Miniaturized Flame Ionization Detector
for Gas Chromatography

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SUMMARY

The Technical University Hamburg-Harburg and ABB Corporate Research are currently exploring the potential to apply silicon–glass microsystems as technology platform for creating a miniaturized flame ionization detector (FID). This device can be used for the detection of hydrocarbons in gas chromatography. Design and first characterizations of such micro-FIDs have been published elsewhere [1]. For a deeper understanding of the performance and further optimization potential the detectors have now been investigated more detailed. The results of those tests show a detection limit of 104 ppb pentane.

Keywords: gas chromatography, flame ionization detector, hydrocarbon detection.

DEVICE DESCRIPTION

Flame ionization detectors are used for quantification of volatile organic compounds in gaseous samples. The measuring effect is based on chemical ionization of organic substances burned in an hydrogen diffusion flame [2].

Ionization Reaction: $CH + O \Rightarrow CHO^{+} + e^{-}$

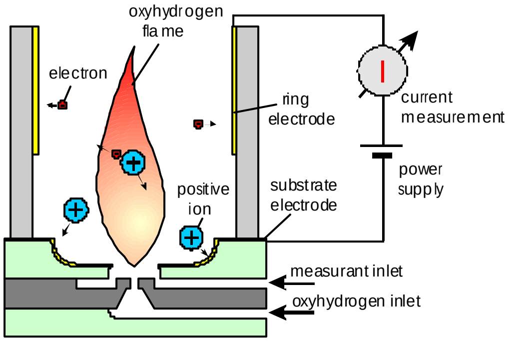

Fig. 1: Measuring principle.

An electric field between the upper ring electrode (anode), which surrounds the flame, and substrate electrode (cathode) accelerates the ions to the electrodes (Fig. 1).

An ion current proportional to the number of carbon atoms present is measurable. Thus, the concentration of organic substances within the sample gas results from the ion current intensity. The required ionization energy to form carbon ions in a flame mostly results from the high carbon oxidation energy released during the combustion reaction of carbon to carbon monoxide and carbon dioxide. The flame temperature itself is insufficient for a direct atom or molecule ionization. That is why flame ionization detectors are especially sensitive to organic substances. The requirement for significant detection signals is the ability to form hydrocarbon radicals. Therefore, inorganic substances and carbon monoxide as well as carbon dioxide are not detected.

CONSTRUCTION OF THE MICRO FID

Main component of the micro flame ionization detector is a micro burner unit, which has minimum fuel gas consumption to maintain a stable miniature flame. Instead of a hydrogen diffusion flame as usual the micro flame ionization detector operates with a premixed oxyhydrogen flame.

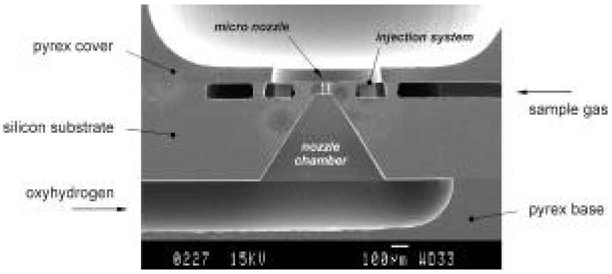

Fig. 2: Sectional view of the micro burner (SEM).

The micro burner is a sandwich construction of a pyrex cover, silicon middle substrate and pyrex base (Fig. 2). All components are manufactured separately and joined by wafer-level bonding techniques. The micro nozzle, required for the miniature flame, is structured into the silicon substrate. A nozzle chamber is etched first by an anisotropic wet chemical etching process in potassium hydroxide solution. Thus, a thin silicon membrane results. A simple opening, structured in the center of the membrane by an anisotropic plasma etching process in SF_6 / O_2 atmosphere, serves as the micro nozzle.

SAMPLE INJECTION SYSTEM

Because sample and fuel gas are not premixed, an integrated passive injection system for gaseous samples is etched simultaneously with the micro nozzle into the silicon substrate by a plasma etch (Fig. 3).

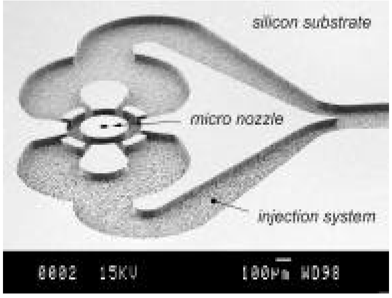

Fig. 3: Sample gas injection system (SEM).

To avoid flame instability caused by direct sample gas injection a radial and homogeneous gas flow into the miniature flame is required. Furthermore, fast and complete mixing between the sample gas and oxyhydrogen is essential for a maximum ion current.

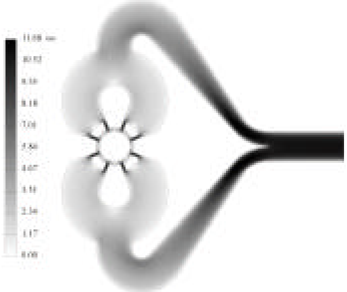

Fig. 4: Flow simulation of the sample injection system.

The special layout of the injection system, which is developed from a three dimensional flow simulation of the micro burner (Fig. 4), is optimized regarding both conditions. Its working principle is based on an integrated pressure stage with eight channels arranged in a circle around the micro nozzle. Due to the smaller channel width at the pressure stage a homogeneously distributed excess pressure builds up in the outer delivery ring. This causes radial sample gas injection through the concentric annular sample gas nozzle into the flame.

OPERATIONAL PARAMETERS

Considering the flame stability and fuel gas consumption as well as a sufficient flame height for an analysis a nozzle diameter of 60 µm and an oxyhydrogen flow of 20 ml/min to 70 ml/min are required. A stable flame of 0.5 mm in width and 2.5 mm in height is formed at an oxyhydrogen flow of 35 ml/min. The flame temperature is about 2700°C. The oxyhydrogen can be generated as-required at low energy consumption of 5 W in a miniaturized electrolyzer, which uses a proton exchange membrane as a high efficient and safe solid electrolyte [3].

PERFORMANCE CHARACTERISTICS

For characterization the FID is mounted in a metal housing on a heating element. A hole centered to the quartz tube of the FID in the housing allows the water vapor generated to disengage. This setup assures electrical shielding and allows for a substrate temperature control. The FID is driven by a controlled constant flow of a stoichiometric mixture of 33% oxygen and 67% hydrogen. The flow of the measurant is also controlled. The mesurant consists of nitrogen with a variable content of pentane. The driving voltage needed to extract all ions generated is 200 V. All characteristics shown are measured at that voltage level. The substrate temperature is held at 90°C to avoid condensation resulting in leakage currents on the electrodes.

OFFSET

The offset of the ion current signal is composed by the leak current of the setup without a flame burning and the zero current (flame burning, but no hydrocarbons in the measurant). The leak current is 0.3 pA. The zero current is approx. 56 pA. It slightly depends on the substrate temperature, the oxyhydrogen flow and the measurant flow.

It is found that it is necessary to heat up the FID substrate to a minimum temperature of 60°C in order to reduce the leak current to the 0.3 pA level. Heating avoids water vapor condensation on the quartz cylinder walls. Water condensation is one reason for increased and drifting leak current.

RESPONSIVITY

For a high-sensitivity FID one can either improve its responsivity or reduce the noise. Therefore it is examined how the responsivity is influenced by changing operational parameters like oxyhydrogen and measurant flow.

The ion current as a function of pentane concentration in the measurant is shown in Fig. 5. Over a wide range the dependency is almost linear.

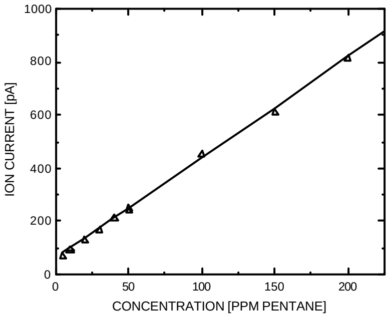

Fig. 5: Ion current as a function of pentane concentration @ 35 ml/min oxyhydrogen flow, 5 ml/min measurant flow.

Increasing the oxyhydrogen flow at the same time increases the ion current as can be seen in Fig. 6. Unfortunately the increase in ion current is mostly due to an increase in offset. As a consequence the responsivity can not be improved by means of higher oxyhydrogen consumption. On the other hand aiming for minimum consumption this does not automatically result in reduced sensitivity.

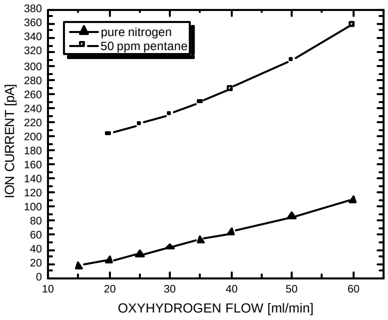

Fig. 6: Response as a function of oxyhydrogen flow for pure nitrogen and 50 ppm pentane @ measurant flow 5 ml/min.

From Fig. 6 the response can be calculated. It is the difference between the current generated by the measurant with hydrocarbons and the zero current. This value is divided by the concentration (here: 50 ppm). The curve obtained is shown in Fig. 7.

Obviously for small measurant flows the dependency between flow and response is not linear. This is not due to an offset variing with the measurant flow. It is caused by a minimum flow needed to inject all the sample gas into the ionization zone of the flame. At to low measurant flows only part of the sample reaches that zone.

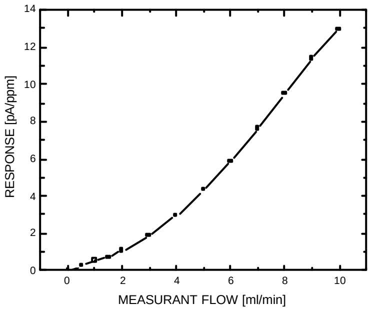

Fig. 7: Response for pentane as a function of measurement flow @ 35 ml/min oxyhydrogen flow, 50 ppm pentane.

NOISE

To determine the detection limit of the device the ion current noise is calculated. For this purpose the standard deviation (SD) of the current is calculated for constant measuring conditions. The SD of the ion current without a flame and therefore the electronic noise of the setup is 9 fA.

The SD of the ion current as a function of hydrocarbon concentration is given in Fig. 8.

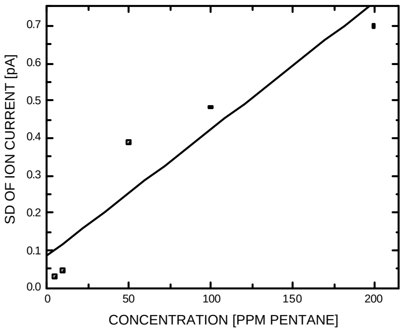

Fig 8: SD of ion current as a function of measurant concentration @ oxyhydrogen flow 35 ml/min, measurant flow 5 ml/min.

A strong increase in current noise with increasing hydrocarbon concentration is observed. Other measurements with constant concentration and variing measurant flow showed a similar dependency. It is found that the increase in noise is mainly caused by the increase in “hydrocarbon flow” which is the measurant flow multiplied with the hydrocarbon concentration.

Therefore a higher oxyhydrogen concentration leads to a higher noise level. Additionally a higher measurant flow rate also contributes slightly to the noise level.

For the calculation of the detection limit later on this effect is very important. For a fixed measurant flow the detection limit depends on the hydrocarbon concentration. Therefore for low hydrocarbon concentrations the detection limit is low. From Fig. 8 it can be derived that the SD for low concentrations for a measurant flow of 5 ml/min is below 0.15 pA

To check if the noise also depends on the oxyhydrogen flow it is measured for zero measurant flow and varying oxyhydrogen flow. It is found that the SD is nearly constant for oxyhydrogen flows of 20 ml/min to 40 ml/min. The SD is 0.1 pA to 0.15 pA. It increases for flows above 40 pA. As the sensitivity is not increased for higher oxyhydrogen flow increasing the oxyhydrogen flow is therefore no option to get a better detection limit. For oxyhydrogen flows below 20 ml/min the flame gets unstable in the current setup resulting also in increasing noise.

SPIKES

One phenomenon that can be observed when the micro FID is used at ambient air is the occurrence of spikes (Fig. 9). It was found that those are caused by dust particles sucked into the micro burner.

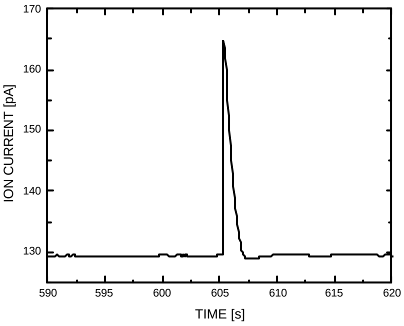

Fig. 9: Spike for constant measurant flow and hydrocarbon concentration.

DETECTION LIMIT

From the figures presented above the detection limit can be calculated as a function of measurant flow. The detection limit is defined as the hydrocarbon concentration that generates an ion current equivalent to three times the SD of the ion current.

Tab 1 shows the detection limits for pentane. For pentane the minimum value is 104 ppb for a measurant flow of 5 ml/min. It is likely that an increase in measurant flow above 5 ml/min will further improve the detection limit.

measurant flow [ml/min]	0.5	1.0	2.0	5.0
3x SD of current [pA]	0.45	0.45	0.45	0.45
response [pA/ppm]	0.28	0.51	1.06	4.31
detection limit [ppb]	1607	882	425	104

Tab 1: Detection limits for pentane as a function of measurant flow for an oxyhydrogen flow of 35 ml/min.

CONCLUSIONS

The detection limit of 104 ppb pentane is well suited for use of the micro FID in gas chromatography. The detection limit is not deteriorated by small measurant flows or relatively small hydrocarbon flows. The oxyhydrogen needed can be generated by an electrolyzer consuming less than 5 W. Therefore a simple water tank can replace the critical hydrogen gas bottles used today. Further work will be focused on developing a setup that avoids the influence of ambient air on the ion current measured.

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