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HYDROCARBON MONITORING AND INSTRUMENT CALIBRATION METHODS

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ABSTRACT

For VOC monitoring several different detectors are well known, for example semiconductor based detectors, pellistors, optical detectors with infrared light, catalytic combustion detectors, flame temperature detectors, photoionisation detectors and flame ionisation detectors (FID). The most widely used detector is the FID.

THE FLAME IONISATION DETECTOR

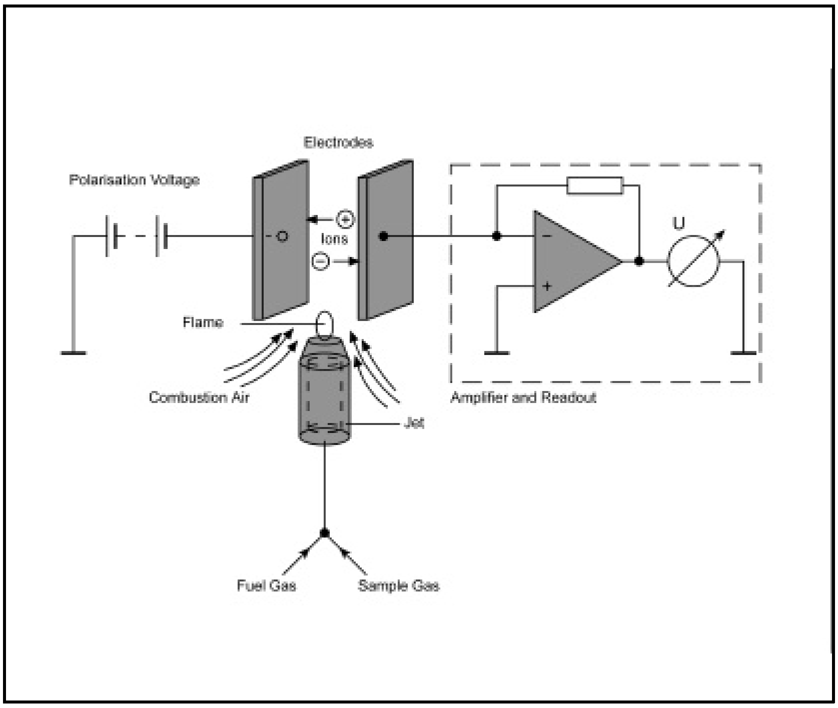


Fig.1 FID-Pinciple of function Z0267502.TIF

The FID works with a flame which burns on the top of the jet. The usual fuel gas is pure hydrogen. The area around the flame is flooded with clean air which contains oxygen necessary for burning. An electric field is applied to the flame with two electrodes. The polarisation voltage, approx. 200-300V is connected to the first electrode and creates an electric field. An amplifier with very high current sensitivity is connected to the second electrode. The distance between the electrodes is approx. 1cm. So if the flame is out, a current between the electrodes is not present because the isolation of the air between the electrodes is very high. After ignition the flame causes an ionisation of the air between the electrodes and a low current with several pA is in existence. The name of this current is basic ionisation current.

If oganic compounds are fed, in addition to the fuel gas, into the flame, they will be cracked and stripped and at the end of the oxidation process CHO^+ ions are produced. The quantity of the CHO^+ ions is absolutely proportional to the quantity of the non oxidised carbon atoms in the organic carbon compounds. Pre-oxidised carbon atoms are only partially registered. Pre-oxidised are carbon atoms which have a bond to an oxygen atom, for example one oxygen atom of Methylethylketone CH_3-CO-C_2H_5 . Carbon monoxide and carbon dioxide do not cause CHO^+ ions. Chlorinated compounds, for example perchlorethylene, cause higher signals which theoretically correspond to the quantity of carbon atoms in the molecule. The specific sensitivity depends on the substance and is called the response factor. Specifically, the response factor is the quotient of the signal outputs between a reference substance and measured substance with the same quantity of carbon atoms. The reference substance is usually propane.

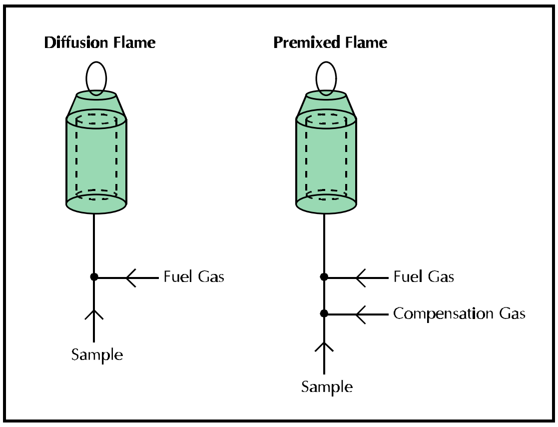
DIFFERENT FID DESIGN

Flame types

In practice several different FID solutions exist. According to the jet inlet gases, two different flame types are well known: the diffusion flame and the premixed flame.

In the diffusion flame, the total flow to the jet contains only sample and fuel gas.

In the premixed flame, in addition to these two gases, a compensation gas is mixed, usually air or pure oxygen. The reason for this solution is the attempt to minimize the oxygen synergism of the FID.



The geometry

The geometry of the detector determines its analytical qualities, like linearity, oxygen synergism and specific sensitivity to the different single organic components. So each manufacturer of VOC-analyzers has developed his own detector to minimize these errors.

At Bernath Atomic there are two different Detectors in existence: The FID with semicylinder and the FID with the explosion protected class Ex(d).

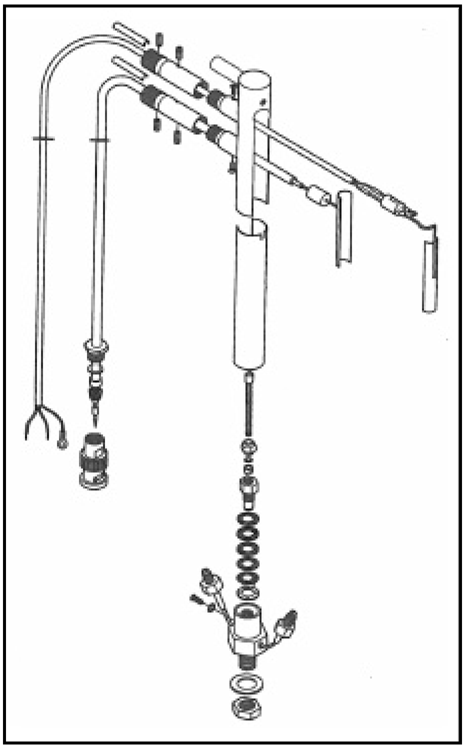


Fig. 3 FID with semicylinder electrodes

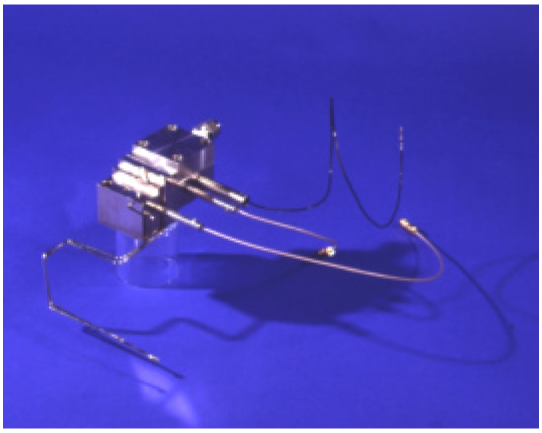


Fig. 4 Ex(d) FID

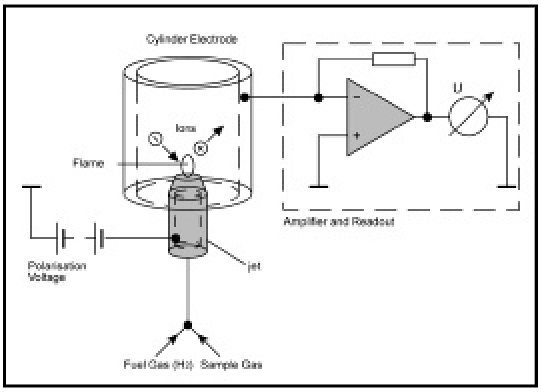


Fig. 5 Ex(d) FID principle of operation

However, it is not only the mechanical dimensions which determine the analytical properties. The quantity of the sample gas and especially the quantity of the fuel gas are also crucial.

FID ERRORS

Linearity

Generally FI detectors have a good linearity within a wide range. The detection limit is usually 10-30ppb. So several manufacturer offer a lowest measuring range of 0-1ppm. The highest possible range is 0-100000ppm (0-10 vol%). In this decade several FIDs show a drop in sensitivity of between 5-50%

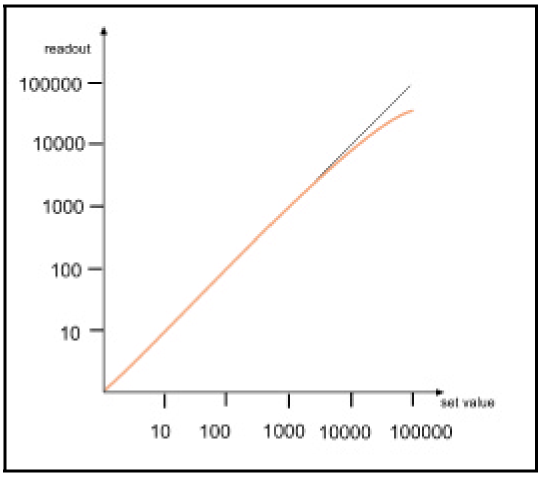


Fig. 7 Drop of the sensitivity

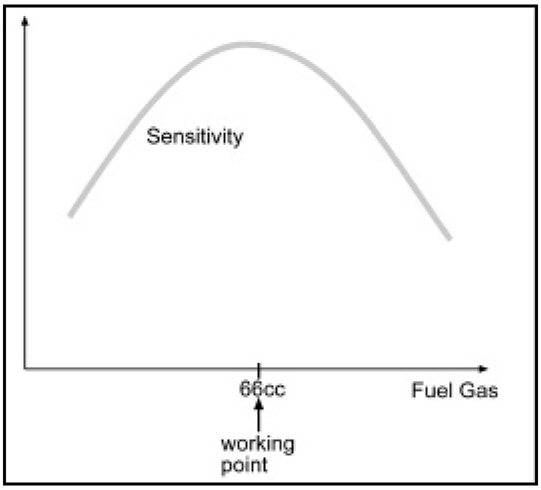


Fig. 6 Sensitivity depends on the fuel gas flow

O2 Cross sensitivity (O2 synergism)

All FIDs display with constant organic carbon concentrations and by fluctuation of the oxygen concentration in the sample, different signal values.

Notable is the reduced sensitivity of up to 20% by middle oxygen concentrations of around 10%. This discovery is therefore especially important because most incineretors have similar oxygen concentrations in their stack.

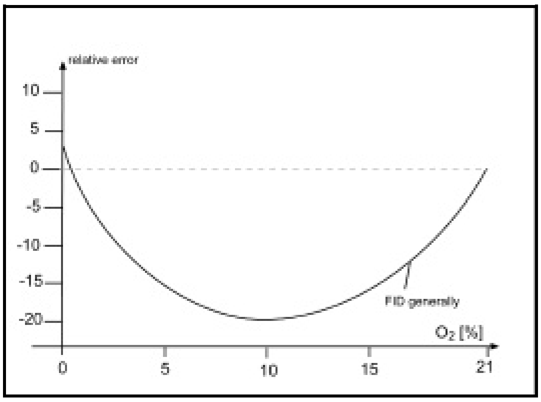


Fig. 8 Oxygen synergism

So it is an important task for each manufacturer to minimize this error. The possible methods are:

- premixed flame,
- make-up gas in the fuel-gas and
- suitable jet material and geometry.

The premixed flame has already been discussed. The addition of compensation gas minimises cross sensitivity to nearly zero per cent.

Make up gas is a non-combustible gas such as helium. Instead of pure hydrogen, a hydrogen-helium mixture is used for fuel gas. The results are satisfactory because the error is less than approx. 3%. However, the disadvantage of this solution is the high consumption of fuel gas and the related costs of these specific gases.

With suitable jet material and jet geometry it is also possible to achieve similar error values to operation with make-up gas.

One example is the jet of the EuroFID

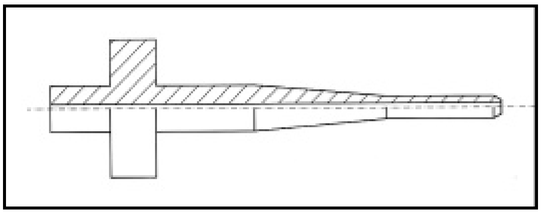


Fig. 9 Jet of the EuroFID

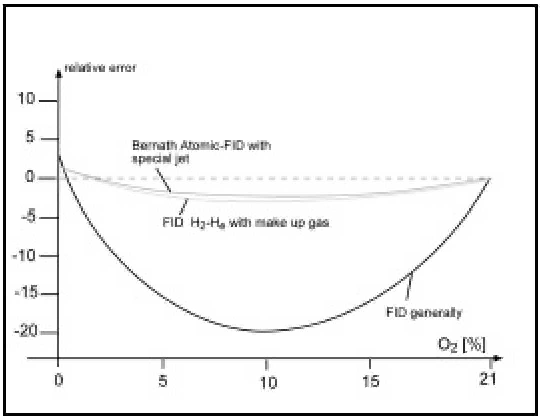


Fig. 10 Oxygen synergism effects of different methods

Total error of a premixed flame

At this point we should talk also about the disadvantages of the premixed flame. This solution creates acceptable oxygen synergism values, but the cumulative other errors are considerable being between 10-30%.

The picture is extracted from a research report of FIDs by Hartmann&Braun

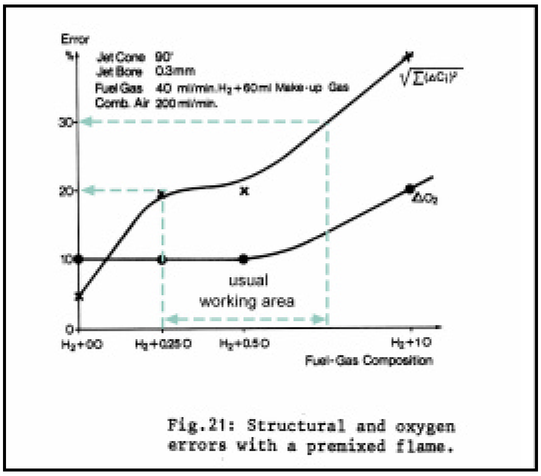
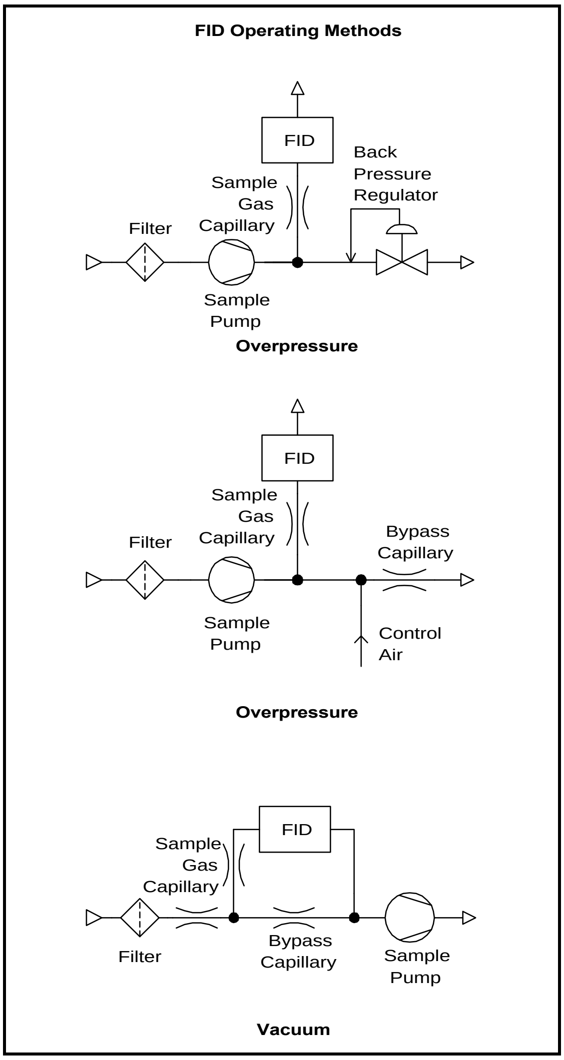


Fig. 11 Total Error of a premixed flame

SAMPLE CONDITIONING METHODS IN THE INSTRUMENT OF THE FID

The FID is a mass-specific detector. In other words, the signal of the detector is dependant on the quantity of the organic carbon compounds. For good repeability a constant sample gas mass flow is therefore important. The FID itself needs only a few ml of sample gas per minute. For industrial sampling this volume is not enough because the response time would be too long. So a bypass system should be used. The main flow is usually 1-3 l/min.

The first industrial hydrocarbon analyzer was developed by Beckman Instruments, USA (today a subsidiary of Rosemount, USA) to measure ambient air concentrations. The sample pump sucked the sample through the filter. A part of the sample flows through the sample gas capillary to the FID. If the pressure on the sample gas capillary is constant, the sample flow to the FID is also constant, apart from the effect of the barometric pressure changes on the exhaust of the FID. To measure in ambient air it was not necessary to heat up all sample ways.



After industry's request to measure hydrocarbon emissions from vehicles as well, it became necessary to heat the sample ways like filter, sample pump, sample gas capillary, FID and the back pressure regulator in order to eliminate condensation of the sample. The temperature was limited by the maximum ambient temperature of the back pressure regulator. Manufacturers like ITT Conoflow, Fairchild etc. produced regulators for up to 94 degrees C ambient temperature, but not higher.

However, certain measuring tasks demanded a heating of up to 190 degree C. Therefore, a new solution was born: the method with control air. Fluctuations in sample flow and pressure are now compensated by control air in the bypass circuit behind the sample take off point and ahead of the bypass capillary. The control air is added to the sample and its flow rate is inversely proportional to the sample flow rate. And it is not necessary to heat up the pneumatic or electropneumatic regulator for control air (no depict). All other parts can be heated up to 200 degree C. The crucial point of this solution is the pump. Usually all sample pumps have moving diaphgrams and elastomers which very quickly tire at 200 degrees C.

To eliminate this disadvantage it was necessary to look for a pump without moving parts. But for the time being only a vacuum pump called ejector was known. This is put behind the FID and creates a vacuum inside the detector. For a constant flow through the sample gas capillary a constant differential pressure on the bypass capillary is necessary. For the regulation of this differential pressure several solutions are well known, but they will not be described here. Several hydrocarbon analyzers are working with this method.

The lastest development of FID operation method is to work with a double stage jet which is a pump without any moving parts This has the practical advantage that the FID is working in an overpressure range.

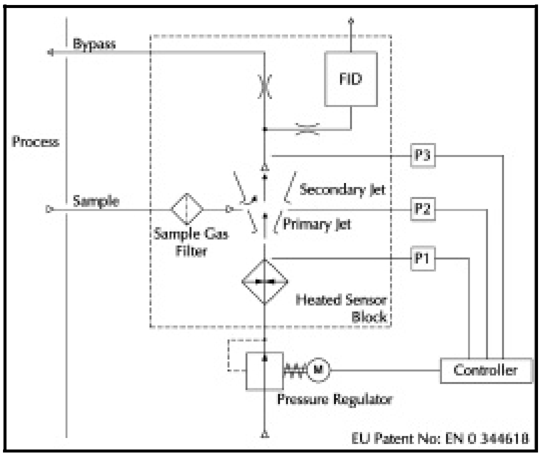


Fig. 13 The latest development:
EuroFID

Instrument error depends on the FID operation

The difference between overpressure and vacuum operation is shown by the following diagram: the vacuum operation has approx. 10% measuring error by the usual working point of -0,5 bars.

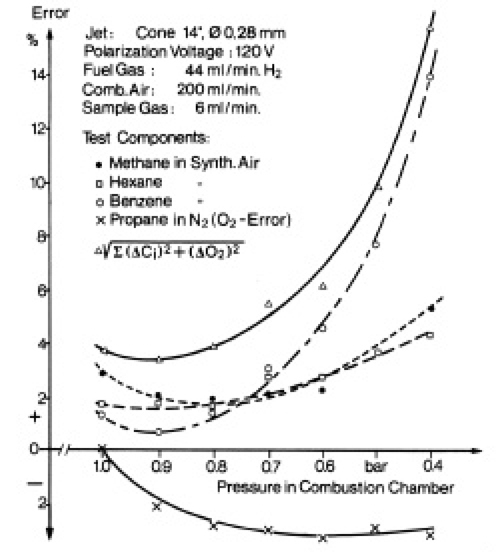
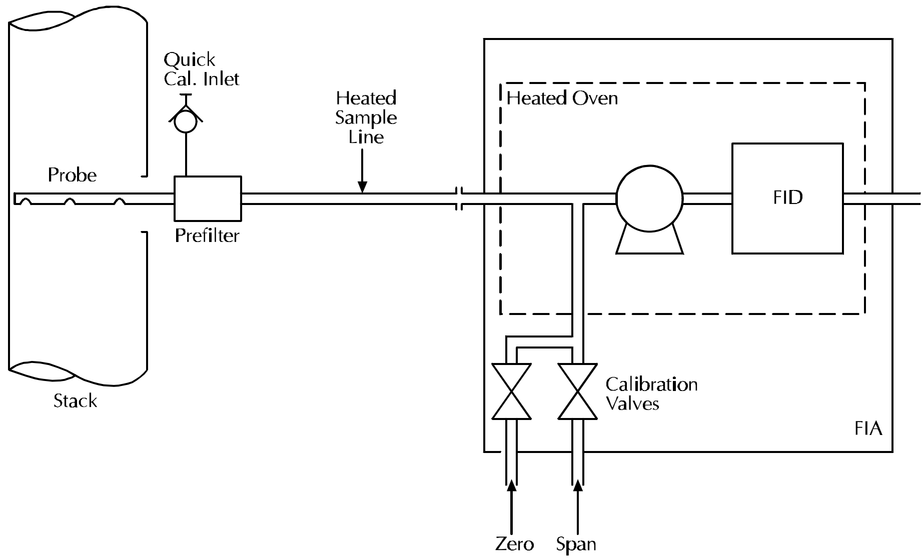


Fig.42: Trend error with vacuum operation of the FID.

The picture is extracted from a research report of FIDs by Hartmann&Braun

CALIBRATION METHODS

The practical instrument installation for emission monitoring is as follow:



A gas sample is extracted from the source through a heated sample line, and if necessary a glass fibre prefilter, to the flame ionisation analyzer (FIA). If the sample contains condensable components, heating of the sample way is necessary.

The analyzer operates according to the principle of comparison. The unknown sample gas concentration is compared with the known concentration of a calibration gas.
It will be assumed that the instrument has a linear characterisation. So the calibration is made with two calibration gases. Usually the first gas is clean air without any concentrations of organic compounds. This gas is therefore called zero gas. The second gas, called span gas, contains organic compounds with a known concentration, for example 80ppm propane in synthetic air (20% oxygen, 80%nitrogen). The quantity of the calibration gases is slightly more than the transfer volume of the pump. The surplus gas flows back into the process. Additionally a check calibration point is available at the prefilter. With it, it is possible to check the filter and heated line properties.

Results are reported as
1. volume concentration equivalents of the calibration gas or as
2. mass concentration or as

3. carbon equivalents or as
4. per cent of low explosion levels.

Usually calibration gases are supplied with a volume concentration certificate, for example 80ppm propane. Propane is the usual calibration gas for FIAs, but any other gas that has a good stability in the cylinder is suitable.

If the sample contains only one organic substances, for example ethylenoxide, the best way is to go around the response factors of the FID, to use the same quality of the calibration gas as the sample.

Calibration by volume concentration:

Example: Cal. Gas is 80 ppm propane

During the calibration the instrument range should be selected to 0-100 and the readout should be adjusted to 80% of the full scale.

If after the calibration the measured value is in the first range (0-10) for example 60%, then 6ppm propane equivalent will be measured.

If the compound of the sample is well known, it is possible, to measure the sample gas concentration in ppm. For it the right calibration value is:

$$(1) \qquad c_V = c_{VK} \cdot \frac{n_{CK}}{n_C}$$

C_V	calibrating value for volume concentration measurement in ppm
C_{VK}	volume concentration of the calibrating gas in ppm
n_C	number of c atoms in the molecule of the sample substance
n_{CK}	number of c atoms in the molecule of the calibrating substance

Example:
our calibration gas is propane C_3H_8 with 80ppm. We want to measure methane CH_4.
The right calibration value is:

$$c_V = 80 \cdot \frac{3}{1} = 240$$

This value can be adjusted in the third meassuring range 0-1000 to 24% of the full scale.

If the response factors are well known, this calibration value can be corrected according the equation as follow:

$$(2) \qquad c_V = c_{VK} \cdot \frac{n_{CK} \cdot r_{CK}}{n_C \cdot r_C}$$

r_C response factor of the sample substance
r_{CK} response factor of the calibrating substance

For our example the reference substance is propane with a response factor of 1. The response factor for methane is 1,22. This value was measured by TÜV with a Bernath Atomic analyzer. According to this response factor, the calibration value is:

$$c_V = 80 \cdot \frac{3 \cdot 1}{1 \cdot 1{,}22} = 196{,}7$$

Calibration by mass concentration “mg/m3"

The calibration is based on volume concentration measuring. To the equation (2) will be added only the mass of 1ppm calibration gas as follow:

$$(3) \qquad c_m = c_{VK} \cdot \frac{n_{CK} \cdot r_{CK}}{n_C \cdot r_C} \cdot \frac{M}{V_{mol}}$$

c_m calibrating value for measuring the mass per unit volume in mg/m^3

M molar mass of the calibration gas in g/mol
V_{mol} molar volume under standard conditions (= 22.41 l/mol)

To our discussed example can be add:

Molar mass of propane: $C3H8$ -> $3 \times 12{,}011 + 8 \times 1 = 44{,}03$ g/mol

The quotient: 44,03/22,41 = 1,96 mg/m^3

The calibration value is:

$$c_m = 80 \cdot \frac{3 \cdot 1}{1 \cdot 1{,}22} = 196{,}7 \cdot 1{,}96 = 385{,}53$$

Calibration by carbon eqivalents “mgC/m^3"

The method is hardly any different at all to the calibration by mass concentration:

$$(4) \qquad c_c = c_{VK} \cdot \frac{n_{CK} \cdot r_{CK}}{n_C \cdot r_C} \cdot \frac{n_C \cdot M_C}{V_{mol}} = c_{VK} \cdot \frac{n_{CK} \cdot r_{CK}}{r_C} \cdot \frac{M_C}{V_{mol}}$$

c_c calibrating value for measuring the carbon concentration in mgC/m^3

M_C molar mass of carbon (= 12.011 g/mol)

Following our example:

$$c_V = 80 \cdot \frac{3 \cdot 1}{1,22} \cdot \frac{12,011}{22,41} = 105,43$$

If the instrument is calibrated to this value, the readout unit is mgC/m3.

Calibration by per cent of low explosion levels “%LEL”.

If we consider the mass concentration of the LEL in g/m3 and consider the drop of the LEL by increased temperatures we come to the equation from (3) as follow:

$$(5) \qquad c_U = c_{VK} \cdot \frac{n_{CK} \cdot r_{CK}}{n_C \cdot r_C} \cdot \frac{M}{V_{mol}} \cdot \frac{1}{c_{mU}} \cdot \frac{1}{10} \cdot \frac{1}{[1-0,0014(h-20)]}$$

C_{mU} mass per unit volume of the lower explosive limit in g/m^3_N
c_U calibrating value when measuring the lower explosive limit in %LEL
h process temperature in °C

Mixtures

The above mentioned equations can be used for mixtures too, but we should replace the mass, quantity of carbon atoms and response factor values with average values of the mixture.

The average molar mass value is:

$$(6) \qquad \langle M \rangle = \left(\sum_{i=1}^{n} \frac{\mu_i}{M_i} \right)^{-1},$$

$\langle M \rangle$	average molar mass g/mol
μ_i	relative mass share of the component i
M_i	molar mass g/mol

The average quantity of carbon atoms is:

$$(7) \qquad \langle n_C \rangle = \langle M \rangle \cdot \sum_{i=1}^{n} \frac{\mu_i}{M_i} \cdot n_{Ci}$$

$\langle n_C \rangle$	average value of the quantity of carbon atoms
n_{Ci}	quantity of carbon atoms of the component i

The average value of the response factors is:

$$(8) \qquad \langle r_C \rangle = \frac{\langle M \rangle}{\langle n_C \rangle} \cdot \sum_{i=1}^{n} \frac{\mu_i}{M_i} \cdot n_{Ci} \cdot r_{Ci}$$

$\langle r_C \rangle$	average value of the response factors
r_{Ci}	response factor of the component i

CONCLUSION

‘State of the art’ VOC analyzers work with overpressure operation in the detector and have a diffusion flame. Other solutions produce unacceptable measuring errors.

The instruments work with a comparison method. The accuracy of measuring results can never be better than the accuracy of the calibration gas.

The quality and concentration of the calibration gas is dependant on the measuring task.
If only one components or a mixture with well known components should be measured, the quality of the gases is the same as the sample. With it response factor calculations are eliminated.

Otherwise we use propane as the calibration gas. Usual readings are for emission monitoring in mgC/m3.

If the oxygen synergism of the instrument is not acceptable, and the oxygen concentration is well known and has a small influence, the calibration gas should contain the same oxygen value. In this way, the oxygen synergism is eliminated.

The concentration of the calibration gas is approx. 70% of the end of scale of the necessary measuring range for the measuring task.