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The application of MEMS technology to on-line analyzers for natural gas

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Abstract

Process Gas Chromatographs have been in use in the natural gas industry since the early eighties. The core analytical elements are commonly manufactured with conventional fine-mechanical tools. Recently MEMS technology has opened the doors to a new level of performance for on-line natural gas analysis.

I MEMS technology

MEMS (Micro Electro Mechanical Systems) technology combines mechanical and electronical techniques on a micro-scale. Using micro-machining processing steps developed by the IC industry, chip-level devices are created which not only allow for a significant improvement of the interaction between these 2 disciplines, but also provides a much better control of the processes which occur on this micro-scale.
MEMS applications have been growing exponentially during the last 3 years. Important application areas are the automotive industry (for example airbag sensors), IT and the medical sector.

Fig. 1 MEMS electrically driven motor with a diameter of a human hair

Gas chromatography is one of the most suited scientific disciplines for MEMS technology. Besides the obvious size reduction (with the associated decrease in production and installation costs) and the reduction in consumables (both power and gas consumption), MEMS technology has a major impact on the analytical performance :

- Miniaturisation of the Thermal Conductivity Detector (TCD), which drives its performance up to levels previously only attainable with FID's, and which indirectly enables the use of capillary columns for on-line C_{6+} analysis.
- Ultra precise integration of columns, detectors and sample injection system – the core analytical components – with the channel system of the base silicon wafer, leading to a significant reduction of the internal dead volume, which is absolutely crucial for the analytical performance of a GC.
- Reduction of the analytical module size allows for a much tighter temperature control of the analytical components, essential for the repeatability of the analysis results.

The following paragraphs explain the advantages of MEMS technology for on-line process gas chromatography in more detail, and give examples of practical MEMS applications with analytical results.

II Advantages of MEMS technology for on-line natural gas analysis

II 1 The use of capillary columns in process natural gas chromatography

Capillary columns is the popular name for open-tubular columns, referring to the small diameter sizes commonly used for this type of columns*.

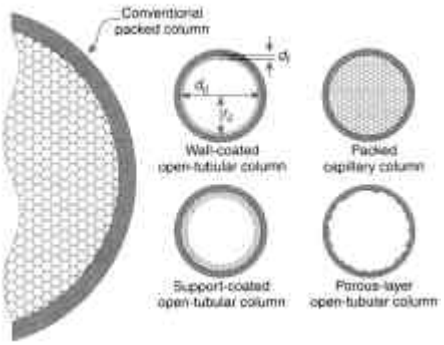

Fig 2 Different types of capillary columns

The most used capillary columns are of type WCOT (wall coated open-tubular) and PLOT (porous layer open-tubular), which offers a better film stability in case a higher loading of the column wall is required. The advantage over a packed column lies in the reduction in pressure drop (typically a factor 25 lower). This allows for much longer lengths and therefore much higher separation power. Nowadays they have replaced the traditional (micro)-packed columns in almost all gas chromatographic fields.

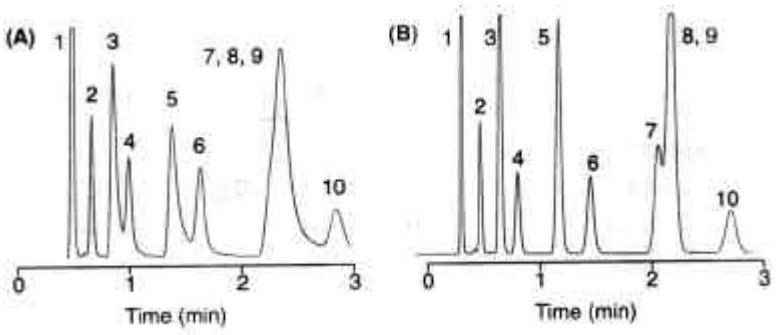

Fig 3 Difference in separation quality between packed and capillary column for identical velocity and temperature settings.

* This is misleading since open-tubular columns could in theory be manufactured at diameters larger than packed columns, but because of its wide spread use, in this document the term “capillary” will be used.

The efficiency of a capillary column increases with decreasing internal diameter. A 10 µm capillary column with a length of 10 m has the same separation characteristics as a 25 µm column of 25 m length.

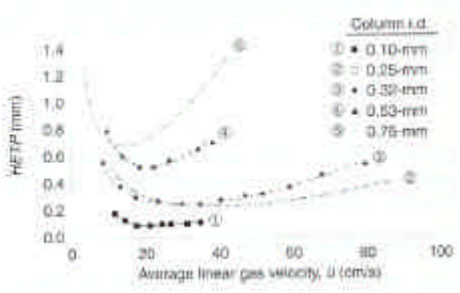

Fig 4 Separation efficiency as function of the average linear gas velocity for different column diameters

The film thickness of the stationary phase is proportional to the internal diameter to maintain the optimal phase ratio for component separation. Efficiency increase therefore results in a strong limitation of the sample size which can be injected onto the column, to prevent saturation of the stationary phase.

In the past TCD's were not sensitive enough to accurately detect the small sample sizes associated with capillary columns. Analytical designers were forced to integrate FID's (Flame Ionisation Detectors), which have a fast response time and low detection limit. Because these detectors require H_2 for the ionisation process, their use is not trivial in hazardous areas. Process analyzers for the natural gas industry therefore were limited to the use of TCD's in combination with (micro-)packed columns.

TCD's based on MEMS technology can compete with conventional FID's for 2 reasons :

- MEMS technology allows for much smaller internal volumes (both the size of the detector chamber and the connections between capillary tubing and detector) which increases the sensitivity of TCD to levels at which they are compatible with the low sample volumes associated with capillary systems.
- The extreme reduction of the sensor size leads to a heat capacity low enough to reach thermal time constants around 5 ms. In general this constant should be a factor 5 smaller than the standard deviation of the most narrow peak. Capillary columns easily produce peak widths less than 1 s, which explains the absolute necessity of MEMS technology for TCD's.

However it has to be noted that even for MEMS TCD's the detection limit is still significantly higher than for FID's . The TCD's have to be put directly in the gas flow to assure fast response times necessary for narrow bore peaks. The inevitable flow variations lead to a relative high noise level. A typical detection limits for a MEMS TCD is 1 ppm for C_5, where FID's can go as low as ppb levels. MEMS TCD's are therefore not (yet ?) appropriate for trace analyses.

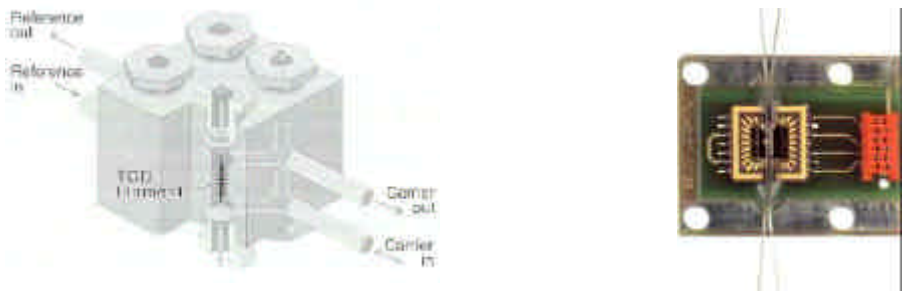

Fig 5 TCD manufactured with conventional mechanical tools (left) and with MEMS technology (right). The internal volume is reduced with a factor 1000.

II 2 Reduction of dead volumes

The second fundamental advantage of MEMS technology for on-line natural gas analysis comes from the level of control it offers on dimensioning of the interconnecting flow paths.

Absolutely crucial for the analytical performance of gas chromatograph system is the number of dead volume spots, and their size, especially between column outlet and detector chamber. Any dead volume will allow the separated components to recombine after the column and therefore destroy the separation performance of the system.
MEMS technology allows to provide a smooth transition between capillary columns and detector inlet port.

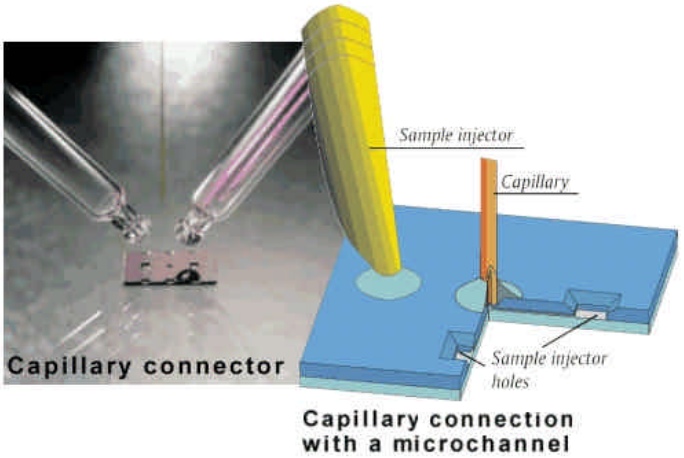

Fig 6 Connection of capillary columns to a silicon channel system. Internal diameter of the capillary column and channel width are the same to reduce dead volume.

Commonly used sizes for both internal diameter of the capillary column and the channel width are 100 and 250 µm.

II 3 Analytical module size reduction

One of the more obvious advantages and major driving force for MEMS applications in general is the intrinsic size reduction of the complete system, which allows for reduction of foot print, overall dimensions and weight, and therefore production costs. For gas chromatography this size reduction allows for a much tighter temperature control of the analytical compartment of the GC, leading to a significant improvement of the repeatability of the analysis data.

III Application of MEMS technology on GC component design

The application of MEMS technology on 2 core components - TCD and capillary column connection - is discussed in detail.

III 1 TCD design with MEMS technology

III 1.1 General description

Most MEMS TCD's are based on a silicon nitride micro-bridge over an anisotropic etched channel. On this bridge the temperature sensitive material is sputtered. To get a more robust structure the bridge is often designed as a grid hanging over the channel. A typical example of such a TCD structure is given in figure 7. Since IC-technology based processes are used, the dimensions for this TCD structure can be minimized to almost every desired value (e.g. bridges of 20 µm wide and channels of 250 µm wide and 100 µm depth). This enables the realization of a very low internal and dead volume detector, which is crucial for an accurate high resolution sensor. Besides this, because of the small filament and channel dimensions the heat capacity of the sensor is extremely low enabling a very fast response time of the detector.

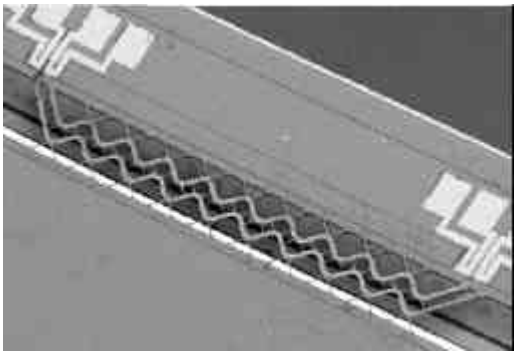

Fig 7 Silicon Nitride micro-bridge on a anisotropic etched channel

The lithographic patterning method leads to a level of uniformity of the sensors which is not possible with conventional techniques. This enables the realisation of high quality arrays of sensors, especially necessary for TCD's since they are always used in a parallel pattern with a reference and measurement cell. Conventionally a Wheatstone configuration is used to neutralize process fluctuations during the analysis, but the high degree of uniformity and ease of integration with the channel system, without introducing dead volume, opens the port also for an array of TCD's. They do not only measure the actual concentrations of the components in the gas, but can also be used as detectors inside the channel system which monitor every step of the analysis, such as injection quality and backflush properties.

III 1.2 Material choice

Most often used sheet materials for MEMS sensor elements are platinum (Pt), nickel (Ni). These films can easily be sputtered or evaporated onto the bridge material (mostly Si_xN_y). Both Pt and Ni require an adhesion layer when deposited onto nitride or oxide. Pt is especially interesting because of its resistance to the commonly used channel etch solutions (KOH, TMAH). Using Pt leads to a very straight forward processing scheme, see figure 8. Ni only has a moderate resistance against the used etchants but addition of a protective layer (e.g. Si_xN_y) over the Ni has been proven to solve this problem.
Besides the protection against the etchants this layer also protects the metal against oxidation during operation.

Fig 8 Standard MEMS processes for resistive temperature sensors on a bridge in a micro-channel. If platinum is used as sensor material step c is not needed

Alternatively tungsten wires, commonly used for conventional TCD's, might be integrated in the MEMS detector cell. Protection with gold is needed to prevent oxidation of the filaments at elevated temperatures. The integration and miniaturisation level of this technique is however less than for the sputtered film sensors.

Thermistors (also knows as NTC's, Negative Temperature Coefficients) are sintered mixtures of manganese, cobalt, and nickel oxides along with trace elements. They exhibit a very large temperature coefficent, and therefore make very sensitive sensors. Their sensitivity decreases with temperature, but offer up to an operating temperature of 150 °C still a very interesting alternative for PTC's.
The use of these kinds of materials however does have major process implications. The material is delivered as powder in a binder solution, which has to be applied to the wafer and sintered afterwards. Figure 9 shows three possible integration methods for the NTC oxide powers in the MEMS channel.

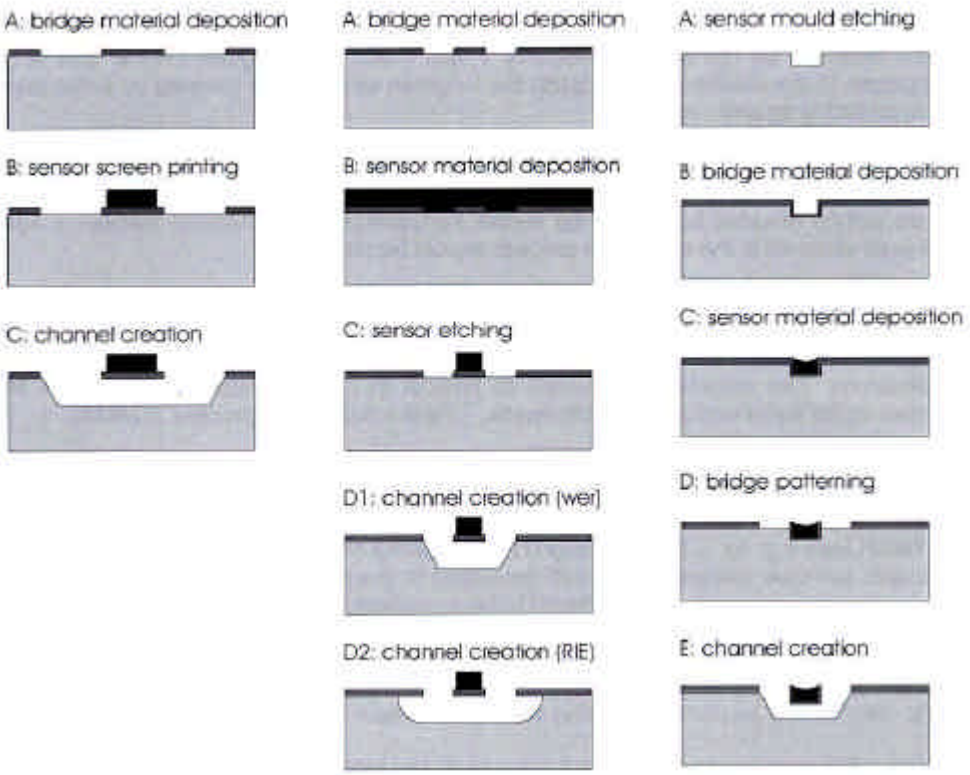

Fig 9 Integration of NTC materials in MEMS channel systems.

Screen-printing technology is a mature production method but still not often used on MEMS wafers. Production problems probably lay more in the field of equipment/wafer compatibility than the material/adhesion field. Furthermore screen-printing only has a moderate resolution (critical dimension about 10 µm) compared to lithography as used in MEMS (about 2 µm). Also the thickness of the layer is determined by the thickness of the screen, which is at least 25 µm.
Etching is a straightforward technique to integrate the desired oxide compounds. The layer is simply deposited unpatterned (e.g. by spinning) and patterned afterwards by etching or lift-off. By using a fine powder (particle size a few µm) the layer thickness can be decreased to several microns, resulting in a fast response time. For this technique a good etch process or lift-off process is essential.
Micro moulding uses reactive ion etching (RIE) into the silicon membrane and coated with the bridge material (Si_xN_y). Thereafter the oxide blend and binder is dispensed over the wafer filling the structure. The waste material on top of the wafer is scrubbed off, after which the remaining material is sintered. If needed the top surface might be protected for scratches or contamination by means of a protection layer (e.g. photo resist), which is removed after filling the structure. The advantage of this approach is that the material can be accurately patterned with standard MEMS resolution of about 2 µm which enables accurate and reproducible sensor elements, necessary for an array design of TCD's.

For all techniques it is important to assure the chemical resistance of the NTC material to the channel-etch etchant. For wet anisotropic etch procedures a silicon nitride or oxide layer might protect the layer. The degree of protection depends however upon the quality of the sintered layer (smoothness, pinholes, contaminations, etc.). Isotropic dry etching provides a more efficient protection with a resist layer.

III 1.3 Channel enclosure

To close the channel often a pyrex glass part is used in which the opposite part of the channel is etched. The glass covers are also realised in wafers. This pyrex wafer can be bonded using anodic bonding technique. This technique gives a hermetic seal with high bond strength, but requires a rather high process temperature (400°C), which might constraint the application of the desired sensor element material. Furthermore the wafers should be completely flat which means that special provisions should be made for the electrical connections to the outside. This can be overcome by etching shallow channels in which the tracks run. After the bonding process they are sealed using epoxy glue.

Figure 10 shows a a possible solution for the wafer scale encapsulation of the TCD. Here an open TCD is mounted (flip-chip) onto a channel plate. The mounting method can be epoxy glue, UV curing glue or thermoplastic glue sheets. This allows the electric connection tracks to run through the adhesive with a good sealing. Of course the adhesive film should be as thin as possible to avoid dead volume due to absorption in the adhesive. Also the gluing process should be well controlled to avoid glue in the micro channels. This can be done using capillary gluing in which the capillary force difference between glue in the narrow glue slit compared to the deeper gas channel is used to guide the glue.

Fig 10 TCD assembly on a channel plate.

The electrical connections of the TCD lay on the top surface of the open TCD chip. Without provisions it will be impossible to reach the bond pads of the TCD if the TCD is flip-chip mounted onto the channel plate. The simplest way to solve this problem is to create holes in the channel plate or place the TCD at the side of the channel plate. After assembly of the TCD to the channel plate and the required electronic board the wire bond can be realized.

III 2 Capillary column connection to MEMS channels

One of the crucial aspects of gas chromatography is the zero dead volume connection of the capillary columns (made of fused silica) to the channel system. Figure 10 shows different options. The use of equal internal diameters for both capillary columns and channels is highly recommended.

Fig 10 Methods to connect the capillary columns to the channel system.

In-line connection.

Due to the capillary guidance in the chip and a well developed capillary glue sequence a robust and reproducible connection is made. However the dead volume of such a connection cannot be guaranteed to be less than 0.05 µl

Orthogonal connection

The gluing sequence and capillary preparation (right angled front side) is much more difficult, but the dead volume reduces to virtually zero.

Removable connection

IV Analytical results for C_{6+} analysis of natural gas wit h MEMS technology

IV 1 Analysis time

The analysis time should be defined as the time within all the components of interest can be detected with baseline separation.

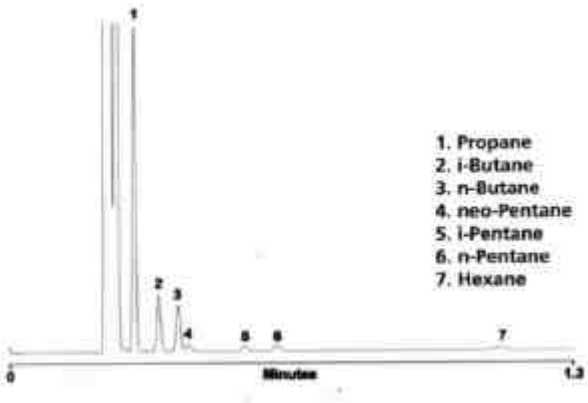

Fig 11 Analysis of the higher hydrocarbons on a MEMS based capillary system.`

A dual-channel capillary system based on MEMS technology can easily complete a full baseline C_{6+} analysis in less than 1 minute. Since the Van Deemter curve (see fig. 3) becomes relatively flat for narrow-bore capillary columns, the linear velocity through these type of columns can be increased significantly without sacrificing much of the separation quality. This allows to increase the analysis speed further more, depending on the accuracy requirement setting.

IV 2 Accuracy

Table I shows the analytical results for a dual-channel MEMS system, calibrated with the so-called 11D gas (standard calibration gas of the PTB). Three gases are analysed, with a deviation of -/+ 10 % in Calorific Value.

Table I Accuracy results for a MEMS bases C_{6+} analysis

	Cal. gas	Test gas #1		Test gas #2		Test gas #3	
		Certificate	Analysis	Certificate	Analysis	Certificate	Analysis
C6+	0.0500	0.0500	0.0499	0.0298	0.0307	0.0500	0.0504
N2	4.0700	13.0000	13.0381	0.7120	0.7637	0.8400	0.8220
CH4	88.8510	81.6870	81.6404	83.5310	83.5374	98.5390	98.5714
CO2	1.5400	1.4200	1.4368	1.8600	1.8639	0.0200	0.0200
C2H6	3.9900	3.1300	3.1268	10.2000	10.1659	0.2660	0.2523
C3H8	1.0000	0.5020	0.5073	2.8100	2.7499	0.0770	0.0815
iC4	0.2020	0.0810	0.0741	0.2370	0.2448	0.0530	0.0505
nC4	0.1990	0.0800	0.0775	0.4740	0.5020	0.0520	0.0527
neoC5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
iC5	0.0490	0.0250	0.0245	0.0735	0.0713	0.0530	0.0497
nC5	0.0490	0.0250	0.0245	0.0727	0.0704	0.0500	0.0495
HV [MJ/Nm3]	39.952	35.605	35.576	44.432	44.391	39.912	39.912
Diff [%]		-10.9		11.2		-0.1	
Error [%]			-0.08		-0.09		0.00

It has to be noted that the uncertainty on the calibration gases cannot be guaranteed to be better than 0.10 % on the Calorific Value.
In general MEMS based GC systems can easily deliver an uncertainty better than 0.10 % for a broad range of gases, based on a single point calibration. This a factor 2 to 3 better than what is achievable with conventional GC technology.

IV 3 Repeatability

Table II displays typical results on the repeatability (as defined by ISO 6976) for the components concentrations and the heating value of a C_{6+} analysis with MEMS based technology. The results are generally a factor 3 to 5 better than what is achievable with conventional GC technology.

Table II Typical repeatability results for a MEMS bases C_{6+} analysis

	Repeatability [%]
N2	0.017
CH4	0.003
CO2	0.113
C2H6	0.056
C3H8	0.113
C4	0.141
C5	0.141
CV [MJ/Nm3]	0.006

V Practical implementation

V 1 Enclosure

The MEMS based unit should be suitable for outdoor installation, close to the sample point. The complete analytical system (analytical module, electronic boards, sample handling and stream select) has to be mounted in a explosion proof enclosure, with ATEX 100 Zone 1 certification and IP 65 classification for environmental impact (water and dust). The unit must have an internal heating module to prevent freezing of the sample gas.

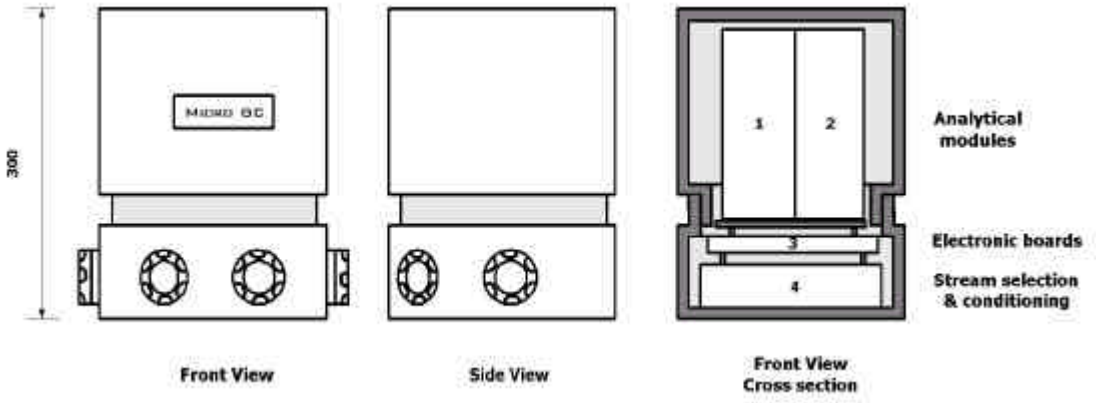

Fig 12 Typical dimensions for a MEMS on-line analyzer for natural gas

V 2 Sample conditioning

The miniaturisation of the analytical module makes it vulnerable for contaminants. Water (in vapour or liquid phase), particles, sulphur, glycol and methanol have to be removed from the sample down to sub-ppm levels. Figure 13 shows the essential components for a efficient protection of the analytical module.

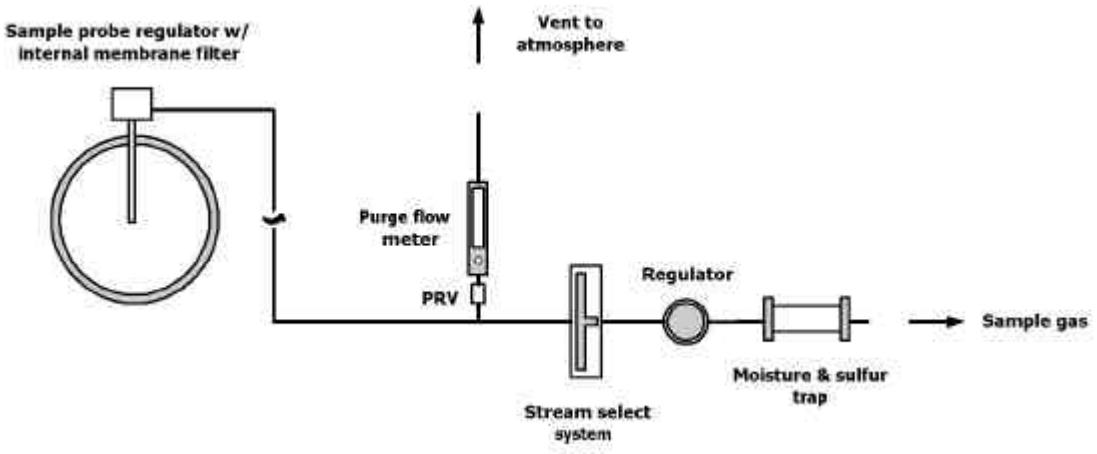

Fig 13 Main components of a sampling system for a MEMS based analyzer

V 3 Other specifications

The analyzer must enable direct ModBus RTU communication and TCP/IP based Ethernet connection. For metrological purposes, a display (locally or remotely) showing the accountable values and alarm status, with internal security switches for data protection, is required, but might also be a request for non-metrological applications.

A power supply of 24 V DC facilitates the integration of the analyzer with the power supply array for transmitters and sensors. The low power consumption of a MEMS analyzer also offers the possibility to run the unit on solar power.

VI Conclusion

MEMS technology enables a new generation of on-line analyzers for natural gas :

- Analytical performance is increased with a factor 3 to 5 :
  - Chip-level TCD's allow for the use of capillary columns
  - Integration of the analytical components on chip-level scale eliminate dead volumes between column outlet and detector, and enable very precise sample volume control
  - Size reduction of the analytical module facilitates the temperature control of the analytical module.
- Overall size and weight reduction with a factor 2 to 3 compared with conventional analyzers. A explosion proof MEMS analyzer can be manufactured on a base of 25 cm with a height of 30 cm
- Reduction of power and utility gas consumption. MEMS analyzers are typically supplied with 24 VDC, which enables easy integration with the power supply array for the field transmitters and sensors. Both helium and calibration gas consumption remain well below 20 l/min.

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