

Determination of water in gases and liquefied gases with the 875 KF Gas Analyzer

Branch

Organic chemistry, chemistry; Pharmaceutical industry; Petrochemistry, biofuels; Plastics, photographic industry; Energy, power plants

Keywords

Titration; KF; coulometric; water content; gas; liquefied gas; endurance test; reproducibility; temperature influence; drift stability

Summary

The 875 KF Gas Analyzer is a **tiamo**[™]-controlled system for determining the water content in gases and liquefied gases. The analyzer module consists of a pipe system including four software-controlled magnetic valves, which allow the control of the sample gas and the rinsing gas flow. Additionally, an oven, a mass flow controller, the titration vessel with indicator and generator electrode (with diaphragm), and a coulometer are included in the module.

This document provides general information on the 875 KF Gas Analyzer and on water determinations in gases. Additionally, it includes useful data that show the stability of hard- and software, the robustness of the system, and the good repeatability.

Definitions and abbreviations

g/l

gaseous/liquid

LPG

Liquefied Petroleum Gas is a flammable mixture of hydrocarbon gases used as a fuel in heating appliances and vehicles. The vapor pressure at room temperature is approx. 0.8 MPa.

MFC

Mass Flow Controller

Mass flow [g/L]

The mass flow is calculated using the gravimetrically determined calibration factor (L/g) and the measured sample volume.

PCV

Precision Control Valve

Volume flow [L/min]

The volume flow is determined with the MFC. As the MFC is calibrated to nitrogen, the value does not correspond to the real sample volume.

Sample

Unless otherwise noted, LPG was used as sample.

Instruments and accessories

875 KF Gas Analyzer	2.875.9020
Accessories for reagent exchange/addition of methanol	6.7209.000
Accessories for rinsing with solvent	6.7209.010

Electrodes

Double Pt Electrode	6.0344.100
Generator electrode with diaphragm	6.0341.100

Reagents

- HYDRANAL[®]-Coulomat AG-Oven
- HYDRANAL[®]-Coulomat CG
- HYDRANAL[®]-Methanol dry
- HYDRANAL[®]-Titrant 5

Predefined methods

As standard, the 875 KF Gas Analyzer is delivered with the following **tiamo**[™] methods:

- Sample measurement
- Reference measurement
- Precision control valve setting
- Gas calibration_liquefied gas
- Gas calibration_gas
- Shut down system
- Drift diagnosis
- System preparation
- Rinsing with solvent
- Reagent replacement
- Addition of methanol

Sample preparation

No sample preparation is required.

System start

As soon as the 875 KF Gas Analyzer is powered on, all programs necessary to run the system are started automatically.

The MFC can be directly used after the system start and does not need any warm-up time.

Nitrogen

A nitrogen supply is needed in order to rinse the tubes and remove any traces of water before sample measurements are carried out. After sample measurements, nitrogen is used to flush water remaining in the tubes into the titration vessel.

To have low and stable drift values, the nitrogen should be as dry as possible. The cartridge in the 875 KF Gas Analyzer does not have a large capacity to absorb water. Therefore, it is recommended to predry the nitrogen.

Ideally the pressure of the nitrogen should be the same as the vapor pressure of the sample (e.g., propane, 0.83 MPa; corresponds to 8.3 bar). In most cases, a pressure of 0.5 MPa is sufficient. Pressures lower than 0.2 MPa should be avoided as the rinsing of the tubes would take a very long time.

Oven temperature

The oven is used to avoid condensation and forming of ice at the precision control valve. Generally the oven temperature is set between 50 and 80 °C.

Calibration

The MFC used to measure the mass flow of the gas is calibrated for nitrogen (ex works by manufacturer). This means that the measured value is correct for nitrogen only and that for every new sample a calibration has to be carried out. To this end, the 875 KF Gas Analyzer includes two predefined methods (one for gas and one for liquefied gas). The sample container is placed on a balance and a certain amount of sample is allowed to flow through the MFC. To calculate the calibration factor, the measured volume of sample is divided by the determined sample mass.

Calibration factor:

$$F_{cal} = \frac{V_{sample}}{m_{sample}}$$

F_{cal} :	Calibration factor [L/g]
V_{sample} :	Measured (with MFC) volume of sample [L]
m_{sample} :	Weighed sample mass [g]

It is recommended to run the calibration using sample from the gaseous phase. Carry out at least 3 times and check if the result is reproducible.

For the calibration, the PTFE capillary is used to connect the sample container to the 875 KF Gas Analyzer. The steel capillary would transmit vibrations to the balance and lead to instable readings.

Please note that the water content in the gaseous phase is higher than in the liquid phase as water migrates to gaseous phase. If the calibration factor is determined with sample from the gaseous phase, the water content of the liquid phase decreases. This means that if the calibration factor is determined with the same sample container as the measurements afterwards, the sample should be taken from the liquid phase. Otherwise the water content of the sample is changed.

Sample measurements

To measure the water content in the liquefied gas, the sample needs to be introduced into the 875 KF Gas Analyzer in its liquid form. Therefore, the sample container must be placed in a way that the liquid sample is flowing into the tube system.

In case a permanent gas is analyzed, it does not have an influence on the result how the sample container is placed.

For sample measurements, the container is always connected with the steel capillary to the 875 KF Gas Analyzer.

The sequence of the predefined method (Sample measurement) is shown in Figure 1.

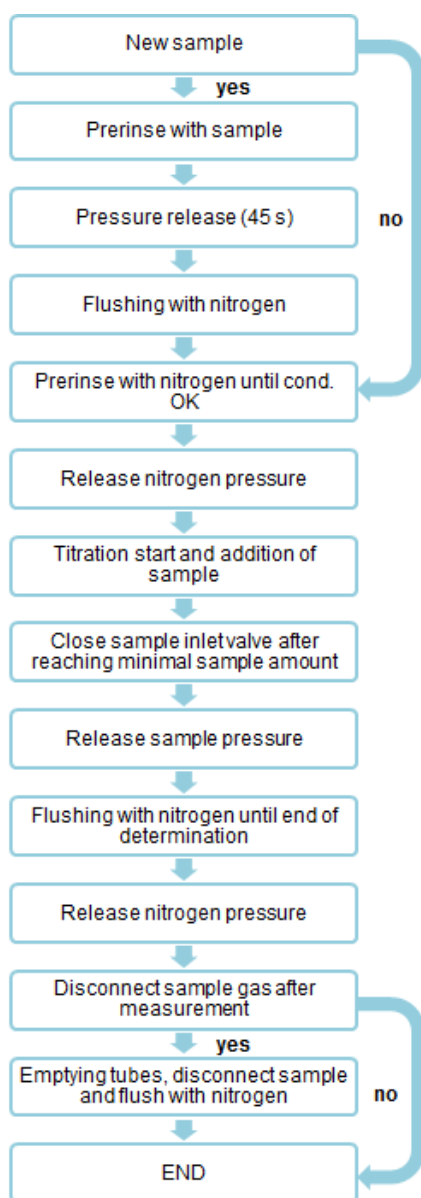


Figure 1: Method sequence of a water determination in gas (l or g)

In the sample table, the minimal amount of sample to be added is defined. As soon as the introduction of sample starts, the MFC measures the volume of gas. After the minimal amount of sample has been added, the sample inlet valve is closed. The remaining sample evaporates, so there is still gas flowing into the titration vessel. If the gas flow is 0 mL/min, the total volume of sample flown through the MFC is stored.

Using nitrogen, the remaining water in the tubes is flushed into the titration vessel.

A typical titration curve is shown in Figure 8. At approximately 180 s the nitrogen flushing starts. The increasing drift points to the presence of residual water in the tubes. Flushing with nitrogen makes sure that the complete water contained in the sample is determined.

The titration curve shows that, due to the low water content of the sample, the drift values are always quite low. Especially when the sample inlet valve is closed and the gas flow decreases, drift values decrease. Without an extraction time, the titration would stop at this point. To obtain correct values, it is crucial to use an extraction time which is long enough. The extraction time is calculated automatically at the start of each determination.

Extraction time:

$$t_{\text{extraction}} = \frac{60 \times (m_{\text{sample}} + 1000 \text{ mg})}{v_{\text{sample}}} + \frac{t_{\text{flushing}} \times m_{\text{sample}}}{6000 \text{ mg}}$$

$t_{\text{extraction}}$ Extraction time [s]

m_{sample} Minimal amount of sample [mg]

v_{sample} Average mass flow of previous sample determination [mg/min]

t_{flushing} Flushing time [s]

60 Conversion factor [s/min]

1000 Calculation factor [mg]

6000 Calculation factor [mg]

Calculation

The predefined methods delivered with the system contain a large number of calculations.

The water content is calculated using the following formula:

$$\text{water [ppm]} = \frac{EP \times F_{\text{cal}}}{V_{\text{Sample}}}$$

Water [ppm]: Water content of sample [ppm]

EP: Determined amount of water at the end of titration [μg]

F_{cal} : Calibration factor [L/g]

V_{Sample} : Measured (with MFC) volume of sample [L]

Long-term test

Procedure

The long-term test of the 875 KF Gas Analyzer took 78 hours in which 360 water determinations were carried out.

The catholyte and the anolyte were not completely exchanged, but the volumes of the two reagents were kept constant.

To avoid an accumulation of water in the catholyte, 2 mL of Titrant 5 were added every day to dry the catholyte compartment.

Results

Reproducibility

The mean value of the 360 determinations was 26.5 µg/g with a standard deviation (SD) of 0.8 µg/g (rel. SD: 3.2%) (Figure 2).

Robustness

To check the influence of the oven temperature, measurements at 50 and 80 °C were carried out. Furthermore, the PCV was opened completely after 42 measurements at 50 °C to test if the position of the PCV has an influence on the measurements. The gas flow through the MFC is limited to 5 L/min. If the gas flow is higher, liquid sample can flow into the MFC and destroy it. To avoid that, the predefined methods automatically close the sample inlet valve if the gas flow is higher than a defined limit (see titration curves in Figure 8 and Figure 9).

The stability of the mass flow measurement was examined with two MFC's (Figure 6 and Figure 7). Those tests were carried out using nitrogen as sample. There is no significant difference in the two slopes of the characteristic curves (98.6% before and 98.3% after the long-term test).

Stability of the drift

The drift is depending on the level of anolyte in the titration vessel, the lower the level (compared to catholyte level), the higher the outflow of catholyte (Figure 4). The catholyte is not dried during conditioning, therefore water and decomposition products of the reagent accumulate. After addition of iodine-containing methanol (titrant 5), the drift decreased significantly.

However, there is no relation between the measured water content and the start drift (Figure 5).

Stability of the introduced amount of sample

The oven temperature has no influence on the sample introduced to the titration vessel. In contrast, the variance of the introduced amount of sample is much higher if the PCV is completely open and the gas flow is controlled by opening and closing the sample inlet valve (Figure 3).

Addition of methanol

The constant gas flow through the methanol-containing anolyte leads to evaporation of methanol and subsequently to a decrease of the reagent level.

To keep the level of the anolyte at 120 mL, methanol was added during the long-term test (32 times 20 mL of methanol). The mean interval between two methanol additions was 11 determinations (approx. 4 h). The drift stabilized after 15 to 20 min after the methanol addition.

Comments

Please note that the PCV does not close the tube completely. Consequently, the gas flow is never 0 mL. The PCV must be treated carefully and never with force as it can be easily damaged.

To check the complete system, a gas with certified water content can be used.

Further information, especially on the calibration procedure, can be found in the manual of the 875 KF Gas Analyzer.

Date

25th of April 2013

Author

Competence Center Titration

Metrohm International Headquarters

Appendix

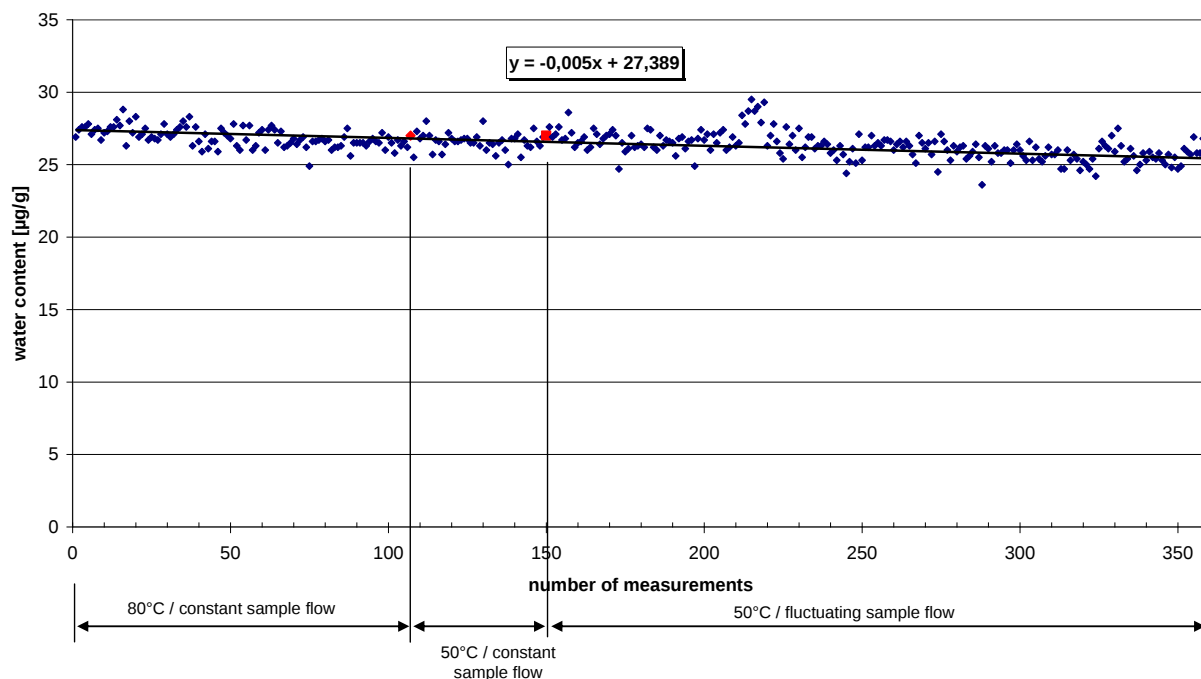


Figure 2: Measured water contents during long-term test

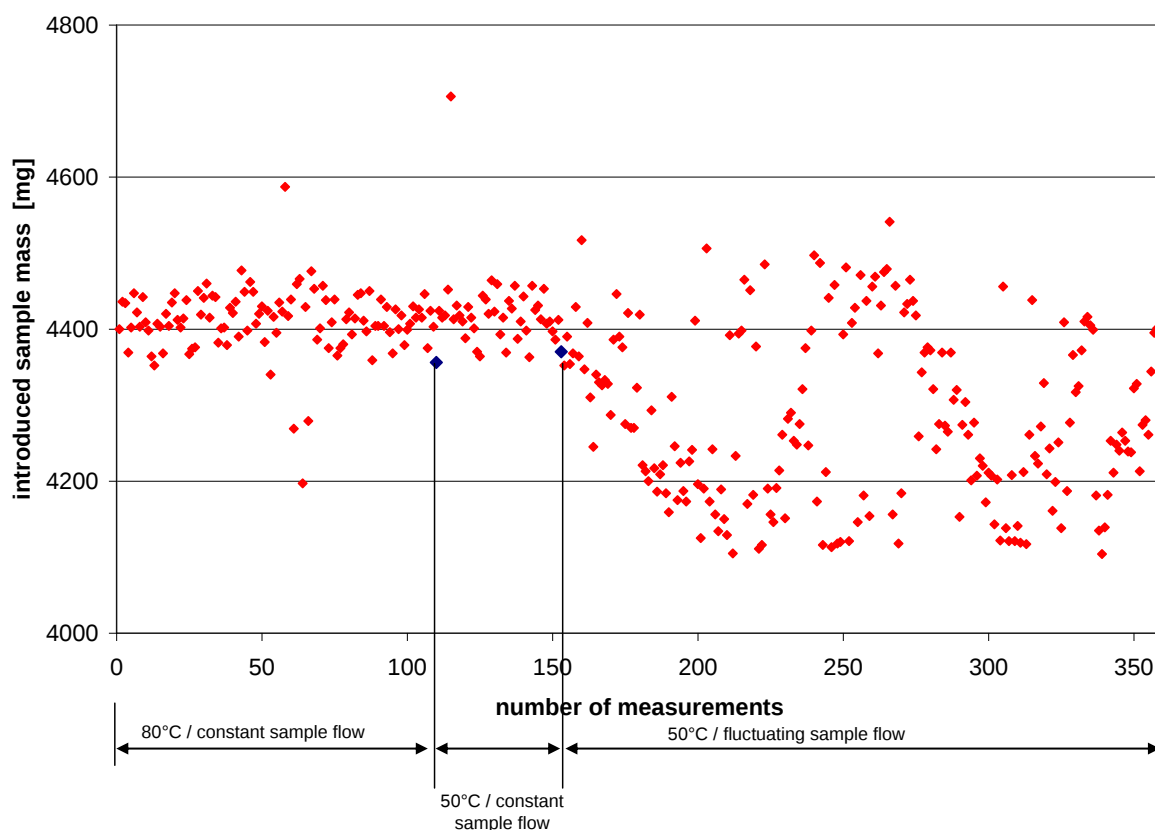


Figure 3: Introduced amount of sample at different temperatures and PCV positions. The sample inlet valve was closed after addition of 4000 mg of sample.

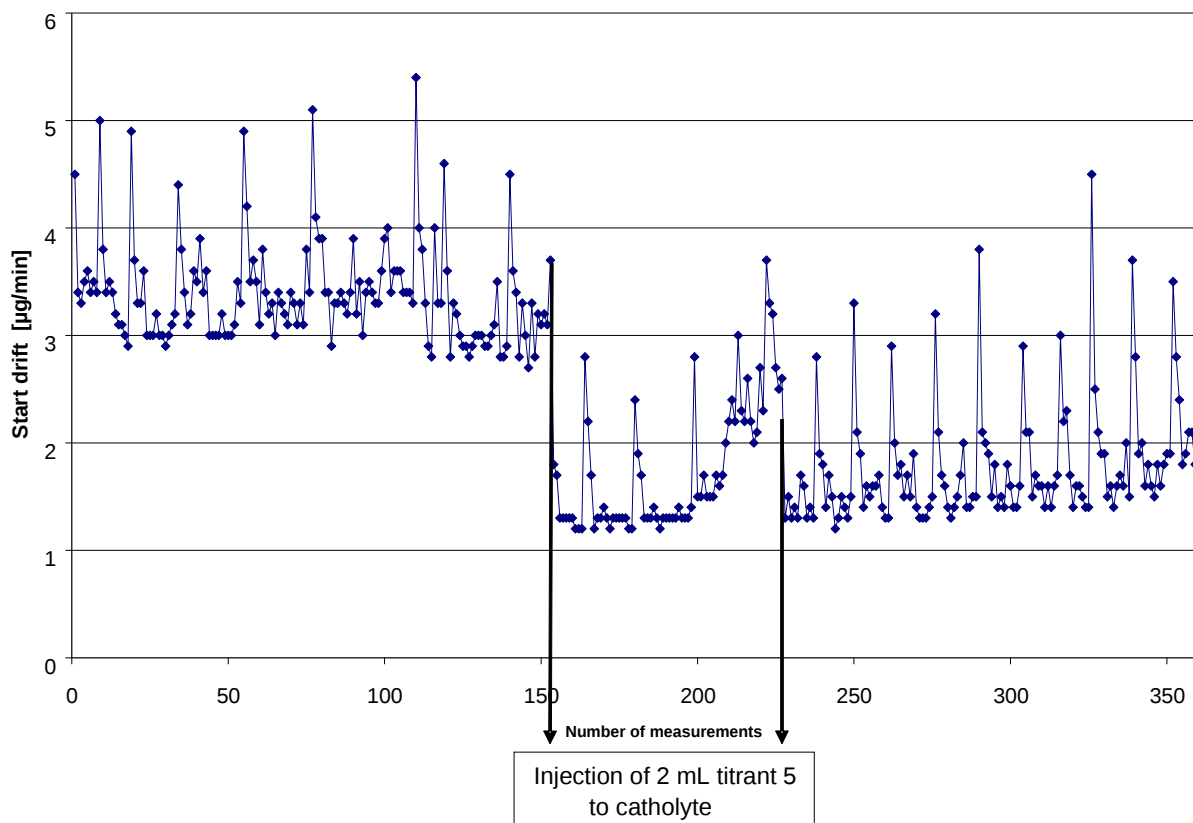


Figure 4: Drift progression; the fluctuation correlates with the level of the anolyte, which leads to a different flow of catholyte into the titration vessel

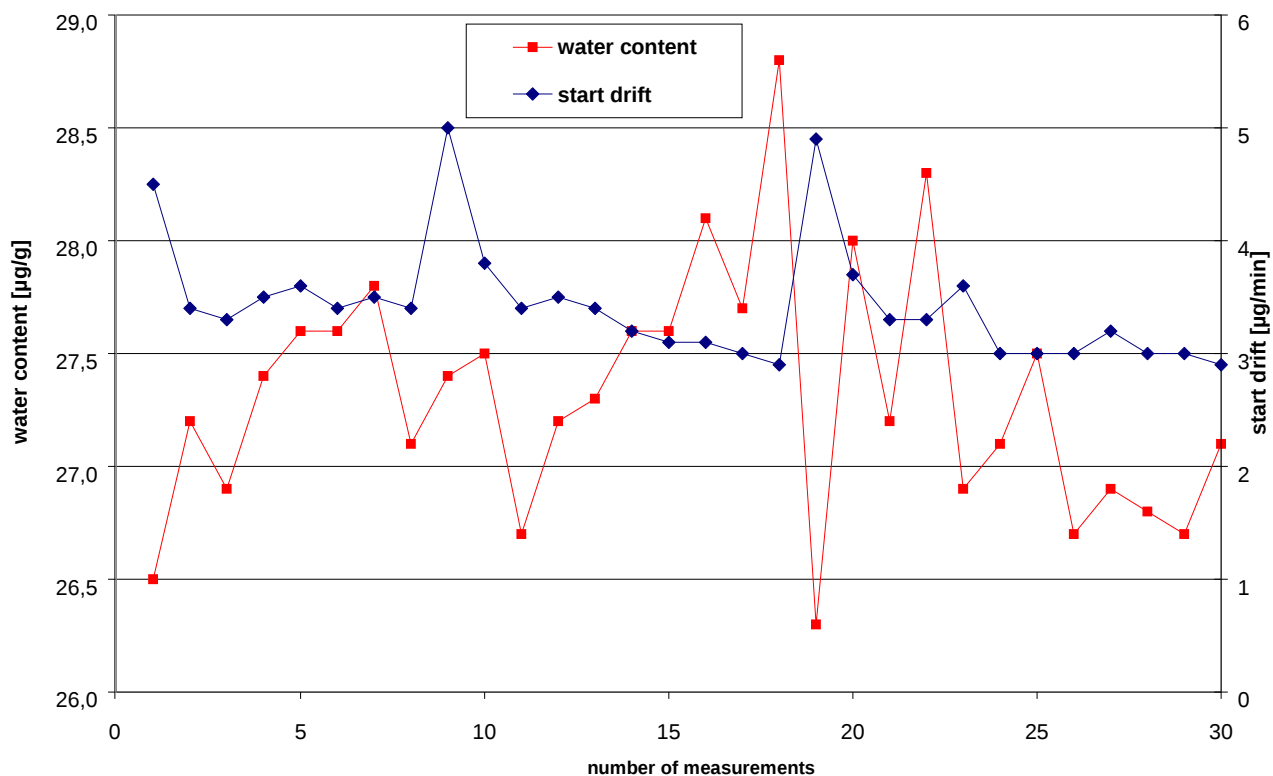


Figure 5: Start drift values and measured water contents after exchanging reagents (first 30 measurements)

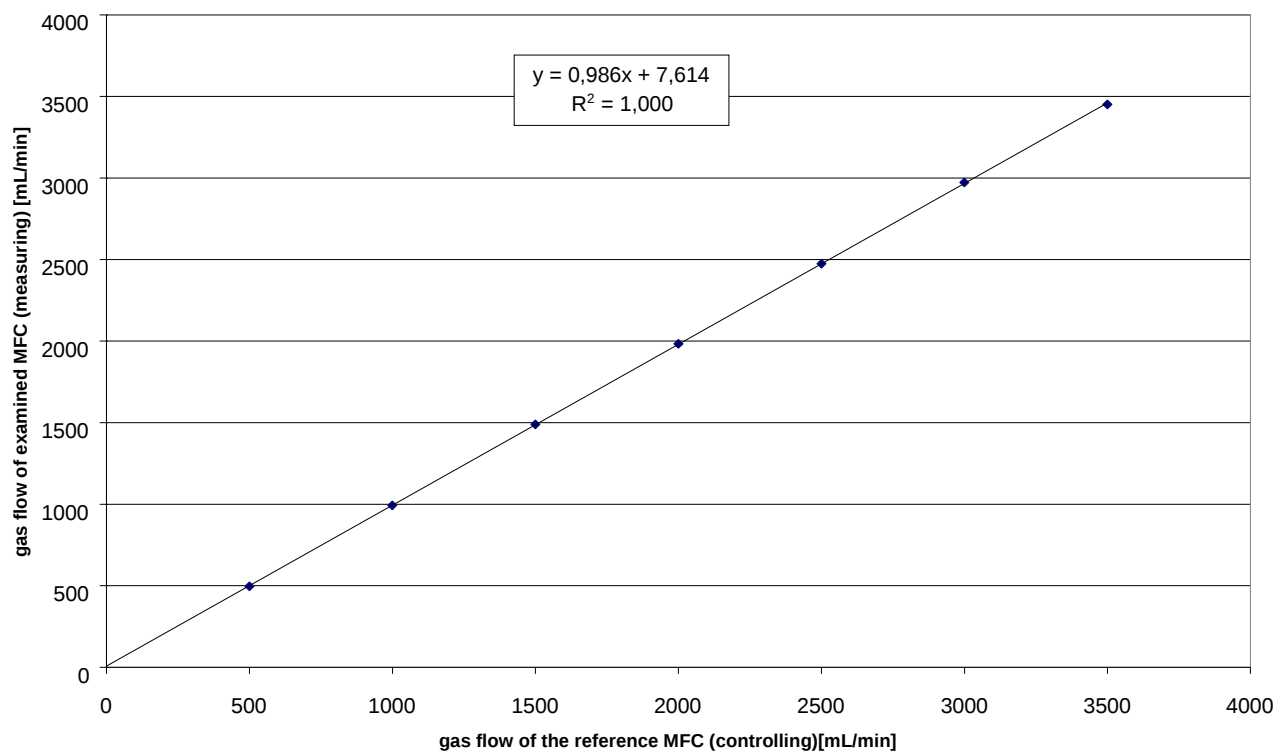


Figure 6: Reference flow versus measured flow – before long-term test

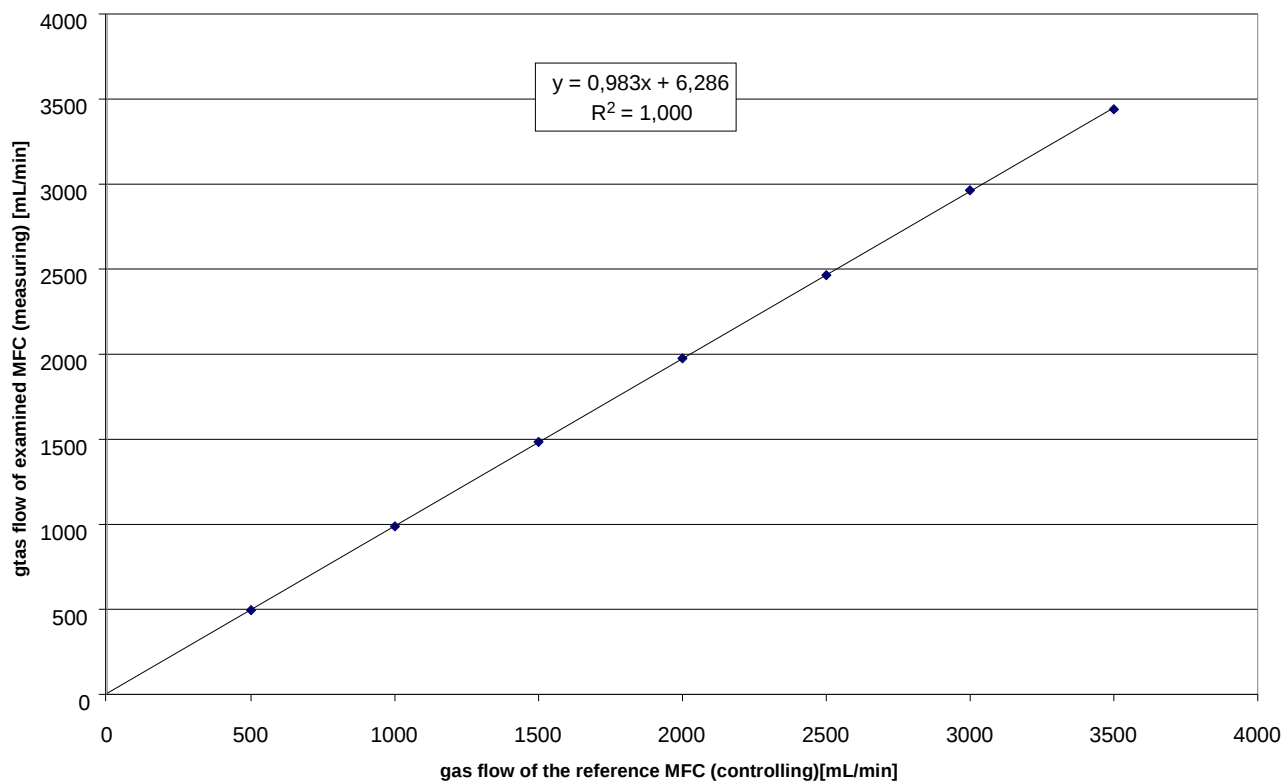


Figure 7: Reference flow versus measured flow – after long-term test

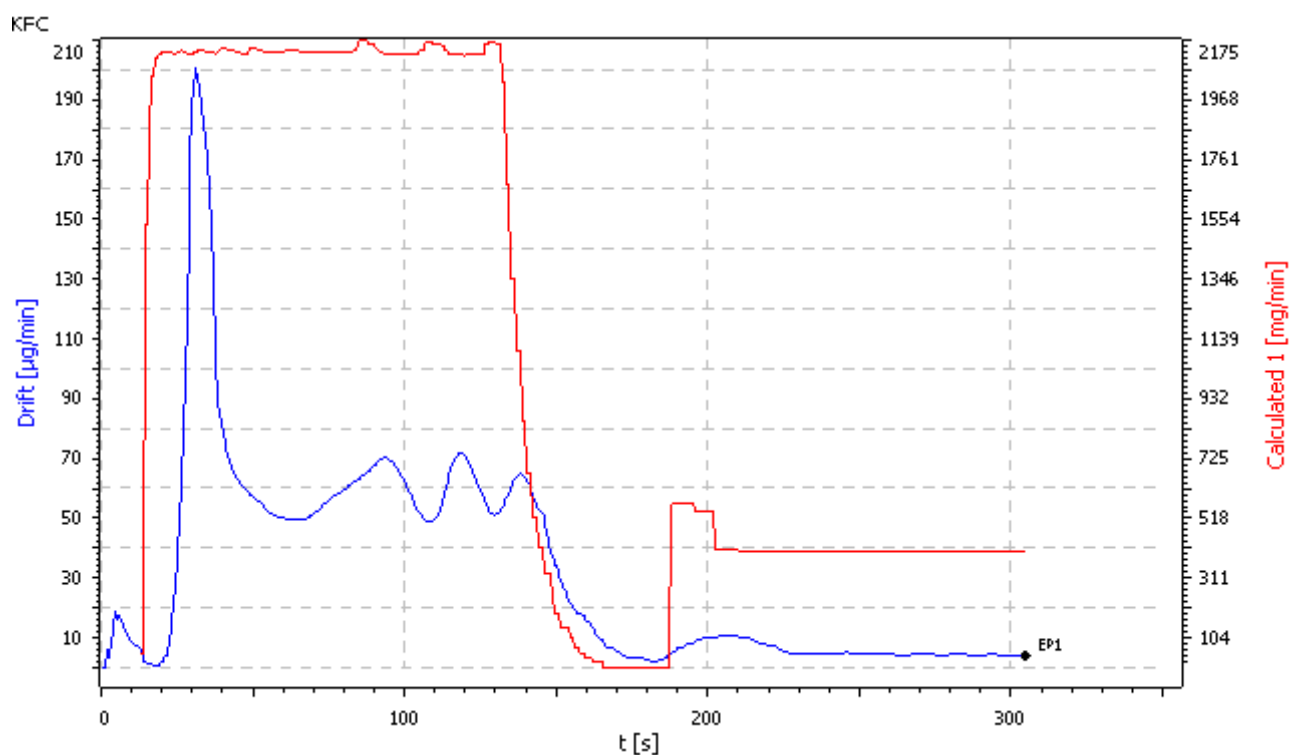


Figure 8: Mass flow and drift curve; oven temperature 50 °C; PCV half turn open; minimal amount of sample 4000 mg

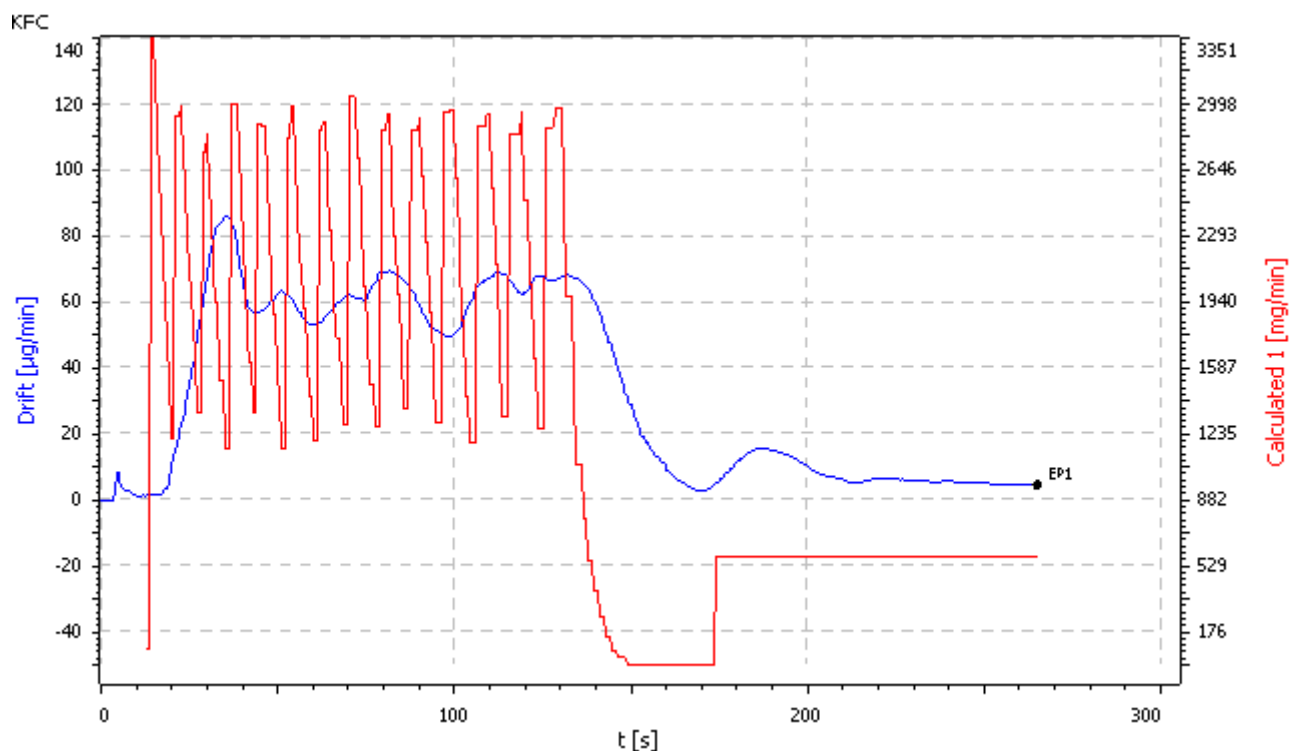


Figure 9: Mass flow and drift curve; oven temperature 50 °C; PCV open five graduation lines; minimal amount of sample 4000 mg