

## **Pressure and Gas Matrix Independent Dilution System for Fuel Cell Gas and Exhaust Distribution Monitoring**

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### **Abstract**

Fuel cells are probably the most efficient way to achieve the difficult purpose of the so-called zero emission vehicles.

In comparison to today's automotive emission monitoring applications, fuel cells emission monitoring meets the most challenge.

In particular the formation of hydrogen from liquid fuels has the most dramatic changes in bulk gas compositions. During startup and instationary conditions gas concentrations of H<sub>2</sub>O, O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, CO and Methanol in the fuel cell may vary from 0 to 60 Vol%, C1 to C4-hydrocarbons from 0 to 5 Vol%.

Whichever physical principles and technologies are applied in the gas analyzing equipment, they are subject to more or less interference caused by the bulk gas.

A new dilution device consisting of pressure reduction stages and four compression stages with regulated dilution inputs is presented in this work.

Measurements of all relevant gaseous bulk compounds are compared in different background matrices by the use of a CI-MS mass spectrometer.

Impurity components in low concentration levels less effected by the matrix but more by the dilution are shown down to 2-ppm levels.

Dynamic and time responses as well as possible memory effects are demonstrated on a methanol-hydrogen reformer.

### **Introduction**

The way to create electric energy from a liquid fuel through fuel cells incorporates several physical phase transitions. Liquid fuel is gasified first, then converted into low molecular weight gaseous compounds like H<sub>2</sub>, CH<sub>4</sub>, CO, CO<sub>2</sub>, and H<sub>2</sub>O via catalytic reactions. Some of these compounds remain gaseous; others are dissociated into ions in a liquid phase and react to new liquid and gaseous compounds on the electrodes, before they leave the exhaust system. Research and development of these systems need the online knowledge of liquid and gaseous distributions and their mass throughput of all compounds in all different stages.

## The Fuel Cell Technology

The main parts of the whole fuel cell system consist of the fuel-processor, the fuel cell itself and finally the electric drive (figure 1).

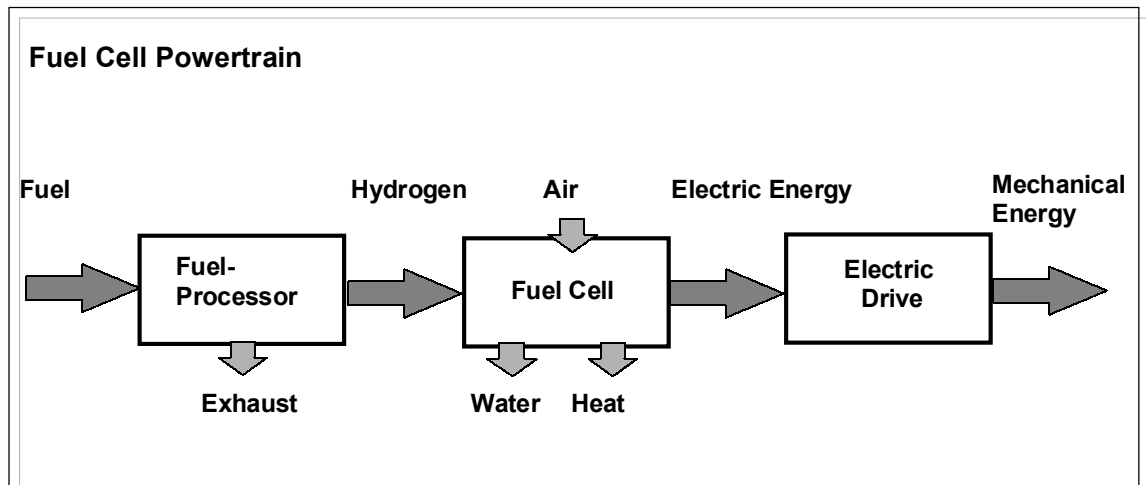


Fig. 1 Schematic structure of a fuel cell powertrain

In the fuel processor occurs the production of hydrogen out of the liquid fuel together with the cleaning of the gas (removal of CO). This happens in three steps via a reforming reaction first, a shift reaction second and a prox-reaction third. Figure 2 describes the process of the formation of hydrogen gas out of methanol in a fuel processor.

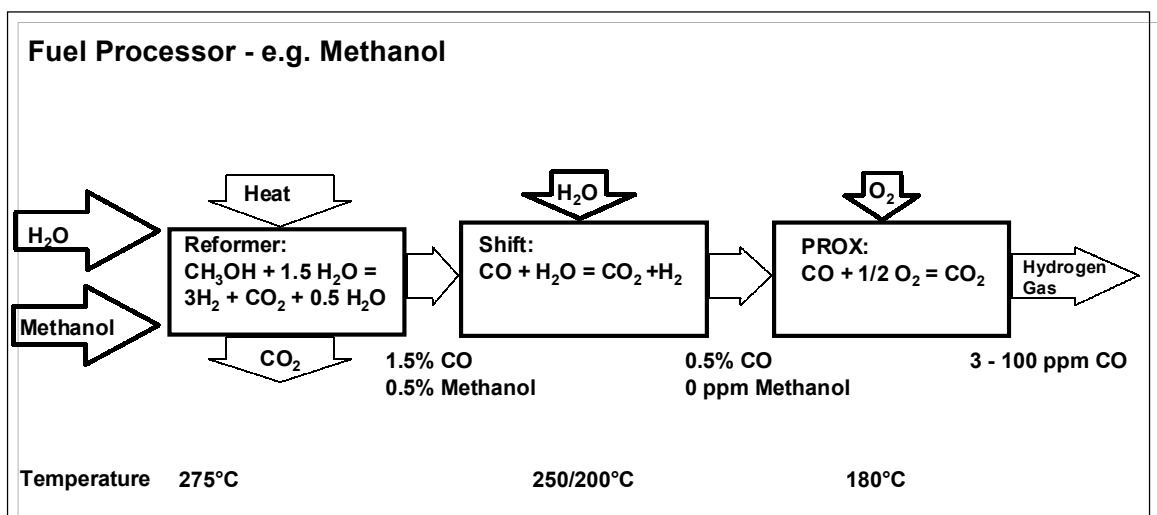


Fig. 2 Typical reactions in a fuel cell processor, e.g. methanol

However, the intrinsic aim of this technology is the production of electricity. It is reached in the fuel cell where hydrogen and oxygen are reacting at electrodes separately under the production of water, oxygen, electricity and heat (figure 3).

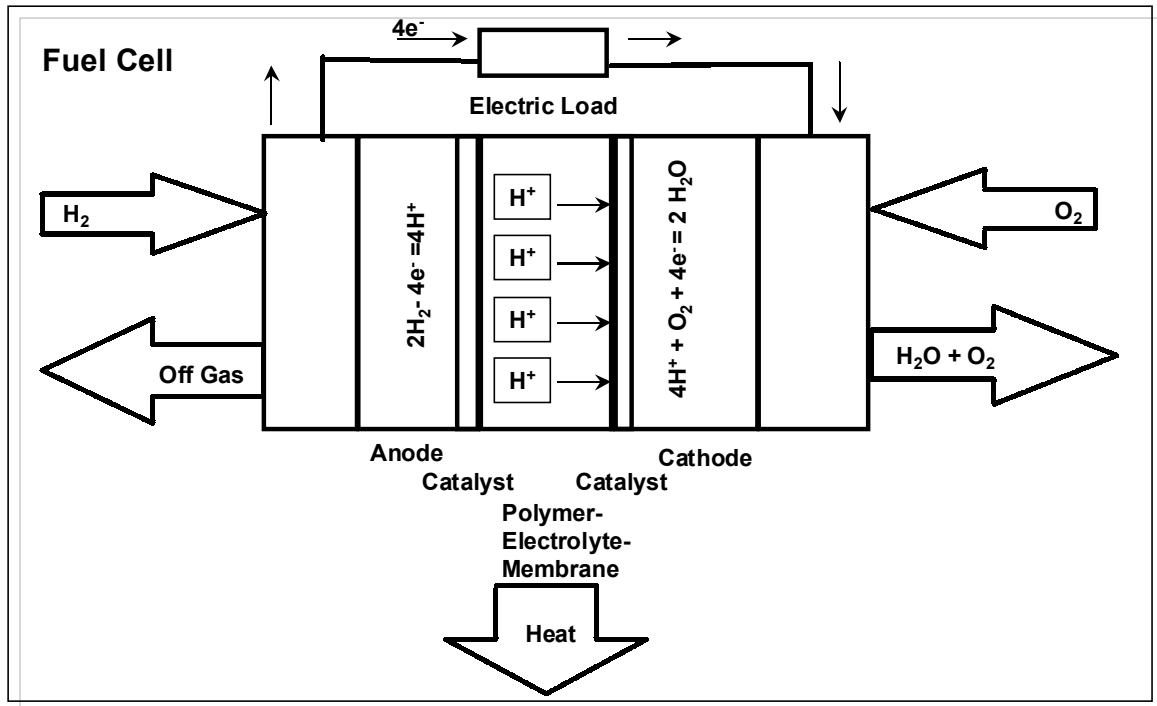


Fig. 3 Typical electrochemical reaction in a fuel cell

The utilization of this electric energy in automotive as well as non-automotive applications will probably arise in the nearer future because of the high efficiency, low emissions of the engines and big reductions of noise.

#### Expected gas concentrations - requests on the gas analyzing system

The estimated wide range of some emitted compounds during the whole process, e.g. methanol-reformation and fuel reformation in the fuel cell system is described in table 1.

Tab. 1 Range of product distribution using different reforming processes

		min [rel%]	max [rel%]
reforming of methanol	H <sub>2</sub> O	0	50
	methanol	0	70
	O <sub>2</sub>	0	25
	N <sub>2</sub>	0	80
	CO	0	2
	CO <sub>2</sub>	0	30
	H <sub>2</sub>	0	45
reforming of petrol	H <sub>2</sub> O	0	80
	O <sub>2</sub>	0	25
	N <sub>2</sub>	0	80
	CO	0	20
	CO <sub>2</sub>	0	25
	H <sub>2</sub>	0	45
	CH <sub>4</sub>	0	2
limiting values of SULEV ( <i>Super Ultra Low Emission Vehicles</i> ) – tailpipe emissions			
CO	< 50 ppm		
HC	< 5 ppm		
NO	< 5 ppm		

The wide range of values given in table 1 explains clearly why a dilution system for the measurement of all gases is necessary, finally to remain in the linear range of the measurement system.

#### **Gasmatrix inertisation by a gas and pressure independent dilution system for analytical fuel cell applications - V&F-Inertizer**

The analysis of the individual gaseous compounds demands many important features:

- A) Quantitative measurements of all bulk gas components with time resolution of less than 1 sec cycle time, especially for startup and dynamic load change of cell output - bulk gases include H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O, not reacted fuel
- B) Analysis of gaseous reaction products in exhaust
- C) Trace impurities in ppm levels e.g. CO, hydrocarbons from methane to naphthalene, C1 to C3 acids, C1 to C3 aldehydes and C1 to C4 alcohols, as well as inorganic gaseous compounds, e.g. NO, SO<sub>2</sub>, H<sub>2</sub>S

From the above it is easy to see that gas analysis in fuel cell systems is more complex than exhaust gas monitoring of internal combustion engines, not in number of

compounds, not in lower detection levels but in the physical properties of the gases involved. Only when a good gas conditioning, or as we call it a „gas matrix inertisation” is done prior to all analytical equipment, reliable and reproducible measurement values can be obtained.

This necessity of matrix inertisation in fuel cell applications arises from five main physical principles in gas analytical theory.

### **1) Solubility of gases in liquids**

Process gas in fuel cells contains high amounts of water. Any cool spot in the gas transfer line falling below the dew point will cause gaseous products like methanol, formaldehyde and acids which can immediately condense into the liquid phase. For that reasons the reduction of the dew point temperature by diluting the matrix is a high necessity in this application.

### **2) Secondary reactions in gas transfer line.**

Sample flow rates from fuel cell systems must be kept at typical ranges from 0,5 to some liters per minute. One reason for this restriction is because of the gas analytical device that should not load up the reformer at very low load conditions of the power train. Another reason is not to bring dangerous gas mixtures carrying high hydrogen concentrations in lesser-controlled and lesser protected areas of analytical instrumentation (see point 5).

Temperatures of heated gas transfer lines must be high (above 170 °C) to avoid condensation at high water concentrations.

Transportation of high hydrogen levels is normally done in stainless steel lines and not in Teflon lines to keep losses of hydrogen by diffusion through organic based materials low.

This setup of constrictions to gas lines and transport does result in undesired secondary reactions. Stainless steel does show some catalytic activity for certain reactions at 200 °C. Small flow rates result in residence times of the gases of typically 300 msec per meter gas line (inner diameter of 4 mm). This allows the gas particles to undergo many collisions with the stainless steel surface until they reach the analytical instrument. A high hydrogen concentration in the sample gas enhances this effect due to the low overall viscosity of the gas mixture.

For 1 Vol% methanol in air we found a decomposition to 8 % Formaldehyde at 200 °C and 1,5 sec residence time and 11% decomposition at 3 seconds residence time in the gas lines. For 100 ppm NO<sub>2</sub> in N<sub>2</sub> we find 3,4 % decomposition of NO<sub>2</sub> into NO at 1,5 sec residence time. For gaseous H<sub>2</sub>SO<sub>4</sub> we have a recovery of only 15 % at the end of the gas line. However not only decomposition is triggered in gas lines. NH<sub>3</sub>, NO<sub>2</sub>, SO<sub>2</sub> mixtures start to react readily under the presence of high H<sub>2</sub>O concentrations to ammonium hydroxide, nitrous acid and sulfurous acid.

### 3) Effects of strong matrix variations in analyzers

Every analyzer (with the exception of a scale which uses gravity as analytical principle) uses electrodynamic principles for the analytical detection, e.g. GC, UV emission, IR absorption, NMR system, high resolution mass spectrometers and even the chemistry in Draeger tubes. Basically the operation of all analyzers consist of a) energy transfer to the compounds under study, b) a selective device to separate the compounds and c) a detecting device for the response of the compound to the initial energy input. The analysis of a compound in a matrix needs a very high separation against the matrix and no system can ignore a matrix variation up to 100 %. The reason for this lies very deep, but very basic in the order of magnitude of physical constants, e.g. electron charge, atomic mass, speed of light and coupling (or better non coupling) of nuclear and coulomb forces. Simply all the atoms and molecules are too much alike in their properties like polarizability, dipole moments, absorption coefficients, ionization potentials, electronegativity, proton affinities and molecular weight. In other words, they do not differ enough in the gasmatrix and hence cannot be treated as isolated from the matrix.

For calculating the trajectory of a space shuttle, you may neglect all other forces like coulomb forces, weak and strong interactions. In this case working with the gravitational force alone, treating all masses as mass points and using rather simple equations is possible, even not curved space with all its complex tensor analysis must be considered (because the shuttle is a very slow moving object) to predict a precise landing on the moon.

For monitoring the startup of a methanol gas reformer in the fuel cell gas system, the gas-analyzing unit has to run through dramatic matrix changes which are coupled to the behaviour of all species we want to determine by their electrodynamic interactions. Air (20 % O<sub>2</sub>, 80 % N<sub>2</sub>) is changed to 5 % O<sub>2</sub>, 20 % N<sub>2</sub>, 60 % methanol, followed by 20 % H<sub>2</sub>, 2 % CO, 20 % CO<sub>2</sub>, 10 % N<sub>2</sub>, 10 % H<sub>2</sub>O, 30 % methanol, 2 % formaldehyde until eventually 55% H<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub> are reached.

### 4) Effects of hydrogen in analyzers

Reformers are capable to produce up to 65 % hydrogen. From all physical properties of gaseous compounds like heat transfer, diffusion constant or viscosity, hydrogen has the very extreme of them.

These differences compared to other gases lead to dramatic changes of pressure readings in many types of pressure gauges, different pumping capacities of pumps, different flow characteristics in flow measurement devices, the changes of concentrations and demixing of mixtures in hydrogen at orifices.

As hydrogen is a strong reducing agent all detecting devices based on charged particle detection like ion multipliers, current detectors, electron multipliers experience a strong shift in sensitivity.

## 5) Moving the sample gas from the explosive limits

Hydrogen gas mixtures are known to have the widest range of explosive limits in respect to their mixing ratios. They may range from 5,6 % to 85 % H<sub>2</sub> depending on pressure and temperature. Reaction barriers to autoignition are also reduced dramatically at the presence of traces of certain metals. Gas transfer lines at 200 °C, stainless steel surfaces and realistically some catalytic active particles on gas inlet filters represent a high risk for the autooxidation of H<sub>2</sub> containing mixtures. Low gas flow rates do limit the overall energy transfer of the gasmixture and hence the hazards to people as gas inlet systems, pressure controllers, pressure reducers and control valves of the instruments can be destroyed in seconds without being recognized by the operator.

Summarizing the basic experimental problem:

One cannot calibrate an analyzer for a CO, CO<sub>2</sub>, O<sub>2</sub> concentration based in N<sub>2</sub> as background and assume to find an accurate reading of these levels when the gas mixture CO, CO<sub>2</sub>, O<sub>2</sub> is based in a background of 50 % H<sub>2</sub> and 35 % water.

Depending on the instruments operation principle and technical setup one may find readings of 20 to several hundred percent of the actual values.

Matrix effects are highly nonlinear and it would overdue the scope of this paper to discuss the mathematical functions for this non-linearity. A simple image may be given by the following considerations.

For accuracies in gas measurements better then 10 %, a gas analysis system should vary the background matrix not more then plus minus 15 % otherwise to be recalibrated in the new matrix.

High matrix variations can only be handled by the:

### “V&F gas matrix inertizer“

A gas matrix inertizer is not simply a dilution system as it might appear at first sight. Several different dilution systems are commercially available and applied for different analytical fields. They are based on physical principles of gas flow patterns, critical jets, diffusion or permeation or flow monitoring and mixing. All these principles do not allow a wide variation in the matrices as they only dilute a gas steam in another gas stream.

For the proper handling of fuel cell gases a device has to compensate three main parameters:

- A) Pressure variations from 0,1 to 1,5 bar
- B) Hydrogen levels from 0 to 60 Vol%
- C) Water vapor levels from 1 to 60 Vol%

The only way to handle these parameters of the gas and thereby dilute its concentrations, is a radical phase transition of the gas into a high vacuum creating a gas with an ideal gas behaviour.

This is done by a step by step mixing with an inert gas component and reducing the pressure of the gas back to atmospheric levels, stepwise.

Fig 4 shows the basic components of the inertizer system.

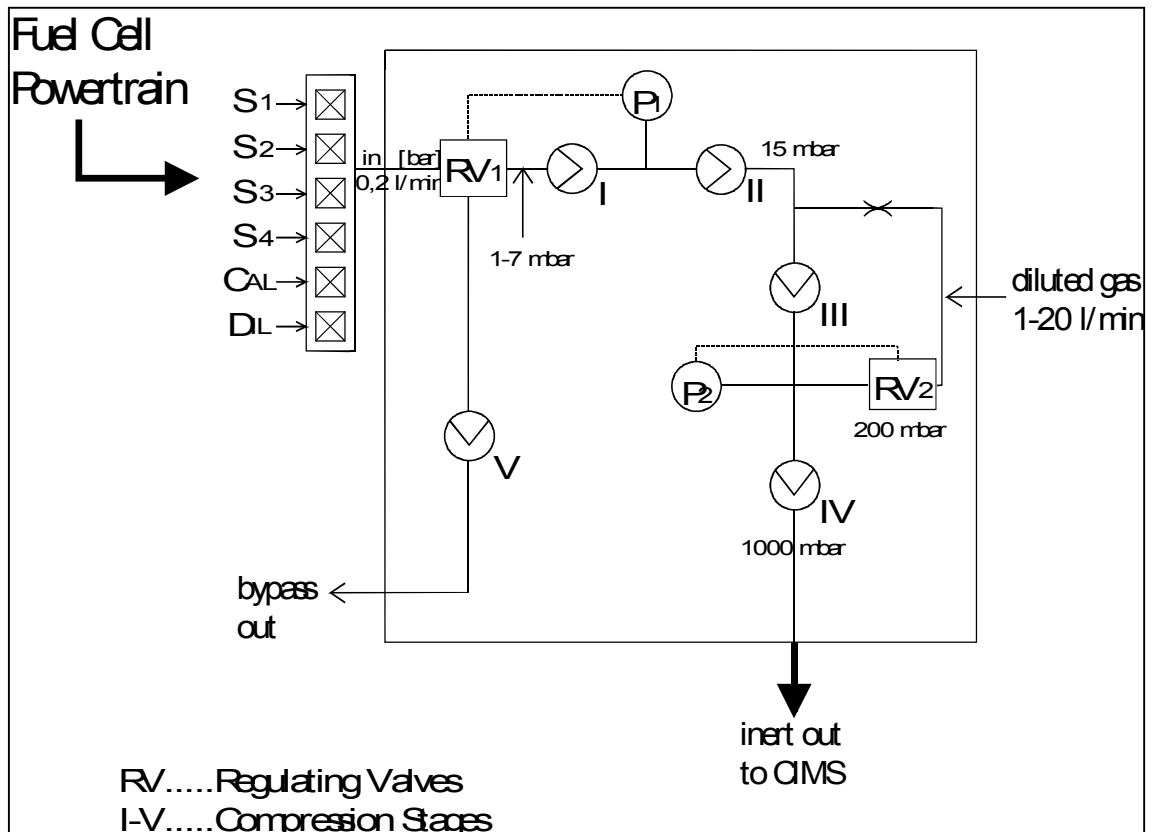


Fig. 4 Schematic setup of the "V&F gas matrix inertizer"

This pressure and matrix independent dilution system (figure 4) operates in the range from 5/1 up to 50/1. It contains a regulating system taking 200 ml of sample gas, transforming this gas into a pressure range of 1 - 7 mbar at 120 °C. Thereafter four compression stages with intermediate dilution increases the gas pressure back to atmospheric pressure at temperatures of 60 °C.



### Analysis of the gaseous compounds emitted by the fuel cell system

The gases of the fuel cell system can be analyzed with the “V&F-CI-MS” – a mass spectrometer for continuous online analysis.

The technology and the main features can be described as follows.

The detection principle of the instrument is the analysis of the molecular weight of the substances. Sample gas is introduced to a high vacuum chamber and transformed into ions that are subsequently mass selected by electromagnetic fields and counted in a particle detector (figure 5).

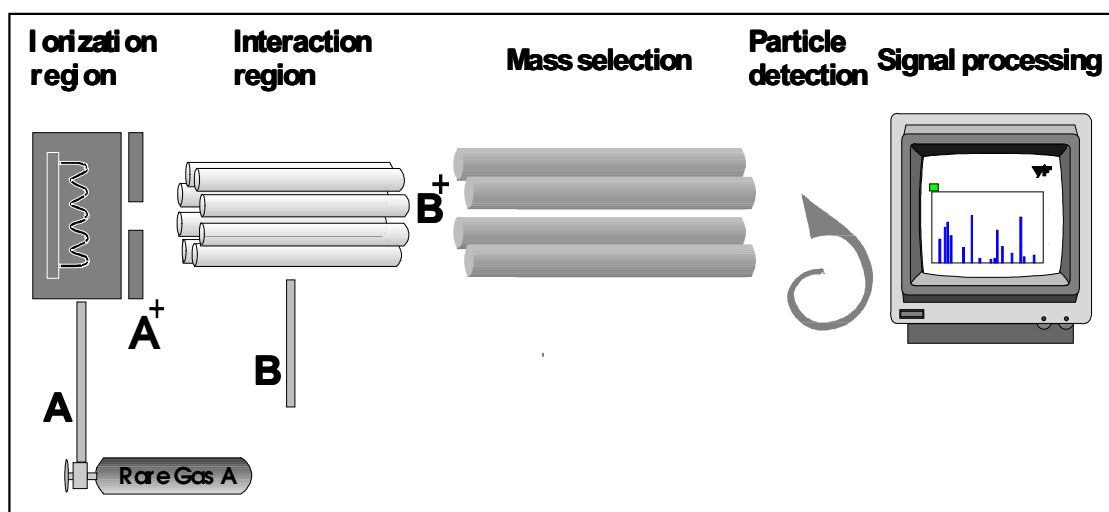


Fig. 5 Schematic setup of the “V&F-CI-MS”

As different molecules may carry the identical molecular weight, like e.g.  $N_2$  and  $CO$  or formaldehyde and  $NO$  or  $CO_2$  and  $N_2O$ , the instrument uses different ionization levels (i.e. different primary ion beams) to distinguish between mass identical molecules.

Every molecule has an individual energy that is necessary to remove an electron and thus convert the molecule into an ion. An additional separation effect is gained through the formation of defined fragment ions. The interaction of the ion beam with the gas sample results in well-defined product ions. A krypton ion beam with 13,9 eV energy, for instance, separates the mass identical molecules  $N_2$  (14,2 eV) and  $CO$  (13,7 eV).

The mass identity of methanol  $CH_3OH$  and oxygen  $O_2$  on mass 32 is solved by ionization with xenon (12,2 eV) that generates an  $O_2^-$  ion on mass 32 and a  $CH_3O^+$  ion on mass 31. Larger hydrocarbons, for example, need ionization energies in the range of 10 eV created by a mercury ion beam.

The method of ionization by different energy levels allows a multiple use of the mass scale and to see molecules from different perspectives (table 2).

Tab. 2 General technical data of the "V&amp;F-CI-MS"

Gas response time:	T 90 $\cong$ 30 msec
Gas transfer temperature:	60° - 210 °C
Measurement cycle / Detection level (ref.: benzene)	1 msec 0,5 ppm      10 msec 0,05 ppm 5 sec 0,05 ppb
Dynamic range:	1:10 <sup>4</sup>
Operation	Selection of up to 40 channels per set from application orientated control library scripts

### Applications for the combination of "V&F-gas inertizer and Airsense 2000"

Figure 6 demonstrates speed, matrix independence and a high linearity for the measuring range 0,01 to 40 Vol% for the gaseous compounds CO<sub>2</sub>, CO and O<sub>2</sub> in four different matrices (table 3).

Tab. 3 Different concentrations of the applied matrices

Mixture	A [%]	B [%]	C [%]	D [%]
CO <sub>2</sub>	0	10	23	0,075
CO	0	0,01	0,2	0,03
O <sub>2</sub>	0	0	0	0,5
H <sub>2</sub>	0	60	30	0
N <sub>2</sub>	100	30	46,8	99,4

Individual monitoring times for the compounds were selected to CO<sub>2</sub>-30 msec, CO-200 msec, O<sub>2</sub>-30 msec. So the overall cycle time was roughly 300 msec. All four different gas cylinders were connected to the inertizer system and a sequencer selected bottle after bottle. Gas response time of the total system was less than 150 msec. The given data (fig. 6) demonstrate the high accuracy of detecting the individual components nearly independent on the chosen matrix.

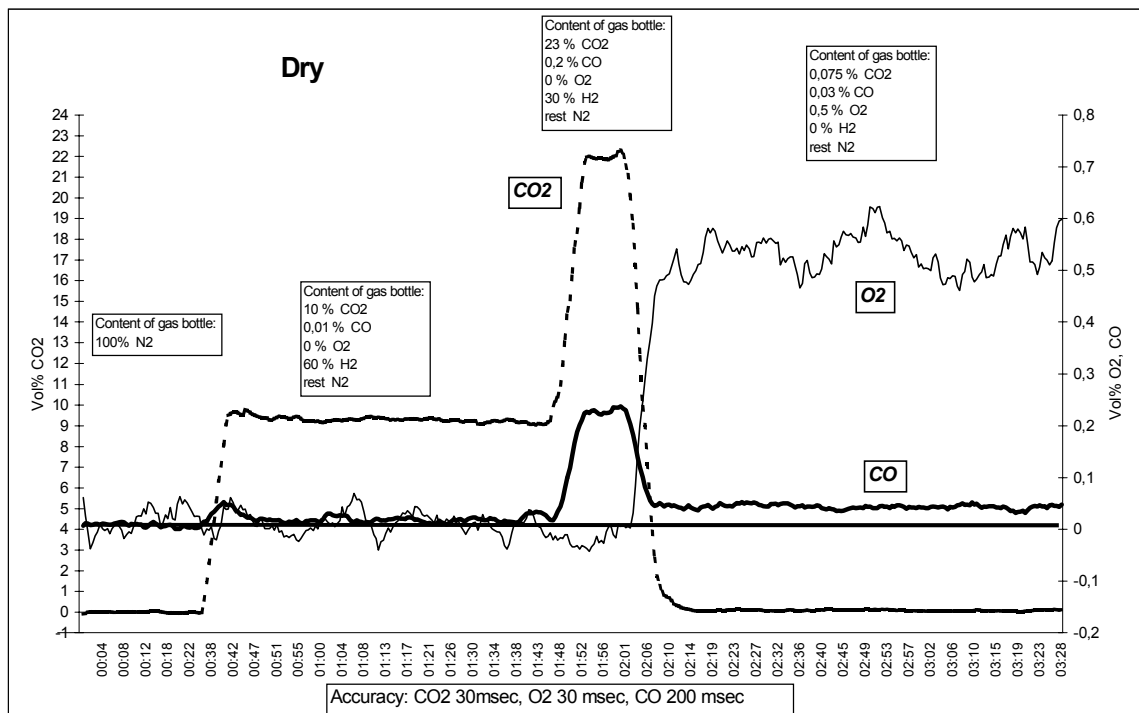


Fig. 6 Concentrations for CO<sub>2</sub>, O<sub>2</sub> and CO in various matrices

Figure 7 demonstrates the water capability of the overall analyzing system. A water vapour was generated from a temperature controlled saturator in the range from 0,8 to 65 Vol% H<sub>2</sub>O, where preheated air was passing through at 1 liter/min picking up the gaseous water thereby. Water saturated air was transferred via 2 meter heated gasline to the inertizer.

The proof of the monitoring capability was done by the simultaneous monitoring of N<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub>O and controlling the sum to 100 Vol%.

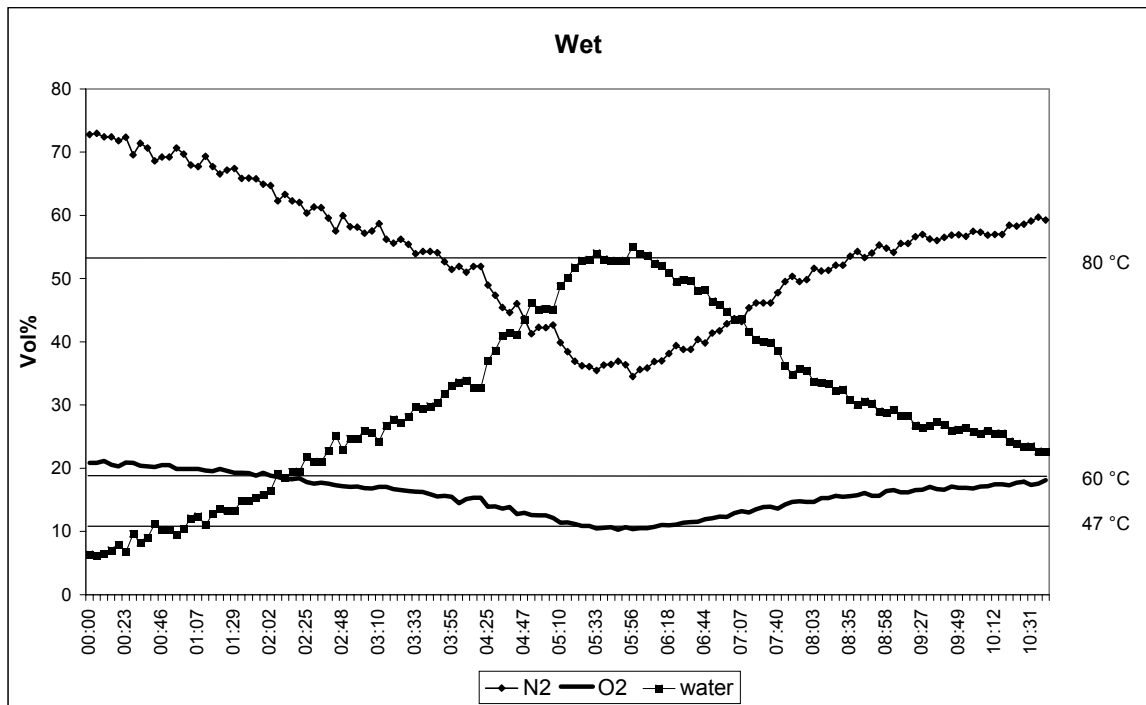


Fig. 7 Water capability of the overall analyzing system

## Conclusions

Research and development of modern fuel cell technologies demand extreme capabilities to analytical equipment. Coupling an inertizing system to a sensitive monitoring technique is the physical layout for an accurate, rapid, highly dynamic and matrix independent bulk gas and trace gas monitoring technique. Experience over the next years may refine individual technical elements but the operating principles will remain as described in this work.