ANALYSIS OF C1 AND C2 HYDROCARBON GAS MIXTURES USING MINIATURIZED GAS CHROMATOGRAPHY AND SNO2 GAS DETECTORS

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ABSTRACT

In this paper the application of miniaturized gas chromatography for analysis of gas mixtures containing hydrocarbons with one and two carbon atoms is presented. The focus is on the quantitative measurement of ethylene gas which is important for post-harvest applications in e.g. fruit logistics.

A miniaturized gas chromatographic column packed with Carboxen 1000 was combined with a SnO_2 gas detector. The system is able to measure absolute amounts of ethylene gas in nl–range. To demonstrate the chromatographic ability of the system a gas mixture containing seven gases with C_1 and C_2 was separated using the measurement system.

KEYWORDS

Miniaturized gas chromatography, µGC, ethylene sensor, Carboxen 1000, hydrocarbon gas analysis, SnO_2 gas detector

INTRODUCTION

The application of selective measurement systems for low gas concentrations has become important in various industrial sectors. For example, information on gas concentrations can be used to estimate ripeness or quality of fruits by measuring the amount of emitted ethylene gas by those fruits [1]. Such quality monitoring approaches give new opportunities in fruit logistics [2]. To obtain acceptance for such measurement applications it is important to make systems available which are small and not-expensive but which have good performance in terms of sensitivity and selectivity.

Miniaturized sensor arrays which consist of low-cost gas sensor elements used in electronic noses are commended for food quality monitoring and other applications [3]. This approach tries to handle selectivity problems of low-cost gas sensors indirectly by using different sensitive layers, but this electronic nose approach has two big disadvantages: Electronic noses need many sensors if complex gas mixtures have to be analyzed, particularly if similar gases are contained in one mixture [4]. The more gas sensors are used, the bigger effort has to be taken related to the electronics and signal processing. The second disadvantage is that electronic noses have to be trained before application. This process needs the exact knowledge about the application gas atmosphere and makes calibration procedures expensive and complex.

A better approach to overcome selectivity limitations of low cost gas sensors is the application of miniaturized gas chromatographic columns. Gas chromatography (GC) is an important method used in gas analysis applications for many years. The main advantage of this method is that the amount of each single gas in one gas mixture is measured separately using at least one non selective gas detector. Thus, signal processing is easy and no training is needed and applications in complex and unknown gas atmospheres are possible.

Miniaturized GC-columns are known for years. The first capillary GC-column fabricated using MEMS-technologies on silicon was applied by Terry in 1975 [5]. Kolesar et al. used a combination of silicon and Pyrex to realize a 90 cm long spiral capillary column with a CuPc stationary phase to separate NH_3 and NO_2 [6]. Stürmann et al. used a silicon/Pyrex combination for a 75 cm long GC-column packed with mixed Carbograph and Carbowax as stationary phase for BTX (C_6H_6, C_7H_8, C_8H_{10}) detection [7]. Agah et al. focused their work on MEMS based capillary columns, also fabricated by using silicon and Pyrex. A 3 m long column integrated on a 3.25 cm x 3.25 cm chip was used for gas analysis of mixtures containing C_7 to C_{10} gases [8]. In general it can be said that the most works focused on capillary columns and the analysis of gas mixtures containing gas molecules with more than two carbon atoms. Although analysis of gas mixtures containing small molecules with one and two carbon atoms is important, this topic was neglected.

The main challenge in analysis of gas mixtures containing C_1 and C_2 molecules is the very short retention time of small molecules when using miniaturized capillary columns. This leads to interferences between the gases and thus, a selective analysis is not possible. Especially when similar hydrocarbons with the same amount of carbon atoms and different numbers of hydrogen atoms are in the same gas mixture, the analysis is difficult. To face this challenge, a combination of a miniaturized packed gas chromatographic column and a SnO_2 detector were used. The experiments were related to a post-harvest application in fruit logistics with ethylene (C_2H_4) as target gas. In the following the GC-column, the detector and the used measurement setup are described and the analysis results are presented.

SYSTEM COMPONENTS

The miniaturized gas chromatographic column used in this paper was applied for BTX (C_6H_6, C_7H_8 and C_8H_{10} in air) detection in former works [7]. It was fabricated using MEMS technologies and a silicon/Pyrex combination with an edge size of 3.5 cm x 3.5 cm and a column length of 75 cm. The GC-channel had a spiral shape, a width of 1 mm and

a height of 0.8 mm. For the new application related to C_1 and C_2 detection the columns were packed with the commercially available material Carboxen 1000 (Sigma Aldrich) as stationary phase. This material is a carbon molecular sieve with spherical particles and a mesh size of 60 to 80. To achieve a good package of the material in the column, a vacuum pump was used to fill the channels. During that step the GC-column was placed on an acceleration table to apply a dense package. After packaging, the columns were integrated into aluminum housings sealed with Viton (fig 1).

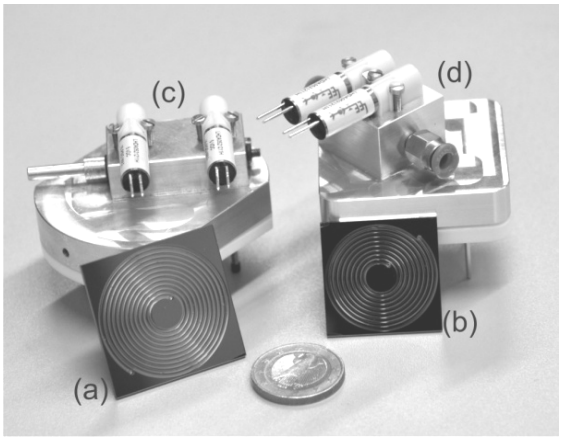

Figure 1: Silicon based GC-columns with aluminum housings and magnetic valves for pneumatic bypass. a) 75 cm column (used in the measurements); b) 50 cm column (also available); c) and d) housings for pneumatic and electrical integration

The choice of hybrid integration was made to provide a flexible and modular setup. This is important when the ability to change the column in the system is needed or if the package material in the column should be changed. Electrical interfaces were integrated into the housings to provide power connection to platinum heaters integrated on the GC-columns for temperature application up to 100 °C. The pneumatic interface was realized using miniaturized magnetic valves (lee-company). The valves can be used to bypass the GC-column if a gas sample has to be applied to the gas detector directly.

The µGC-column was combined with a newly developed gas detector. The gas detector was based on a commercially available low-cost SnO_2 metal oxide (MOX) gas sensor element in a TO - 8 housing. The sensor was integrated into an aluminum detector chamber. Additionally, a combined temperature / humidity sensor was integrated into the detector chamber to provide the monitoring of the absolute humidity concentration in the chamber. The detector assembly is shown in fig. 2. The measurement of temperature and relative humidity inside of the chamber are important because of the cross-sensitivities of MOX-sensors to humidity. Knowing the absolute humidity allows to reduce the measurement error or to recognize humidity peaks in the chromatograph.

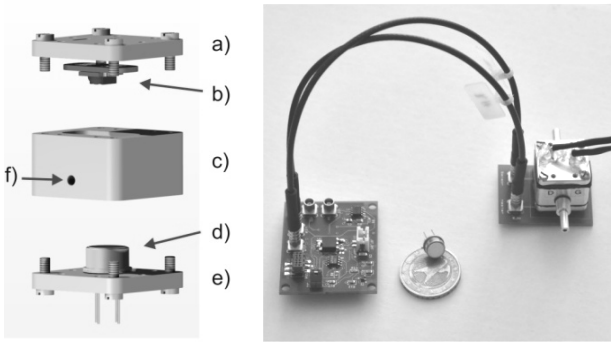

Figure 2: Ethylene detector. Left: Detector chamber. a) and e) top and bottom lid; c) main body with measurement chamber; d) MOX gas sensor; b) temperature and humidity sensor; f) sample inlet/outlet. Right: Detector with electronics

The detector was equipped with regulation electronics which hold the temperature of the sensitive layer of the MOX-sensor constant using the heater resistance R_H itself as temperature reference. This minimizes the influence of the ambience temperature changes without the need of an additional temperature sensor integrated in the gas sensor.

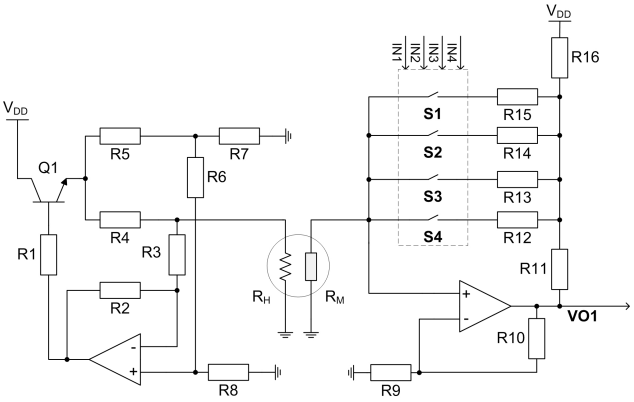

Figure 3: Schematic of control & measurement electronics for the gas detector containing heat regulator and four range linear resistance measurement circuits.

To provide a linear conversion of the resistance R_M of the MOX sensitive layer into a measurement signal, linear signal processing electronics were developed. This circuit has the advantage of a constant resolution over its entire output swing. Standard voltage divider circuits usually used for MOX- signal processing do not provide this property. The measurement range of the circuit can be adjusted digitally to fit the output voltage to the input resistance range and provide a flexible measurement and the possibility to change the used sensor element against other elements which are sensitive to other target gases. Both electronic circuits are presented in fig. 3. The left part of the schematic shows the regulator circuit and the right part shows the measurement circuit.

EXPERIMENTAL

After the GC-column and the gas detector were connected pneumatically, the assembly was integrated into a laboratory measurement setup (fig. 4).

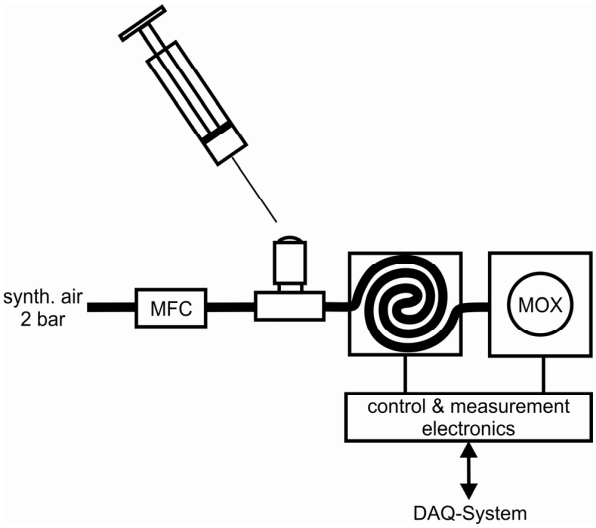

Figure 4: schematic of the used measurement setup. Synthetic air used as carrier gas; flow rate regulated using an mass flow controller; sample injection using syringe and septum at GC input; MOX based detector at GC output.

Synthetic air with a pressure of 2 bar was used as carrier gas connected to a mass flow controller (MFC). The output of the MFC was used as carrier gas feed line which was connected to the input of the gas chromatographic column. Here a simple septum was integrated for sample injection. The data acquisition and device control was automated using a desktop PC and an USB DAQ device. For system control and data acquisition a LabView implementation was used. Two series of measurements were made to show the properties of the column/detector combination. The first one dealt with the reaction of the system to an absolute amount C_2H_4. To examine this, a constant carrier gas flow of 20 sccm was adjusted and the GC-column was heated up to 45 °C. A gas analytic syringe was used to take gas samples out of a 350 ml gas sampling tube. As sample gas C_2H_4 in synthetic air was used (10 ppmv, 100 ppmv and 500 ppmv) flowing with a constant flow rate of 100 sccm through the sampling tube. Five samples of each concentration were taken (0.2 ml, 0.4 ml, 0.6 ml, 0.8 ml and 1ml) and were injected into the carrier gas flow.

In the second measurement run the separation abilities of the column were demonstrated. For these measurements a standard analytic gas mixture containing the gases CO, CO_2, CH_4, C_2H_2, C_2H_4, and C_2H_6 with a concentration of 1% each in N_2 was used. Measurement runs were made at a carrier gas flow of 20 sccm and column temperatures of 20 °C, 35 °C, 45 °C and 60 °C.

RESULTS

Figure 5 shows the results of the first measurement series. For each measurement run the resulting chromatography peak related to ethylene gas was analyzed by calculating the integral of the peak. The resulting peak area was plotted against the absolute amount of injected C_2H_4. A linear regression was used to analyze the linear behavior of the measurement data.

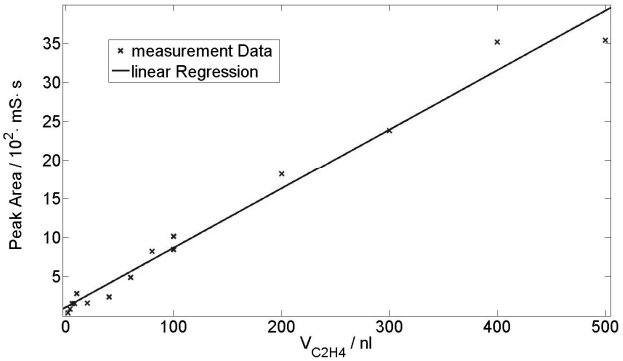

Figure 5: Measured peak area related to C2H4 versus injected C2H4 and a linear regression plot with $R^2 = 0.98$.

The resulting line in fig. 5 shows this behavior. The goodness of fit is R^2=0.98. The lowest amount of ethylene which was injected during the experiments was 2 nl. Increase of the injected ethylene volume in 2 nl steps could be resolved by the system.

The chromatographic results are shown in figure 7 where the system reaction to the injection of the gas mixture containing CO, CO_2, CH_4, C_2H_2, C_2H_4, and C_2H_6 is shown.

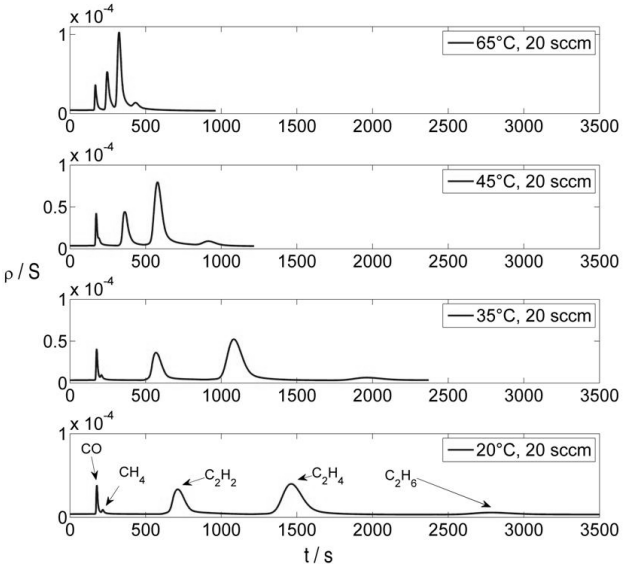

Figure 7: Chromatograms measured using the described system components. Injected mixture of CO, CO_2, C_2H_2, C_2H_4, C_2H_6, 1 % in N_2

At a column temperature of 20 °C five peaks can be seen. Single gas calibration measurements and comparison of the chromatograms with available Carboxen 1000 chromatographic results [9] lead to an assignment of the peaks in sequence to CO, CH_4, C_2H_2, C_2H_4 and C_2H_6. CO_2 and N_2 peaks were not observed

because the used detector does not react to these gases.

The correlation between the column temperature and the retention time of the single gases can be observed. The higher the column temperature, the smaller the retention time. The peaks are becoming narrower as well as higher. This shows the functionality of the GC-components described. The resolution of the chromatographs is listed in Table 1. The results show a good chromatographic resolution. Only the resolution between the CO and CH4 peak is under 100%.

Table 1: Peak resolution R of the chromatograms from fig.7 for 20°C and 45°C. 100% resolution achieved for R ≥ 1.5

T/°C		$CO;CH_4$	$CH_4;C_2H_2$	$C_2H_2;C_2H_4$	$C_2H_4;C_2H_6$
20	R	1.1	4.8	3.71	3.9
45		0.89	3.17	10.28	19.82

The different peak heights in fig. 7 are caused by the different sensitivity of the used SnO_2 sensor element to different gases. In this work C_2H_4 was in focus, so that gas peak is the biggest one. By changing the temperature of the sensitive layer of the sensor element or by changing the sensor element itself, the sensitivity can be fitted to other target gases.

CONCLUSION

A 75cm long miniaturized gas chromatographic column packed with Carboxen 1000 was combined with a SnO_2 gas detector. The integrated devices were tested focused on quantitative ethylene gas detection. The linear relation between the injected ethylene amounts and the resulting system chromatography peaks was shown in experiments. The measurement resolution of the system was at least 2 nl related to C_2H_4. It was demonstrated that a gas mixture containing the gases CO, CO_2, C_2H_2, C_2H_4, C_2H_6 in N_2 can be separated using the described system with clearly separated peaks and column temperatures under 50 °C. Chromatography resolution is over 100 % for temperatures up to 45 °C except CO and CH_4.

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