shown in figure 9.

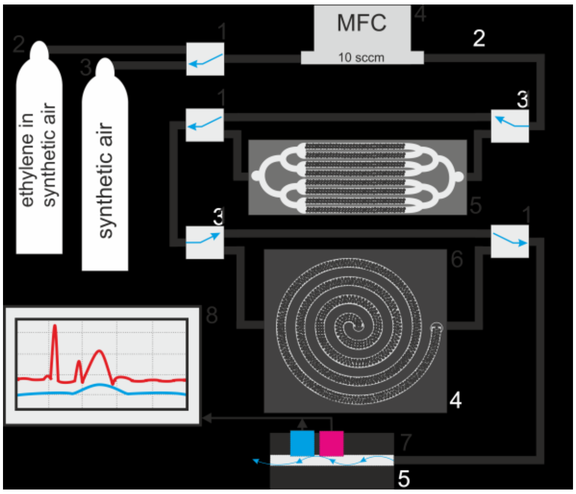

Figure 9: (1): Measurement setup; Valves; (2,3): Gas bottles; (4):Mass Flow Controller (MFC); (5): µ-Preconcentrator (PC); (6):Packed gas chromatography column (GC); (7): Measurement chamber with MOX and humidity sensor; (8)Gas chromatogram .

As the sample gas, ethylene with a concentration of 400 pp**b**v in synthetic air is used. As the carrier gas, synthetic air is used to get more comparable results with the use in the container. The mass flow controller provides a flow rate of 10 sccm that is needed to get the best separation behavior possible for the GC for both stationary phases.

The first step is the adsorption. During the adsorption the sample gas with ethylene is led through the PC for a few minutes and through the bypass of the GC. After that, the PC is closed and the synthetic air is led through the bypass of the PC and through the GC. After adjusting the baseline the PC is heated. This is the desorption process. After the desorption process the PC is connected to the GC to inject the gas sample. The gas sample flows through the GC and the several compounds are getting separated from each other. At different times they are causing an output signal on the gas sensor and the humidity sensor.

RESULTS

The main problem of the described large-capacity PC-device is that increasing its volume leads to an increase of the influence of vaporized water on the non-selective MOX sensor (metal oxide sensor; SnO_2). By increasing the volume of the PC, not only the amount of ethylene trapped in the PC increases but also the trapped amount of vaporized water. In this case the water influence is so high that subsequent software compensation by using the data of a humidity sensor is not possible. The choice of the right stationary phase of the GC is crucial to increase the separation capability for ethylene and vaporized water.

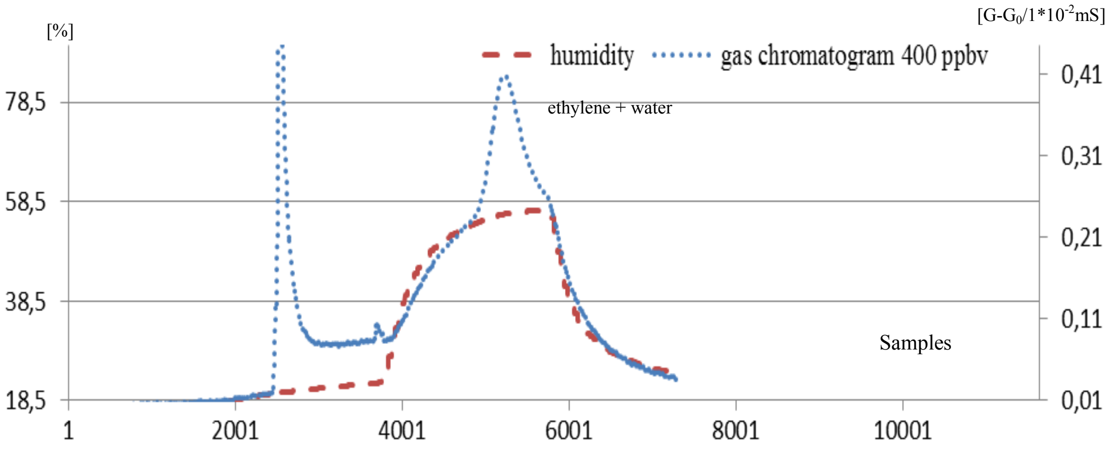

*Figure 10: Blue dotted line: Measurement result for **400 ppbv** ethylene for the 75cm long GC filled **with Carboxen 1000 (old)** and the new PC); Red dashed line: Humidity (bottom). The ethylene peak coincides with the water peak. Sample rate 4 Hz.*

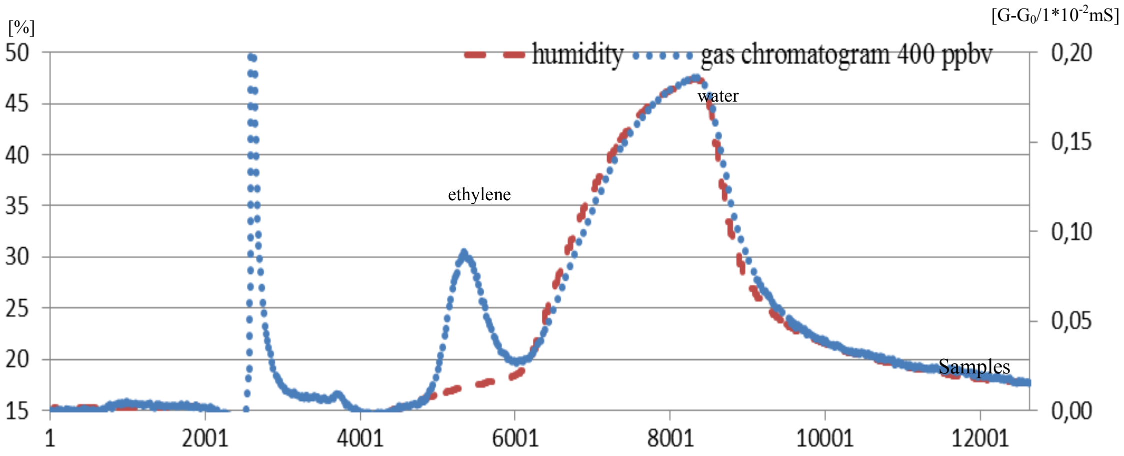

*Figure 11: Blue dotted line: Measurement result for **400 ppbv** ethylene for the 50 cm long GC filled **with Carbosieve SII (new)** and the new PC; Red dashed line: Humidity; The ethylene peak is separated from the water peak. Sample rate 4 Hz.*

During the adsorption process the PC is at room temperature. The breakthrough of ethylene and so the maximum possible ethylene concentration in the PC is reached after 22 minutes. Due to the separation behavior of the PC it is advantageous to run this procedure at this exact time to have the maximum amount of ethylene with the smallest possible amount of vaporized water trapped in the PC because the water breakthrough comes about 10 minutes later. After heating the PC to about 200°C for 10 minutes, it is connected to the GC to inject the gas sample. The GC is heated to provide a constant temperature of 45°C.

The results are shown in figure 10 and 11. With the use of CSII instead of C1000 it is possible to separate ethylene and vaporized water.

Therefore, it is now possible to use the new large-capacity-on-chip PC. The latest measurement shows that at the gas distributors lowest available ethylene concentration in synthetic air of 400 pp**b**v of is detectable. The noise equivalent initial ethylene concentration is about 3.8 pp**b**v–corresponding to ±3σ of the noise signal–. Therewith the minimal needed detection limit for fruit logistic processes of 50 pp**b**v is reachable. With the humidity sensor the water peak can be identified with high accuracy (e.g. figure 10 and 11).

SUMMARY

With the realization of the large-capacity-on-chip preconcentrator device the detection limit of ethylene measurement was increased strongly in comparison to earlier publications. With this new PC-device for the first time a small GC-system was able to measure 400 pp**b**v, which was the smallest concentration available at gas distributors. The mean value of the noise signal corresponds to an ethylene concentration of 1.3 pp**b**v. The noise limit of the measurement is at 3.8 pp**b**v (= 3σ). We conclude from this and from figure 11 that 50 pp**b**v can be resolved.

However with the enlargement of the PC the influence of the vaporized water due to the cross selectivity of the non-selective sensor increases as well. Subsequent software compensation with the data of a humidity sensor was no longer possible. The stationary phase was changed from C1000 to CSII to overcome the influence of water. The separating behavior of CSII showed to be much better than from C1000 when it comes to the separation of ethylene and vaporized water.

OUTLOOK

A next design of the PC-device is in discussion to improve the heating profile to be more uniformly.

One of the main goals is to getting the system out of the laboratory to the field tests in the container. Therefore, a new electronic control unit and a complete new housing with pumps will be designed.

Furthermore, a complete new µ-capillary column will be realized with micro system technology to decrease throughput times of the gases together with an increase of the separating capability.

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REFERENCES

[1] J. R. O. do Nascimento*, et al.*, "Beta-amylase expression and starch degradation during banana ripening," *Postharvest Biology and Technology,* vol. 40, pp. 41-47, 2006.

[2] A. Sklorz*, et al.*, "Application of a miniaturised packed gas chromatography column and a SnO2 gas detector for analysis of low molecular weight hydrocarbons with focus on ethylene detection," *Sensors and Actuators B: Chemical,* p. 7, In Press; Corrected Proof 2012.

[3] W. Engewald and J. Pörschmann, "5. Solid Stationary Phases" *Journal of Chromatography Library,* vol. 48, pp. 103-141, 1991.

[4] J. Hildenbrand*, et al.*, "A compact optical multichannel system for ethylene monitoring," *Microsystem Technologies,* vol. 14, pp. 637-644, 2008.

[5] R. Jedermann*, et al.*, "Sea transport of bananas in containers–Parameter identification for a temperature model," *Journal of Food Engineering,* 2012.

[6] R. Jedermann*, et al.*, "Supervision of Banana Transports by the Intelligent Container," *idea,* vol. 75, p. 84, 2010.

[7] M. M. Blanke and R. Shekarriz, "Gold Nanoparticles and Sensor Technology for sensitive Ethylene Detection," in *XXVIII International Horticultural Congress on Science and Horticulture for People (IHC2010): International Symposium on 934*, 2010, pp. 255-262.

[8] A. B. A. Dow*, et al.*, "A microfluidic preconcentrator for enhanced monitoring of ethylene gas," *Sensors and Actuators A: Physical,* vol. 167, pp. 226-230, 2011.

[9] A. Sklorz*, et al.*, "Detection limit improvement for NDIR ethylene gas detectors using passive approaches," *Sensors and Actuators B: Chemical,* 2012.

[10] B. Esser*, et al.*, "Selective Detection of Ethylene Gas Using Carbon Nanotube-based Devices: Utility in Determination of Fruit Ripeness," *Angewandte Chemie International Edition,* vol. 51, pp. 5752-5756, 2012.

[11] J. Luong*, et al.*, "Multidimensional gas chromatography for the characterization of permanent gases and light hydrocarbons in catalytic cracking process," *Journal of Chromatography A,* 2012.