

Gas Sensor Array for Low-cost Gas Chromatography in Food Industry Processes

Marie-Luise Bauersfeld, Carolin Peter, Jürgen Wöllenstein
Fraunhofer-Institute for Physical Measurement Techniques IPM
Heidenhofstrasse 8, 79110 Freiburg, Germany

Mark Bücking, Jörg Bruckert, Jürgen Steinhanses
Fraunhofer-Institute for Molecular Biology and Applied Ecology IME
Auf dem Aberg 1, 57392 Schmallenberg-Grafschaft, Germany

Abstract

A portable low-cost gas chromatographic measurement system will be presented. The system consists of a novel chromatographic column - which enables measurements at room temperature and ambient air - with a downstream micro machined gas sensor array and offers the separation and identification of volatile organic compounds. The targeted application is the monitoring of flavours directly during food processes. The measurement system was characterized by using flavours like methyl pyrrole, hexanal, pinene, ethyl butyrate and limonene as well as ethylene and methyl mercaptan as test gases. Reliable and reproducible identification of the gases in the concentration range of a few ppb has been achieved.

Introduction

Today, food quality plays a more and more significant role for the consumer. Therefore fast monitoring of food quality in the industry gets more important. To protect consumers and always ensure the optimum grade of quality, critical steps during production have to be controlled, to recognise and eliminate failures. Till this day more than 6000 volatile compounds are known which create the aroma of food [1]. Nowadays a multiplicity of aroma characterization methods exists. These are on one hand human sensory test methods and on the other hand analytical methods like gas chromatography (GC) with coupled odorimetry (GC/O) and / or mass spectrometry (GC/MS). Conventional analytical methods are mostly complex, expensive and some volatile compounds are not so good separable by gas chromatograph as per human sense of smell.

The judging of aromas is objective by human. Because of that there are tests to describe flavours by so-called "electronic noses" [2]. This should offer a sensory fingerprint of each aroma by pattern recognition. But the development of those systems for special applications need mostly an especially requirement on qualification of able sensor elements and those calibration [3]. In the past decade, activities directed towards development of low cost chromatographic measurement system using metal oxide gas sensors as detectors have increased substantially. A development so-called HRGC/SOMSA-method (high resolution gas chromatography/selective odorant measurement by multi sensor array) consists of gas chromatographic column and sensor array. On this base exists research for controlled food quality [4, 5, 6]. However, a continuing drawback of such implementations has been the incompatibility of the chromatographic column with ambient air.

Novel chromatographic columns allow measurements at room temperature and ambient air and enable the use of low cost semiconductor gas sensors as detector unit in the gas chromatographic system (Fig. 1). Furthermore the combination of different sensors in a single array offers the possibility to detect aromatic flavours which are, due to their similar chemical behaviour, not separable by the used chromatographic column over time.

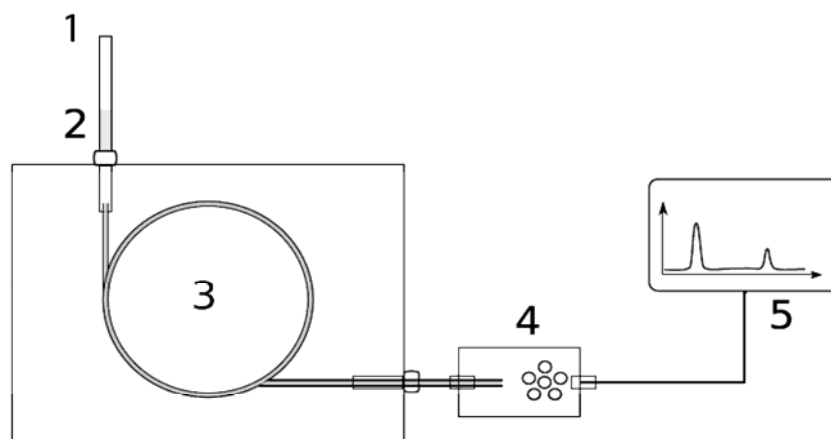


Figure 1 Schematic diagram of the portable low-cost gas chromatographic measurement system. 1 sampling, 2 drying agent, 3 GC column, 4 gas sensor array, 5 data evaluation.

Set Up of Measurement System

The functionality of the present measurement system for detection of special aromatic compounds, which are released during food processing, based on combination of gas chromatography with downstream micro machined gas sensor array. The single components are described in this part.

A. Gas Sensor Array

Flavours are volatile gas mixtures, which can be chromatographically separated. Due to their similar chemical behaviour many flavours are not resolvable about the retention time. For the detection of these compounds commercial gas sensors as well as self produced sensors have been tested. The goal of development was that a gas sensor array composes a well-defined fingerprint for each aromatic compound of a gas mixture by different reactions of gas sensor types. The used self produced gas sensor array is fabricated on one chip and consists of four independent semiconductor gas sensors with metallic oxide. To increase the selectivity of every sensor those are manufactured with different gas sensitive layer like tin oxide (SnO_2), tungsten trioxide (WO_3), SnO_2 with Platinum as catalyst and chromium titanium oxide ($\text{Cr}_{2-x}\text{Ti}_x\text{O}_{3+z}$, CTO) [7]. The goal of technological development is the optimizing of these sensors in respect of sensitivity, selectivity and long time stability. Another important parameter is the operating temperature which influences the sensitivity of the sensors. The optimal operating temperature was validated for every using flavour.

B. GC Column

In addition to gas sensor array the choice of chromatographic column influences the possibilities of measurement system. For gas sensors as detector in this unit it is necessary to use oxygen. But until today many columns are destroyed by oxygen due to use of polymers. A novel commercial available column enables the use of oxygen and an optimal chromatographic separation at 40°C .

C. Sampling Supply

Conventional gas chromatographic systems use an injection into the column for sampling supply. For the target portable system is this option not practicable. In this case a special pump controlled suction mechanism is used. The sampling supply occurs in a sampling loop, which is split in a supply with flushing gas and in a supply with the test gas respectively.

For the first labour tests fluid flavours was evaporated and afterwards according to requirements mixed. For that a defined air stream is managed over the fluid sample to concentrate with vapour phase of flavour [8]. The flavour concentration depends on the temperature of the fluid. The resulting flow with a speed of $150\text{ml}/\text{min}$ is routed as carrier gas stream into the column and arrives at the measurement chamber with gas sensor array.

D. Tested Gases

Aromatic compounds and gases which are important for later applications - in food chain management - of this measurement system were chosen. Special attention is the combination of two flavours which are not separable by the retention period through the chromatographic column. On the base of this the functionality of the gas sensor array as detector and for the differentiation of flavours is demonstrated. Flavours which enclosed direct in fruit and secondary flavours which result of production are chosen. The tested flavours like methyl pyrrole, ethyl butyrate, pinene, limonene and hexanal as well as ethylene and methyl mercaptan including a short description of natural existence and possible applications are display in table 1.

Table 1 Tested Aromatic Compounds and Gases

Aroma	Natural existence	Application
Methyl pyrrole	result from roasting processing	monitoring of roasting processing, e.g. coffee
Ethyl butyrate	apple	degree of ripeness of fruits
α -Pinene	spruce needle, coriander, caraway	add in medicaments and essential oil
Limonene	citrus fruits	degree of ripeness of fruits
Hexanale	result from decomposition of fatty acids	manufacturing process of nuts
Ethylene	biological hormone in fruits and vegetables	degree of ripeness of fruits
Methyl mercaptane	result from bacterial degradation of proteins	detection of perishable food

Results of Measurement

The described measurements are done with labour set up. The sampling supply takes place an admixture of flavours in carrier gas stream of synthetic air. Synthetic air is also use as flushing gas. The sensor chamber has a volume of 4ml, which means a 37fold gas change per minute for a carrier gas flow of 150ml/min. Through the operating temperature of gas sensors between 300°C for WO₃ and SnO₂ with Pt and 450°C for CTO and SnO₂ the chamber heated up and adhesion on chamber wall are insignificant. During the measurement the flavour concentrations in table 2 are tested. These are generated by a gas generator [8].

Table 2 Tested Flavour and Gas Concentrations

Gases	Concentration [ppb]
Methyl pyrrole	720
Ethyl butyrate	399
α -Pinene	66
Ethylene	50
Limonene	22

To demonstrate the differentiation of flavours through the developed gas sensor array the first step was to measure with pure flavours. A calculated Principal Components Analysis is present in figure 2. This gives the proof that the measurement of each flavour is discriminable and that the use of the develop gas sensor array enable the separation of the tested flavours. In the figure it is describe that each measuring point is a well-defined point in the scatter plot of the coordinate system. In addition the plot shows that more than one principal component is, for the differentiation of the flavours, necessary. Through both principal components the flavours are graphical separable. Together they safe 96.52% information of all measurements.

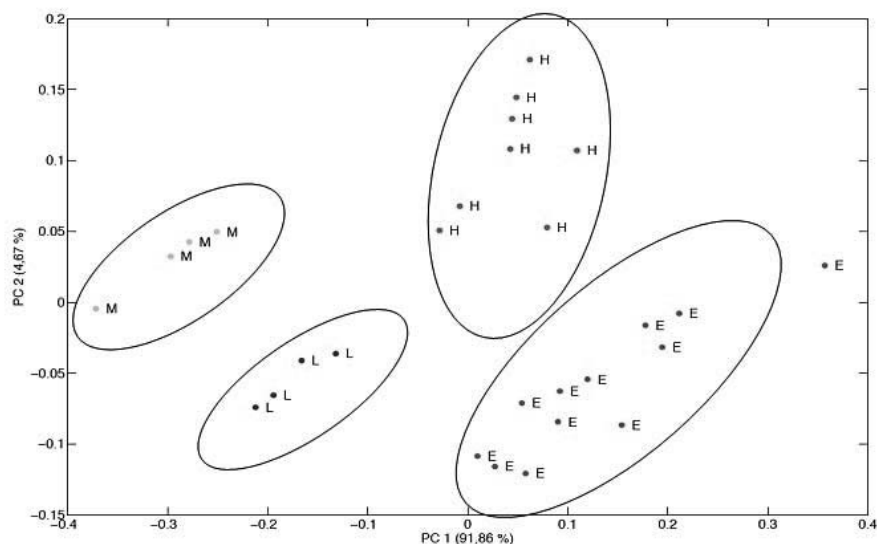


Figure 2 Principal Components Analysis of the analysed flavours (Scores Plot). H: hexanale, E: ethyl butyrate, M: methyl pyrrole, L: limonene. Out of these four, ethyl butyrate and hexanale are not separable over time by a chromatographic column.

An important factor of a gas chromatographic system is the repeatability. In figure 3 the repeat of two measurements is presented. The upper graph shows the sensor reaction of a SnO₂ sensor and the lower graph of a CTO sensor. Both are manufactured by Fraunhofer IPM. Notable is that in the measurement with the CTO sensor the transition point between methyl pyrrole and ethyl butyrate is visible (Fig. 4).

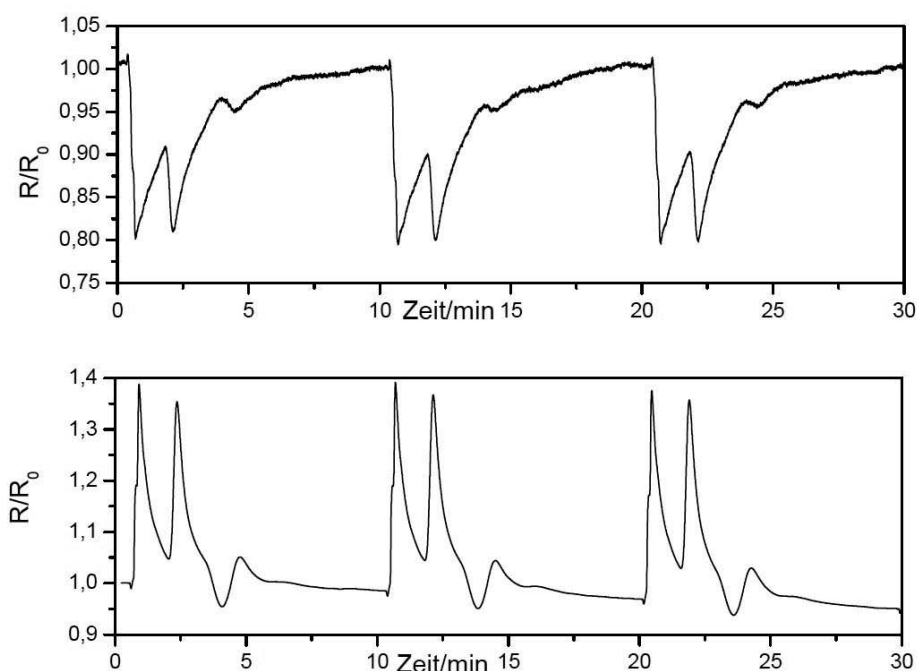


Figure 3 Chromatogram: Reaction of (up) IPM SnO₂ and (down) IPM CTO gas sensor to gas mixture which is separate over time by used chromatographic column and as a function of the nominal resistance. The measurement was repeated thrice. The first peak is a mixture from methyl pyrrole and ethyl butyrate and the second peak is α -pinene. After 4min is the limonene impact. The operating temperature of both sensors is 450°C.

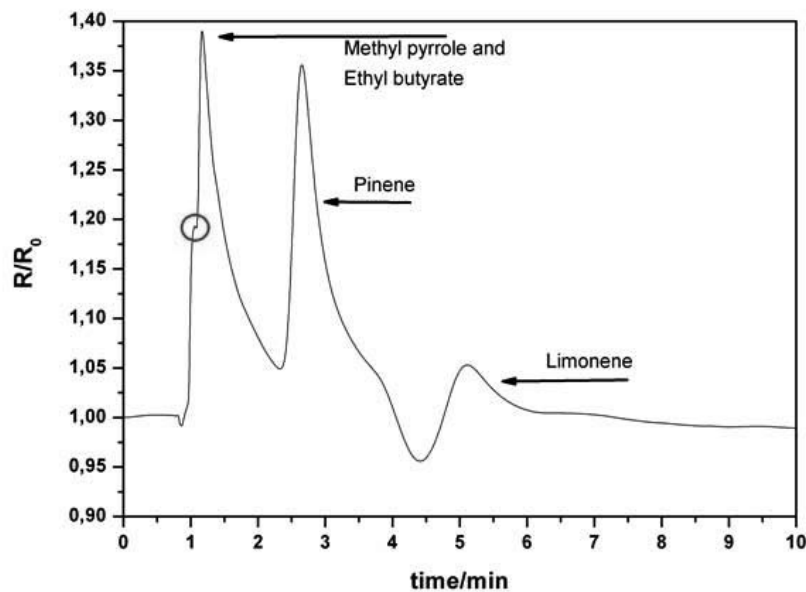


Figure 4 Response of IPM gas sensor based on Chromium Titanium Oxide as sensitive layer to different flavours. The marked area signals the change from methyl pyrrole to ethyl butyrate. The operation temperature during the measurement was 450°C.

Figure 5 illustrates the comparison between commercial gas sensors as well as self produced sensors and various aroma concentrations. In this figure the significant different response of the represented gas sensors, which can use for well-defined fingerprint of each aromatic compound, is shown.

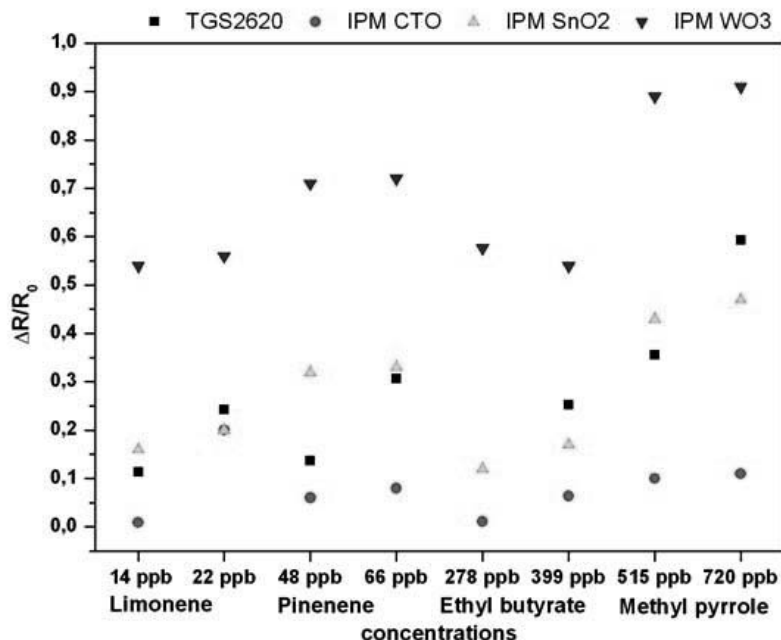


Figure 5 Comparison between commercial gas sensors as well as self produced sensors and various aroma concentrations. The operating temperature during the measurements are 325°C for Figaro TGS 2620, 300°C for IPM SnO₂ and WO₃ as well as 450°C for IPM CTO.

Furthermore the sensitivity of the developed measurement system is tested with the gas ethylene. Ethylene is a biological hormone which influences fruit ripeness, microbial growth and biological

senescence. Due to its chemical behaviour it is often used in agricultural and food logistics for controlled fruit ripeness.

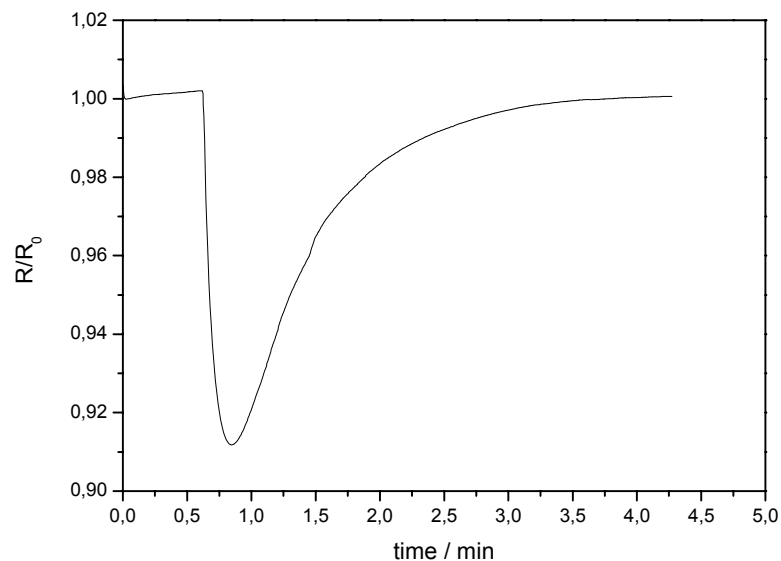


Figure 6 Sensor response of Figaro TGS 2602 to 50ppb ethylene and as a function of the nominal resistance. The operation voltage during the measurement was 5V.

Conclusion

The presented measurement system enables reliable and repeatable detection of gas concentrations, down to the ppb-range, as well as assignable to the aromatic flavours. Next to food industry, similar processes in the pharmaceutical area offers further markets for the novel gas chromatographic measurement system.

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