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High sensitive and selective ethylene measurement by using a large-capacity-on-chip preconcentrator device☆

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ABSTRACT

Using a large-capacity-on-chip preconcentrator device for selective ethylene measurement leads to some challenges. The dramatic increase of the water influence and the gas chromatography effect of the preconcentrator must be known and compensated before a good measurement with this new device can be performed. Nevertheless, after facing these challenges the small gas chromatograph presented in this paper was for the first time able to detect an ethylene concentration of 170 ppbv. Deduced from this measurement a detection limit below 50 ppbv can be reached, which is absolutely mandatory for shelf life prediction of climacteric fruits. New stationary phases were tested. The used packed gas chromatography column is now capable of separating vaporized water and ethylene gas from each other, which was a 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 €.

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1. Introduction

The dynamic prediction of the shelf life of climacteric fruits like bananas during their transportations is of great interest for suppliers worldwide [4,5]. 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 reduce the shelf life significantly.

Early knowledge of a container with spoiled food in a 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. The concept of such a container is shown in Fig. 1.

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 (ppbv) is absolutely mandatory (e.g. Fig. 2) [1].

Latest work on the subject of the coupling of a packed μ-gas chromatography column (μGC) and a μ-preconcentrator (μpc) was presented by us in 2012 [2]. The detection limit of this system was at 6 parts per million by volume (ppmv).

GC-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 μpc, besides the indirect increase of sensitivity, the process of injection gets easier and more reliable. In the following, new solutions to overcome the latest detection limit are presented. The focus is set on the development of a completely new large-capacity-on-chip preconcentrator (PC) and to overcome fatal influence of vaporized water on the non-selective sensor.

2. Gas chromatography

The main parts of a gas chromatograph are an injection unit, a GC 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 that is filled with the stationary phase. Different stationary phases depending on the GC-design—if it is a packed or a capillary column—are applied. In our case of a packed

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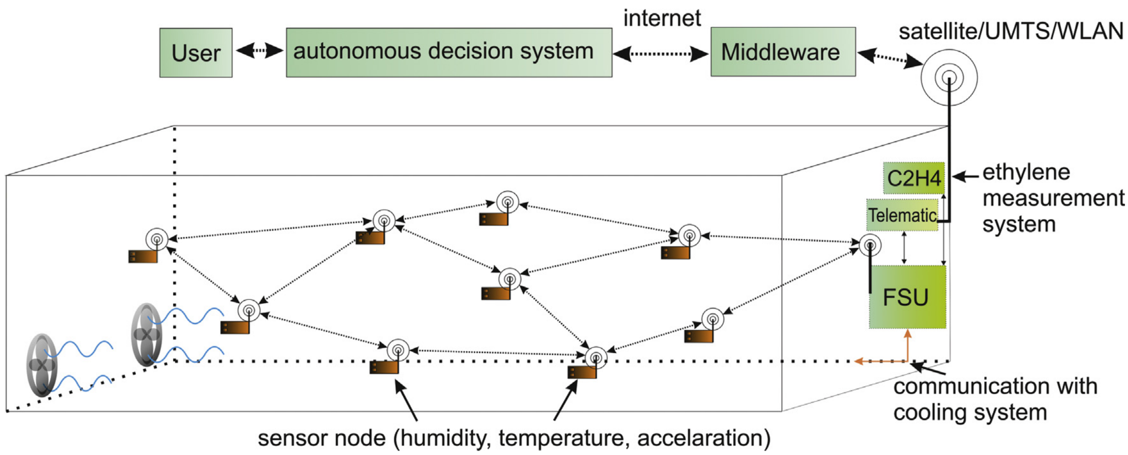

Fig. 1. Principle of the "Intelligent Container". A sensor network in the container sending their data to the FSU (mainframe of the container), an ethylene measurement unit is near the FSU. With a telematics the container communicates via WLAN, GPRS or satellite with a middleware.

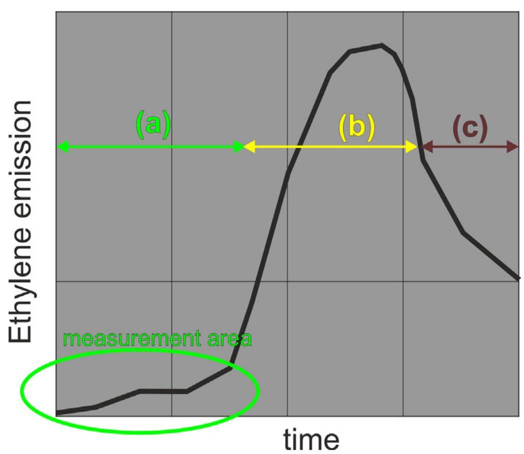

Fig. 2. Ethylene emission of bananas during their different states of ripeness. (a) Bananas are green (pre climacteric state). (b) Bananas are yellow (ripe, climacteric state). (c) Brown sugar spots (post climacteric state); the measurement is in (a) where the logistic process takes place, the ethylene concentration in a container is here in a range of ppbv [6]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

GC, carbon as an adsorbent is common. Carbon comes in several particle sizes, pore sizes and forms that 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 PC which is also needed to increase the sensitivity of the system. The first generation of our μpc is shown in Fig. 3. It was filled with 8 mg CSII and was a simple two-layer glass silicon compound with a 50 Ω platinum heater on the bottom.

The used packed-μGC is shown in Fig. 3. It has a platinum heater at the bottom and is 0.9 mm high and 1 mm wide. As the stationary phase, CSII and C1000 were used.

As mentioned before, these are adsorbent materials based on carbon. CSII (e.g., Fig. 4) have a particle size of 80–100 mesh, a pore size of 6–15 Å and a surface area of about 1200 m^2/g. C1000 have a particle size of 60–80 mesh, a pore size of 10–12 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.

3. Preconcentrator device

In order to overcome the limits in the sensitivity, two completely new large-capacity-on-chip preconcentrator devices were realized. The new design for both PCs are shown in Figs. 5 and 6. Fig. 5 shows a cross section. Both PCs consist of a three layer system of glass, silicon and glass in a triple stack bonding. On the bottom side a Platinum Resistor (PtR) is used for temperature measurement.

In Fig. 6 the design is shown in a 3D CAD-picture. The design for the inlet (Fig. 6b) and the design of the sieve (Fig. 6c) are also shown. The sieve at the outlet of the device holds the CSII particles inside the channels. The open space at the inlet of the channel helps to fill them. Two different sizes were realized: one with 8 channels and the other with 4. In both cases the channel sizes are the same.

The silicon walls between the channels are used as the heater for the desorption process. In Fig. 7a simulation of the heating process is shown. The important simulated parameters for the heating behavior are shown in Table 1.

Out of this simulation an adsorption temperature of 200 °C is reachable. The power consumption should be in a reasonable range. Inside the Container we have a power supply for the heater that provides 24 V and 1 Å.

Fig. 8 shows the single steps of the manufacturing 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 are etched open from the back. For temperature measurement and regulation a platinum thin film resistor with a resistivity of about 1 kΩ is used (PtR). Ultrasonically drilled holes in the top glass wafer are used for contacting the silicon-heater and as pneumatic feed through to the channels.

Fig. 9 shows the realized PC with and without its housing.

Table 1
Calculation of the heat production and power consumption of the silicon heater.

@ 300 K	0.01		0.02	
Voltage [V]	13	24	18	24
Current [A]	1.5	2.4	1.0	1.3
Resistivity [Ω]	8.6	9.9	16.8	19.1
Power [W]	19.6	58.0	19.3	30.2
	Max. temperature			
[K]	680	1000	680	800
[°C]	407	727	407	527

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