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Sensitivity of a planar micro-flame ionization detector

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ABSTRACT

The sensitivity of a MEMS μFID with reduced fuel gas consumption for portable applications like mobile GC or THA is examined. It is shown that sensitivity depends on flame size and type of sample gas supply (either separate supply or premixed with the hydroxygen). In contrast to conventional FIDs, the sensitivity of the μFID increases with decreasing molecule size. The sensitivity to methane can be optimized up to conventional values. Measurements with the μFID as a second detector in a μGC module prove the additional functionality of such a system.

1. Introduction

Because of its outstanding properties, the flame ionization detector (FID) is the preferred method for hydrocarbon detection either as a detector in gas chromatography (GC) or as a stand-alone instrument for total hydrocarbon analysis (THA) [1]. The FID is characterized by a very low minimum detectable limit (MDL) ($<1 \times 10^{-10}$ gram carbon per second [gC/s]), high sensitivity (0.015 coulomb per gram carbon [C/gC]) and a broad linear measurement range (10^7) [2]. Moreover, it is insensitive to modest changes of operating parameters, such as fuel and oxidant gas flow, environmental air pressure, and temperature.

The measurement principle is based on the chemical ionization of organic substances in a hydrogen flame and measurement of the ion current generated in an electric field [2]. First, hydrocarbon molecules are decomposed into single carbon radicals by pyrolysis. Then, these radicals react with oxygen to form CHO^+ ions. It follows that the detector signal is proportional to the number of carbon atoms present in the sample gas. This is also known as the “equal per carbon” response of the FID, which is important for reliable THA. Since flame temperature is insufficient for ionization, ionization relies on the large amount of energy released during oxidation of the hydrocarbon radicals. As a result, the FID is insensitive to inorganic compounds and already oxidized substances such as carbon dioxide.

The hydrogen flow rate is typically set at 30 ml/min. A 10-fold amount of air is supplied around the central hydrogen nozzle, not only to supply the oxygen for fuel lean combustion, but also to shield the flame from contamination. The sample gas is premixed with the hydrogen.

The current trend in gas analysis goes towards instrument portability and miniaturization. However, only few miniaturized FIDs have been reported [3–10]. Portable THAs are commercially available, but the conventional FID with its high consumption of explosive gases and corresponding storage does not allow for a small device. The portable THA FID3006 by Sick (Waldkirch, Germany) [11] consumes 20 ml/min H_2, measures 290 mm × 240 mm × 380 mm (cylinder frame for gas storage not included) and weighs 13.2 kg. In micro-GC (μGC) [12] the FID is replaced by the thermal conductivity detector (TCD) [13,14]. Since FID is an absolute detection method, detection limits increase with decreasing sample flow rates. Although in conventional GC large injection volumes guarantee exceptional FID detection limits, in μGC FID and TCD performances are comparable. Yet, if a truly portable FID with drastically reduced gas consumption becomes available, it will not only enhance THA, but also improve qualitative analysis by μGC-μTCD-μFID, which combines a non-selective and a hydrocarbon-selective detector. Therefore, a miniaturized FID has been developed by means of low-cost MEMS technology (μFID) [15–18]. This paper focuses on the improvement of the MDL by increasing sensitivity. In addition, the sensitivity of the μFID to different hydrocarbon molecules is compared using a μGC.

2. Experimental

2.1. Design

The miniaturized hydrogen flame burns in the silicon plane of a glass–silicon–glass sandwich (Figs. 1 and 2). The exhaust opening

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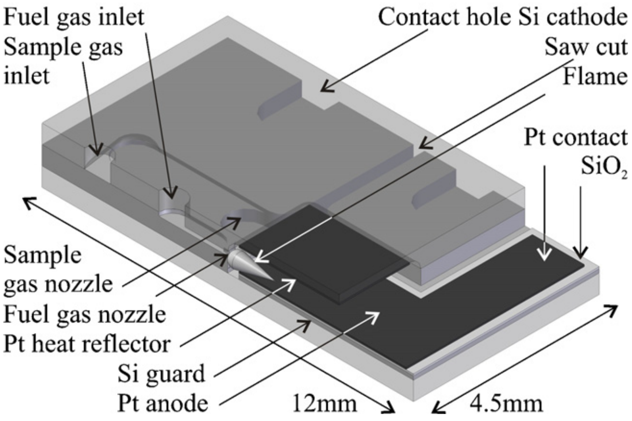


Fig. 1. 3D representation of half the planar μFID.

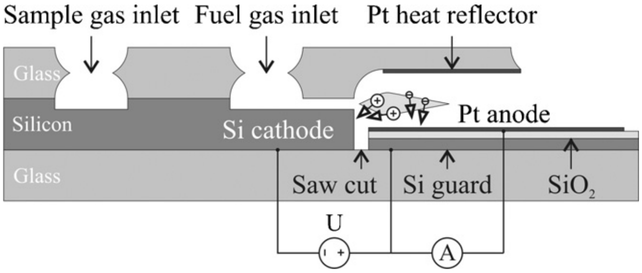


Fig. 2. Cross-sectional view of the planar μFID. The cross-section corresponds with the cut bisecting the system in Fig. 1.

is small and prevents contamination from the environment. Therefore, there is no need for the excessive airflow shielding the flame as in conventional systems and the μFID can be driven with oxygen for combustion only. Thermal isolation by low thermal conductive glass minimizes heat loss from the system. In addition, the platinum electrode also acts as a heat reflector and as a catalyst for combustion. Therefore, not only oxidant gas flow, but also the hydrogen consumption can be reduced considerably from 30 ml/min for conventional FIDs to 20 ml/min or less for the planar μFID. Small amounts of hydrogen and oxygen can then, e.g. be supplied by the electrolysis of water [19], which reduces both the explosive risk to a minimum and the storage volume almost 2000 times. The latter is based on the densities of water (1.0×10^3 kg m^{-3}), hydrogen (9.0×10^{-2} kg m^{-3}) and oxygen (1.4 kg m^{-3}) at 273 K and 101.325 kPa [20].

The nozzle height is given by the etch depth of 100 μm. The nozzle width is a lithography mask design parameter and can be varied to correspond with a certain gas flow to avoid flash-back or lifting of a premixed flame. A nozzle width of 40 μm yields a nozzle area of 4.0×10^{-9} m^2 compared to 2.0×10^{-7} m^2 of a standard 0.5 mm diameter FID. Separate sample gas nozzles are provided to be able to vary the sample gas flow over a wide range without changing the outflow velocity of the hydroxygen. Because of flame stability, the sample gas nozzles are symmetrically arranged on either side of the flame (Figs. 1 and 3) and are relatively wide (800 μm) to obtain small outflow velocities.

To enable anodic bonding of glass and silicon, borosilicate glass becomes conductive at elevated temperatures. Unfortunately, this complicates the measurement of the ion current, since the leakage current flowing through the borosilicate glass maybe many times larger. However, the leakage current can be intercepted by a third electrode, the so-called guard electrode [15]. Therefore the silicon substrate is divided into two parts (Fig. 2). The part containing the nozzle serves as the cathode, whereas the silicon part underneath the flame is the guard electrode. On top of the guard electrode the platinum anode is deposited. Both electrodes are separated by a non-conducting thermal oxide layer. In this way, the platinum anode is completely surrounded by the silicon guard and only the ion current will be registered by the picoammeter.

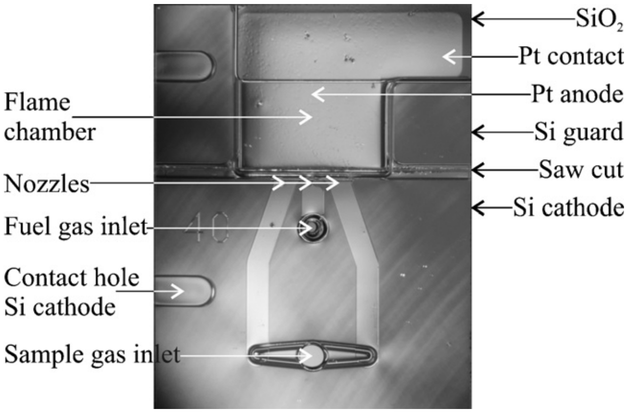


Fig. 3. Top view photo of the planar μFID without platinum heat reflector.

To ensure a wide range of gas flows to be controlled by mass flow controllers (MFCs) during system development, gas inlets are designed for orthogonal connection of large diameter tubing. Later on, these can be replaced by in plane capillaries for easy interconnection with other planar components, like for example a micromachined separation column [13], and for low-cost flow control by pressure regulation. A detailed description of the MEMS fabrication process can be found in [16]. Fig. 3 shows a photograph of a planar μFID. To obtain a clear view on the flame during characterization, devices were not equipped with the platinum heat reflector on the top glass substrate (see also Figs. 3–6). The bottom glass substrate was omitted completely to facilitate fabrication (see also Figs. 4–6).

2.2. Measurement setup

For characterization of the planar μFID the measurement setup was modified in three different ways (Figs. 4–6). Fig. 4 is schematic representation of the measurement setup for separate fuel and sample gas supply to the μFID. With the setup shown in Fig. 5 fuel and sample gas can be premixed before entering the μFID. Finally, Fig. 6 depicts the setup, in which the μFID is connected to the micro-TCD (μTDC) outlet of a μGC module (GCM5000 by SLS Micro Technology, Hamburg, Germany). Its micromachined separation column of 270 mm length and 0.3 mm diameter is packed with HayeSep A (Vici, Hayes Seperations Inc., Bandera, TX, USA). The column can be temperature ramped. Starting at 40 °C it was programmed to reach 165 °C in 62.5 s (2 K/s). According to the manufacturer the μGC module has an MDL of 50 ppm. The helium (6.0 purity, Air Liquid, Paris, France) carrier gas flow was set to 1 ml/min. The injection volume is fixed at multiples of 1 μl. In this work, the maximum number of 8 injections was chosen. The μFID was connected to a Keithley (Cleveland, OH, USA) 487 picoammeter with build in voltage source (Fig. 2), which was set at 200 V.

The hydrogen (5.0, Air Liquid, Paris, France) and oxygen (4.8, Air Liquid, Paris, France) flow rates were controlled individually by MFCs from Bronkhorst (Ruurlo, The Netherlands) and set to 22 and 8 ml/min, respectively, for the μGC experiment. For all other experiments, hydrogen and oxygen were stoichiometrically mixed to obtain a total hydroxygen flow of either 30 or 39 ml/min.

The samples consisted of nitrogen with small amounts of organic compounds. To obtain different concentrations of these substances, both the sample gas flow and a flow of pure nitrogen (5.0, Air

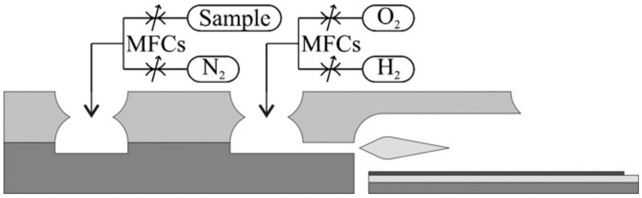


Fig. 4. Measurement setup for separate fuel and sample gas supply. The picoammeter with integrated voltage source was connected according to Fig. 2.

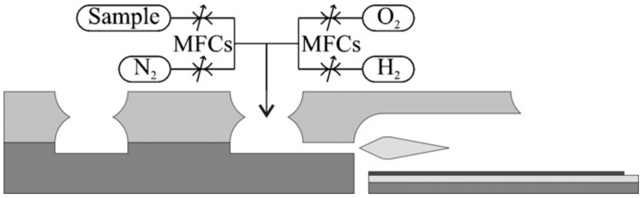


Fig. 5. Measurement setup for premixed supply of fuel and sample gas.

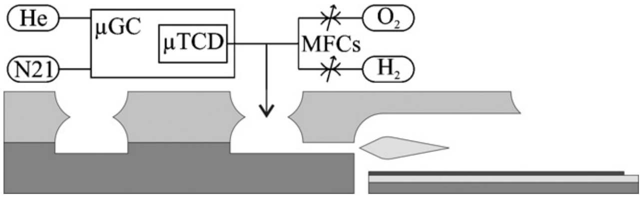


Fig. 6. Measurement setup for μGC-μTCD-μFID measurements.

Liquid, Paris, France) were controlled individually. The sum of these flows (total sample gas flow) was either 5 or 10 ml/min. Besides nitrogen with a small amount of only one hydrocarbon molecule (100 ppm pentane, 100 ppm methane, 0.1% methane, 1% methane and 10% methane, all supplied by Real Gas, Martinsried, Germany), two mixtures of different hydrocarbon substances in nitrogen (N17 and N21, both supplied by Air Liquid, Paris, France) were examined. N17 consists of nitrogen with 100 ppm methane, ethane, propane, *n*- and *i*-butane, *n*-pentane and *n*-hexane. N21 contains 10% methane, 1% ethane, 1% propane and 1% *n*-butane in nitrogen. The latter was used in the μGC experiment only. Flames were externally ignited through the outlet by a lighter.

3. Results and discussion

3.1. Sensitivity and minimum detectable limit

The MDL is defined as the amount of sample generating a signal two times as large as peak to peak noise. The MDL (in g/s) can be calculated by dividing two times peak to peak noise (in A) by the sensitivity (in C/g). Since the FID is a "carbon counter" (its response is proportional to the amount of carbon in a sample), the amount of sample is measured in grams carbon (gC). The initially published MDL of 1.2×10^{-9} gC/s [16] is about a factor 20 larger than the MDL of conventional devices [2,9]. However, this result was obtained under non-optimized conditions (experiment A in Table 1), which left room for improvement.

This work focuses on improvement of the MDL by increasing sensitivity. Several parameters with an expected effect on sensitivity were investigated. For experiments A–K (see Table 1) sensitivity was determined using a certain off-the-shelf sample gas, which was diluted in three steps to pure nitrogen keeping the total sample gas flow constant. The ion current was recorded for all four different carbon mass flows, including zero. The latter was used for offset correction, before the measurement points were approximated by a linear fit through zero, of which the slope represents sensitivity. Unfortunately, no low-noise measurement environment was available and no additional measures were taken to minimize noise. Therefore, noise recordings and consequently MDLs have to be interpreted with care.

Unless indicated otherwise, all measurement points represent a 1-min average with a sampling interval of 1 s. Peak to peak noise equals the difference between the maximum and the minimum reading of that same 1 min interval. After having set a new carbon mass flow, the ion current reading was allowed to reach steady state, before measurements were taken.

First, the fuel gas flow was increased from 30 to 39 ml/min hydroxygen (compare experiments B and C in Table 1 [17]) to produce a larger flame with stronger ionizing power. Of course, this is in conflict with the objective to minimize fuel gas consumption with a planar μFID. Nevertheless, there will be applications, where the detection limit is more important than fuel gas consumption. By increasing fuel gas consumption, sensitivity was raised from 4.8 to 6.6 mC/gC (Fig. 7, Table 1). Since noise did not increase as much, the MDL reached an optimum value of 4.5×10^{-10} gC/s. A comparison between experiments A and B leads to the conclusion that higher total sample gas flow (10 compared to 5 ml/min) reduces the ionizing power of the flame (4.2 compared to 4.8 mC/gC).

Then, instead of using the separate sample gas supply nozzles on either side of the fuel gas nozzle (Figure 3), the sample gas was premixed with the hydroxygen (compare experiments D and E in Table 1 [17]). This is likely to reduce the amount of carbon that passes the flame without being ionized. To maintain a stable flame, the hydroxygen flow needed to be set at the higher value (39 instead of 30 ml/min) and a larger nozzle (60 instead of 40 μm width) was needed to prevent blow-off. The difference in sensitivity is significant: 3.0 mC/gC for separate, but 10.2 mC/gC for premixed sample gas supply. For reasons yet unknown, also noise is larger for premixed samples.

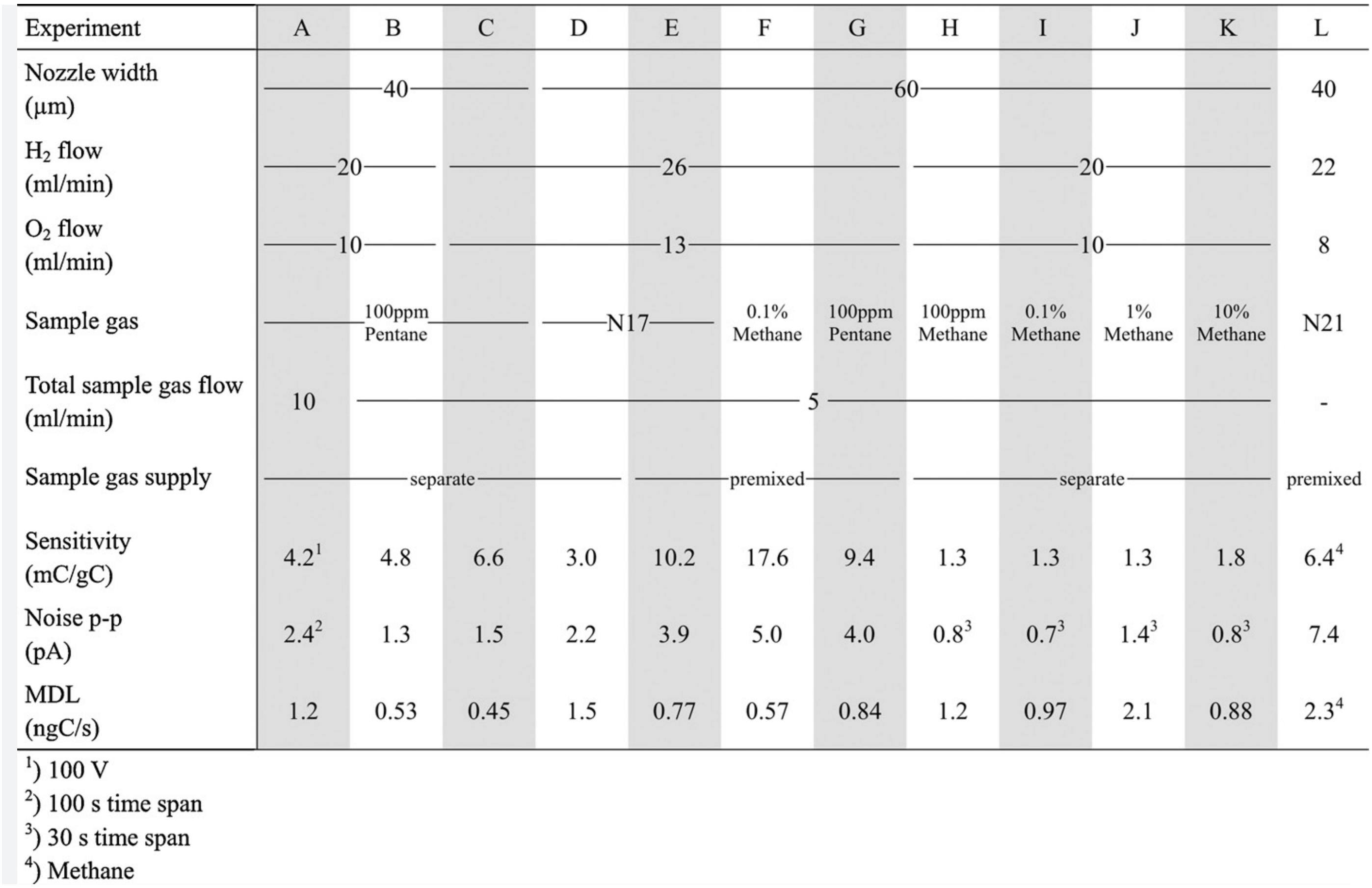
The relatively low sensitivity of experiment D (3.0 mC/gC compared to 6.6 mC/gC of experiment C) can be explained by the large nozzle area (60 μm nozzle width in experiment D compared to 40 μm nozzle width in experiment C) and the corresponding low outflow velocity of the fuel gas. As a consequence ions are produced closer to the nozzle and many of them are captured by the guard electrode (Fig. 2). The comparison of responses to different sample gases (N17 and 100 ppm pentane in nitrogen) appears to be acceptable, since response factors differ only slightly (see below).

3.2. Response factor

As mentioned before, the conventional FID is characterized by an "equal per carbon" response. This is a useful property, when the total carbon content of an unknown organic mixture has to be determined as in THA. Along with μGC, THA is another important application of the μFID. An "equal per carbon" response implies a constant sensitivity (in mC/gC) for organic compounds with different carbon numbers. To verify this behavior for the μFID, the sensitivity towards methane and pentane was determined in experiments F and G, respectively. The sensitivity towards methane of 17.6 mC/gC (experiment F) is the largest measured so far. The sensitivity towards pentane (9.4 mC/gC, experiment G), however, is only half of it and obviously the "equal per carbon" rule does not apply. Since sensitivity is larger for smaller molecules, it is assumed that larger molecules are not completely broken down to single carbon fragments in the microflame.

Since the sensitivity of 10.2 mC/gC to N17 (experiment E) is similar to the sensitivity of 9.4 mC/gC to pentane (experiment G), the comparison of experiments C and D (see above) is indeed acceptable.

Table 1
Overview of experiments.



Experiment	A	B	C	D	E	F	G	H	I	J	K	L
Nozzle width (μm)	40			60								40
H_2 flow (ml/min)	20		26					20				22
O_2 flow (ml/min)	10		13					10				8
Sample gas	100ppm Pentane			N17		0.1% Methane	100ppm Pentane	100ppm Methane	0.1% Methane	1% Methane	10% Methane	N21
Total sample gas flow (ml/min)	10	5										-
Sample gas supply	separate				premixed			separate				premixed
Sensitivity (mC/gC)	4.2^1	4.8	6.6	3.0	10.2	17.6	9.4	1.3	1.3	1.3	1.8	6.4^4
Noise p-p (pA)	2.4^2	1.3	1.5	2.2	3.9	5.0	4.0	0.8^3	0.7^3	1.4^3	0.8^3	7.4
MDL (ngC/s)	1.2	0.53	0.45	1.5	0.77	0.57	0.84	1.2	0.97	2.1	0.88	2.3^4

^{1}) 100 V
^{2}) 100 s time span
^{3}) 30 s time span
^{4}) Methane

[a] 100 V.
[b] Methane.
[c] 100 s time span.
[d] 30 s time span.

3.3. Linearity

To determine whether the sensitivity remains constant over a larger range, sensitivity was determined for off-the-shelf sample gases containing nitrogen with methane in four different concentrations (experiments H–K in Table 1). These concentrations were 100 ppm, 0.1%, 1% and 10% (four measurement points each). For these experiments a device with 60 μm nozzle width was run with 30 ml/min hydroxygen and separate sample gas supply. As a consequence many ions were captured by the guard electrode and sensitivities were relatively low. Note that also noise levels were small. Except for 10% methane in nitrogen, which yields a sensitivity of 1.8 mC/gC, the sensitivity (i.e. the slope of the linear approximation through zero) is 1.3 mC/gC for all samples (Table 1). Fig. 8 shows the sensitivities corresponding to each non-zero measurement point. From this figure it becomes clear that sensitivity

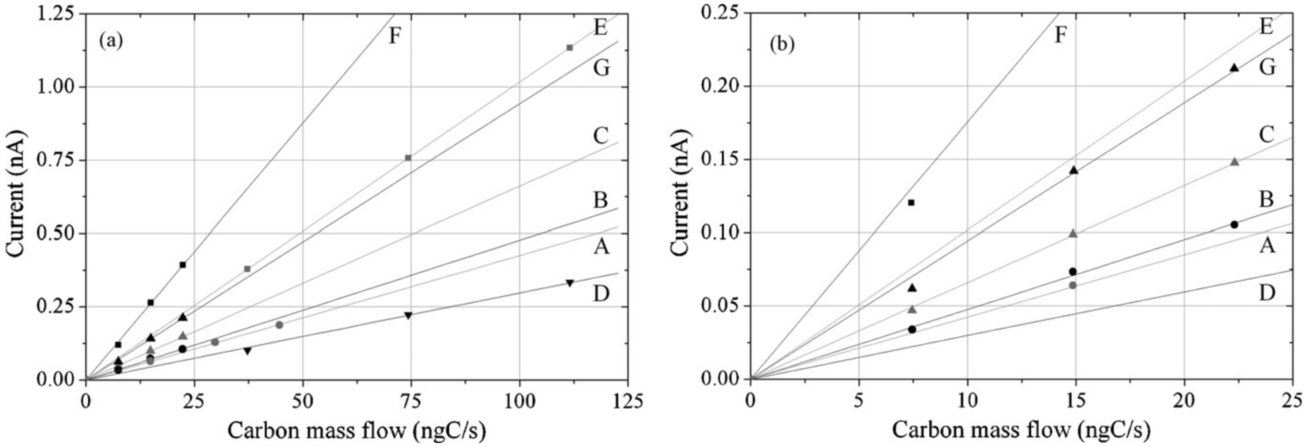


Fig. 7. (a) μFID sensitivities corresponding to experiments A–G from Table 1 and (b) enlargement of (a).

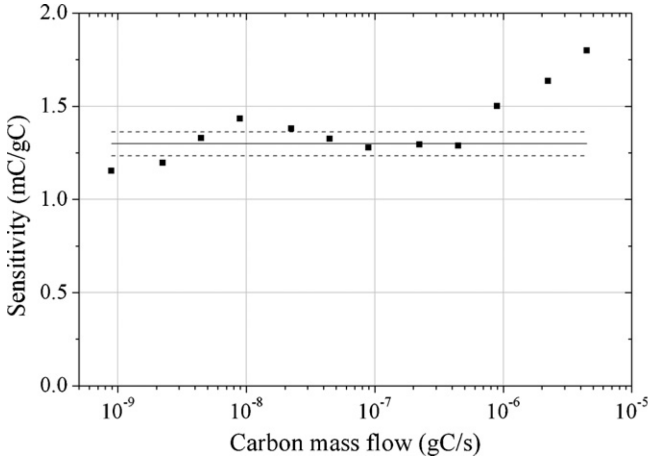


Fig. 8. μFID sensitivities corresponding to non-zero single measurement points of experiments H–K from Table 1.

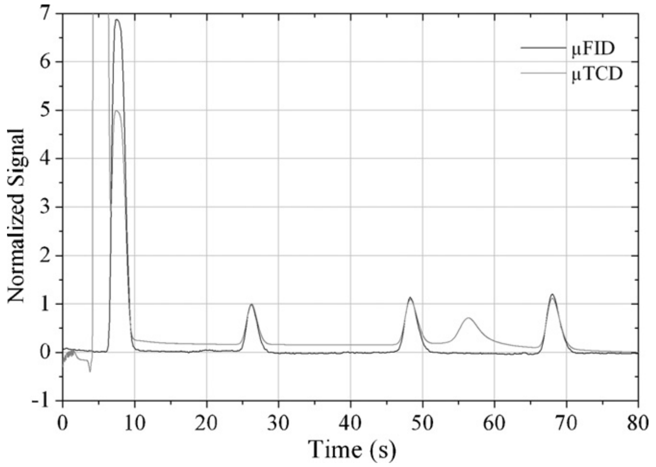


Fig. 9. μFID and μTCD chromatograms of N21 (10% methane, 1% ethane, 1% propane and 1% butane in nitrogen) recorded with the μGC module of SLS Micro Technology.

deviates more than 5% (dashed horizontal lines) from the average of the lower three sample gas concentrations (solid horizontal line). Above a carbon mass flow of 5×10^{-7} gC/s sensitivity increases continuously. Apparently, at larger carbon mass flows, the sample contributes significantly to combustion increasing the ionizing power of the flame.

3.4. *μGC-μTCD-μFID*

To prove the functionality of the μFID as a detector in μGC, the μFID is compared with the built-in μTCD of the μGC module. Fig. 9 shows chromatograms of the sample gas N21 recorded by both the μFID (experiment L in Table 1) and the μTCD [18]. Both signals have been normalized with respect to the ethane peak (26 s retention time).

Several advantages of the μFID over the μTCD are apparent. First, its signal is insensitive to the injection procedure. Then, the μFID has a constant baseline. Since the μFID is insensitive to nitrogen (4 s), the methane peak (8 s) can be measured easily.

The usefulness of a μGC-μTCD-μFID system can be illustrated by examination of the unknown peak after 56 s retention time. Since it was not registered by the μFID, the substance must be of inorganic nature. Furthermore, an additional measurement showed that this peak does not scale with the injection volume and must therefore be contained in the carrier gas.

Table 2
μFID response factors to and normalized thermal conductivities [20] of different hydrocarbons.

	Hydrocarbon			
	CH_4	C_2H_6	C_3H_8	C_4H_{10}
Response factor	1[a]	0.63	0.55	0.45
Thermal conductivity	1[b]	0.61	0.48	0.45

[a] Corresponds to 6.4 mC/gC.
[b] Corresponds to 31 mW/(m K).

From the areas under the peaks in the chromatogram and the carbon content of the injected volume the sensitivity towards the four different constituents of N21 can be determined (Table 2). As before, sensitivity increases with decreasing molecule size. Note that the μFID and μTCD chromatograms are very similar. Moreover, μFID response factors to different hydrocarbons correlate extremely well with corresponding values for thermal conductivity [20] (Table 2). This result might be of significance for a better understanding of the FID response mechanism [21].

Due to the relatively large peak to peak noise, the methane MDL calculated from the chromatogram (Fig. 9) is somewhat higher than determined before in experiments A–K (Table 1). Because of the absolute nature of the FID ("carbon counter"), MDLs are given in gC/s. For comparison of the μFID with the μTCD, which measures concentration, MDLs have to be expressed relatively. An MDL in ppm can be obtained if one requires the peak height (in A) to be twice peak to peak noise. From the ethane peaks of Fig. 9 it follows an MDL of 760 ppm for the μFID and 89 ppm for the μTCD. Yet, even a conventional FID can hardly compete with TCD in μGC. The MDL of an absolute detector, like the FID, increases with decreasing injection volume, whereas the MDL of a relative detector, like the TCD, does not depend on it directly. Therefore, the μFID will not replace the μTCD as a detector in μGC, but it is advantageous to combine both in 2D μGC as shown above.

4. Conclusions

This paper presents a miniaturized FID, with reduced gas consumption. Especially oxidant gas consumption is reduced considerably from 300 ml/min of air to 13 ml/min of pure oxygen without loosing sensitivity. Presently, noise is still relatively large and as result the MDL is still about a factor 10 away from state-of-the-art. Sensitivity varies somewhat from average in a range from 1×10^{-9} to 5×10^{-7} gC/s. Above 5×10^{-7} gC/s sensitivity increases continuously with the carbon mass flow.

It is shown that sensitivity can be raised (from 4.8 to 6.6 mC/gC) by increasing the hydroxygen flow (from 30 to 39 ml/min in experiment C) and by doing so, the optimal MDL of 4.5×10^{-10} gC/s was obtained. Sensitivity can also be increased by premixing the sample with the hydroxygen. Highest sensitivity (17.6 mC/gC) was obtained for premixed methane (experiment F). The sensitivity to pentane under equal conditions is lower (9.4 mC/gC, experiment G). It is assumed that larger molecules are not completely broken down to single carbon fragments in the microflame. This is a common characteristic of portable FID systems [22] and impairs reliable THA. Yet, it does not cause any trouble quantifying methane, which is the main application of such mobile FIDs.

This behavior was confirmed by using the μFID as a second detector in a μGC-μTCD. Compared to methane as the reference substance (response factor 1), the μFID response factors of ethane, propane and butane measure 0.63, 0.55 and 0.45, respectively, and correlate very well with corresponding values for thermal conductivity.

In contrast to a relative detection principle (e.g. TCD), of which the MDL is independent of the sample volume, the MDL of an absolute detector (e.g. FID) increases with decreasing sample volume. Therefore, the μFID will not replace the μTCD as a detector in μGC. However, it is shown that the functionality of a μGC can be extended by adding a μFID.

Future work will concentrate on minimizing noise. Noise might arise from organic residuals originating from MEMS fabrication. Therefore, special care has to be taken in substrate cleaning while fabricating. Furthermore, to improve the thermo-mechanical stability of the system, the silicon underneath the flame will be removed, such that there is only glass on either side of the flame. The lower glass substrate will be provided with an electrode structure consisting of a thin metal film guard and measurement electrode with an electrically isolating SiO_2 layer in between. This will also release the thermal stress on the wire contacts.

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