VSL

Evaluation of a natural gas analyser
on-line Gas Chromatograph from BACS

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Summary

From Thursday November 29th 2012 until Wednesday December 13th 2012, validation tests were performed on an on-line Gas Chromatograph, type number KC 50.310-000, from BACS. The tests were performed at the VSL laboratories in Delft (NL). The test protocol was based on the requirements of ISO10723 and GOST 31371:2008. The GC is tested for efficiency (peak separation/resolution), repeatability, reproducibility, linearity, and accuracy. Also longer term stability tests are carried out and the performance of the GC is monitored after a shut-down and restart of the GC.

It is concluded that the GC system tested shows good peak separation and repeatability. Also the reproducibility of one day is good, and typically about twice the repeatability of the component at the tested amount–of–substance fraction level. The reproducibility over several days is again typically a factor 2 greater than the reproducibility in one day. The reproducibility over several days is of less relevance, as usually GC systems for natural gas analysis are calibrated each day with a single, well established calibration gas mixture.

For a number of components, the GC system shows appreciable non-linearity. This non-linearity can be addressed by a multipoint calibration, but this is not the calibration mode used in the field. Hence, in the field a calibration gas mixture needs be chosen that resembles the gas composition of the natural gas to be analysed. This is by the way a requirement of the GOST 31371.6 (2008) and ISO 6974-2 (2002) standards. With such a choice of a calibration gas mixture, the GC can be operated with satisfactory performance.

The uncertainty associated with the gas composition measurement is satisfactory and meet in most cases the requirements of GOST and ISO standards. Where these criteria are not met, the uncertainty as determined during the tests is good enough for accurate determination of gas properties, such as density (for volume conversion), calorific value and Wobbe index.

After a system shutdown of more than 15 minutes, it takes one hour before the performance of the GC achieves the level required in GOST 31371-2008.

From the performed tests it can be concluded that the on-line Gas Chromatograph, type number KC 50.310-000 from BACS will meet the requirements of GOST 31371, ISO 6974 and ISO 10723 in case an appropriate calibration gas mixture will be used.

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1   Introduction

From Thursday November 29th 2012 until Wednesday December 13th 2012, validation tests were performed on an on-line Gas Chromatograph, type number KC 50.310-000, from BACS. The tests were performed at the VSL laboratories in Delft (NL).

The tests have been performed in accordance with VSL's procedure for a Factory Acceptance Test [1], based on the requirements of ISO 10723 (Natural gas – Performance evaluation for on-line analytical systems) [2].

The results of the linearity test and accuracy are compared with the criteria for the maximum allowable uncertainty of ISO10723 [2] and GOST 31371:2008 [3].

The GC is tested for efficiency (peak separation/resolution), repeatability, reproducibility, linearity, and accuracy. Also longer term stability tests are carried out and the performance of the GC is monitored after a shut-down and restart of the GC.

Throughout the report, the gas composition is expressed in amount–of–substance fractions, also known as "mole fractions". These fractions are expressed in 10^{-2} mol mol^{-1}, also known as "mole %". Whereas the notation between citation marks is according to international standards deprecated, this notation is used throughout the report as this is common in the natural gas industry.

2 Validation approach

2.1 Description of the gas chromatograph

The GC is configured with two channels. Both channels are equipped with a sample loop, a GC column and a TCD. A single analysis therefore consists of the analysis of two samples of natural gas.

Table 1: GC configuration

Parameter	Channel 1	Channel 2
Column	PLOT – Poraplot Q	WCOT – 5 CB
Column Length	10 m	8 m
Column flow	4 mL/min Helium	4 mL/min Helium
Column head pressure	170 kPa	170 kPa
Column temperature	75 °C	65 °C
Injection volume	200 nL	200 nL
Injector temperature	100 °C	100 °C
Analyzed components	$N_2 + O_2$, CH_4*, CO_2, C_2H_6, C_3H_8	C_4-C_6
Analysis time	2 minutes of purging and sampling, followed by 2 min and 50 sec of run time	

* CH_4 is separated on column 1, but the calculation of the fraction is done "by difference" according to GOST 31371

2.2 Overall performance and system efficiency

For the testing of the performance, a natural gas mixture containing N_2, CO_2, CH_4, C_2H_6, C_3H_8, n-C_4H_{10}, iso-C_4H_{10}, n-C_5H_{12}, iso-C_5H_{12}, neo-C_5H_{12} and n-C_6H_{14} is injected. The separation and peak shape is checked and the resolution will be calculated according to equation (1) [4] for the critical pairs of peaks such as N_2 / CH_4 and n-C_4H_{10} / neo-C_5H_{12}. The resolution R is defined as

$$R = \frac{t_2 - t_1}{\omega_1 + \omega_2}$$

(1)

where t_1 and t_2 denote the retention times and ω_1 and ω_2 the peak widths at half height of peaks 1 and 2 respectively.

2.3 Repeatability test

Series of 10 repeat injections of the same synthetic natural gas mixture are performed. For all components, the dataset is screened for outliers (absolute deviation exceeding 3 times the repeatability standard deviation) and stragglers (absolute deviation exceeding 2 times, but not 3 times the standard deviation). The outliers are not used for the calculation of the repeatability standard deviation, but the stragglers are kept in the dataset.

2.4 Reproducibility test

The repeatability test as described previously is repeated for a natural gas mixture at different times (reproducibility conditions). From the results of the different data sets the reproducibility is calculated.

2.5 Initial calibration and linearity test

A primary standard gas mixture (PSM) is used to calibrate the GC. This mixture has been prepared by VSL in Delft, according to ISO 6142 (Gas analysis – Preparation of calibration gas mixtures- Gravimetric method) [5]. The composition of this mixture is given in table **2**. The uncertainties are expressed as expanded uncertainties with a coverage factor k = 2.

Table 2: Composition of the calibration gas mixture (uncertainty with $k = 2$)

Component	Fraction (mol %)	Uncertainty (mol %)
N_2	3.009	0.012
CO_2	0.8042	0.0030
CH_4	92.42	0.22
C_2H_6	2.507	0.010
C_3H_8	0.8034	0.0032
$i\text{-}C_4H_{10}$	0.1506	0.0010
$n\text{-}C_4H_{10}$	0.1001	0.0007
$neo\text{-}C_5H_{12}$	0.0201	0.0003
$i\text{-}C_5H_{12}$	0.0698	0.0007
$n\text{-}C_5H_{12}$	0.0801	0.0008
$n\text{-}C_6H_{14}$	0.0402	0.0008

For the testing of the linearity of the GC, VSL used a set of 6 PSMs. The compositions of the mixtures are based on the criteria of ISO 10723 and cover typical compositions of natural gas world-wide. The nominal composition of the 6 mixtures used is shown in table 3.

Table 3: Nominal compositions of the 6 VSL validation gas mixtures[1] (uncertainty with k=2)

	Mixture I mol %	Mixture II mol %	Mixture III mol %
N_2	10.000 ± 0.040	7.000 ± 0.028	5.000 ± 0.026
CO_2	3.000 ± 0.018	6.500 ± 0.026	8.000 ± 0.032
CH_4	72.00 ± 0.07	78.00 ± 0.08	82.00 ± 0.08
C_2H_6	10.000 ± 0.038	7.000 ± 0.028	3.500 ± 0.014
C_3H_8	2.800 ± 0.012	0.1000 ± 0.0005	0.3000 ± 0.0015
$i\text{-}C_4H_{10}$	0.8000 ± 0.0032	0.6000 ± 0.0024	0.4000 ± 0.0016
$n\text{-}C_4H_{10}$	0.8000 ± 0.0032	0.6000 ± 0.0024	0.4000 ± 0.0016
$i\text{-}C_5H_{12}$	0.3000 ± 0.0018	0.1000 ± 0.0008	0.2000 ± 0.0012
$n\text{-}C_5H_{12}$	0.3000 ± 0.0018	0.1000 ± 0.0008	0.2000 ± 0.0012

	Mixture IV mol %	Mixture V mol %	Mixture VI mol %
N_2	3.500 ± 0.022	0.500 ± 0.005	0.2000 ± 0.0028
CO_2	4.500 ± 0.018	0.500 ± 0.004	0.2000 ± 0.0020
CH_4	86.20 ± 0.09	94.20 ± 0.09	97.75 ± 0.10
C_2H_6	5.000 ± 0.020	1.500 ± 0.006	0.2500 ± 0.0012
C_3H_8	0.7000 ± 0.0028	2.100 ± 0.008	1.400 ± 0.006
$i\text{-}C_4H_{10}$	0.03000 ± 0.00018	0.2000 ± 0.0012	0.06000 ± 0.00036
$n\text{-}C_4H_{10}$	0.03000 ± 0.00018	0.2000 ± 0.0012	0.06000 ± 0.00036
$i\text{-}C_5H_{12}$	0.02000 ± 0.00020	0.4000 ± 0.0024	0.04000 ± 0.00040
$n\text{-}C_5H_{12}$	0.02000 ± 0.00020	0.4000 ± 0.0024	0.04000 ± 0.00040

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[1] Usually 7 gas mixtures are used, but one appeared empty during the tests. As long as the characteristic of the analyser can be modelled with a straight line or parabola, 6 gas mixtures are sufficient [2,6].

The non-linearity of the natural gas analyser is determined on the basis of the relative residuals, as defined in ISO 6143 [6]. The relative x–residual is defined as

$$f_{x,i} = \frac{x_i - \hat{x}_i}{u(x_i)} \tag{2}$$

and likewise the relative y–residual as

$$f_{y,i} = \frac{y_i - \hat{y}_i}{u(y_i)} \tag{3}$$

According to ISO 6143 [6], for all i both relative residuals should be smaller than 2. The simplest model that meets these criteria is used for assessing the non-linearity. The values for the coefficients and their associated covariance matrix are obtained by minimising χ^2, defined as

$$\min \chi^2 = \sum_{i=1}^{n} \left(\frac{(x_i - \hat{x}_i)^2}{u^2(x_i)} + \frac{(y_i - \hat{y}_i)^2}{u^2(y_i)} \right) \tag{4}$$

where $\hat{x}_i$ and $\hat{y}_i$ denote the predicted values of x_i and y_i respectively. These predicted values are related to one another as follows

$$\hat{y} = f(\hat{x}; a) \tag{5}$$

Where f denotes the function used to model the analyser. The vector a denotes the coefficients.

2.6 Calculations and reference data

Based on a single analysis, the calculations performed by the GC have been checked against manual calculations using the reference data from ISO 6976 [11]. The purpose of this check is to verify the correctness of the reference data entered into the GC software and the integrity of the implementations of the calculations in the software.

2.7 Stability test, including GC shutdown/restart

One of the natural gas mixtures is analyzed with a two hour time interval during one week. During this day the GC is calibrated once per day, according to the normal operation routine. From the peak areas and the calculated fractions the stability of the system is determined.

During these tests the power has been turned off and on again to demonstrate the effect of a temporary power failure.

2.8 Uncertainty evaluation

For all uncertainty evaluations, the law of propagation of uncertainty of the GUM (*Guide to the expression of uncertainty in measurement*) [7] is used. The calculation of the parameters of the calibration curves and their associated uncertainties is performed in accordance with ISO 6143 [6].

The calibration and measurement capability (CMC) is determined by mimicking the analysis of a natural gas sample of the GC at three different locations of the calibration curve: the lower end, the middle, and the upper end. For these values of y, the corresponding value for the fraction x is determined by means of interpolation of the calibration function. The uncertainty associated with the fraction is obtained by propagating the uncertainties associated with the coefficients of the calibration curve and the uncertainty associated with the response.

Given a response y_0, the associated x–value (x_0) is to be calculated. This calculation can be done iteratively, using for example the bisection algorithm [9, p. 27]. An implementation of the bisection algorithm is given in [8, pp. 353-543]. The idea behind the method is that the solution is bracketed by two guesses. The interval is cut into two equal parts at each iteration. If there are multiple roots, bisection will find only one root. For well-established analysers,

there should be only one root in the interval. The initial guesses can be obtained, for example, by taking the range of the calibrants used to set up the calibration curve. It is considered good practice to use calibration curves only for *interpolation*. At convergence,

$$y_0 = f(x_0; \mathbf{a})$$

The uncertainty associated with x_0 is computed from [10]

$$u(x_0) = \left(\left[\frac{\partial f}{\partial x}(x_0; \mathbf{a}) \right]^{-2} \left[u^2(y_0) + (\nabla_a f(x_0; \mathbf{a}))^T V_a (\nabla_a f(x_0; \mathbf{a})) \right] \right)^{\frac{1}{2}}$$

where

$$(\nabla_a f(x_0; \mathbf{a}))^T = \begin{pmatrix} 1 & x & \dots & x^m \end{pmatrix}$$

V_a denotes the covariance matrix associated with the parameter vector $\mathbf{a}$.

For the calculation of the calibration and measurement capabilities (CMCs), three values of y_0 are chosen: one at the lower end of the interval given by the y_i, one at the higher end, and one in the middle. The standard uncertainty associated with each of the values is taken from values of y_i as obtained when calibrating the natural gas analyser.

3 Results and discussion

3.1 Overall performance and system efficiency

The overall performance of the analyser is determined by injecting a natural gas sample and to verify the chromatograms first. The main purpose of this "system efficiency" check is to verify that the peaks are all visible, correctly assigned to the components (through the retention time), and well separated. Figure 1 shows the chromatogram on channel 1. All relevant peaks are correctly identified. The peak separation between nitrogen and methane (figure 2) is verified by zooming in.
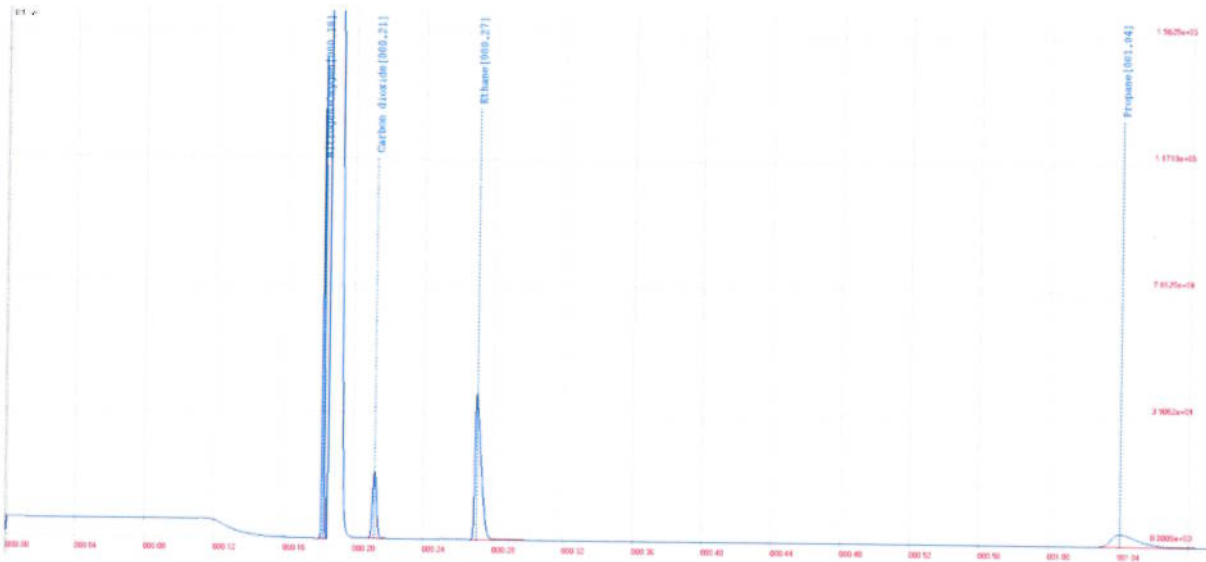

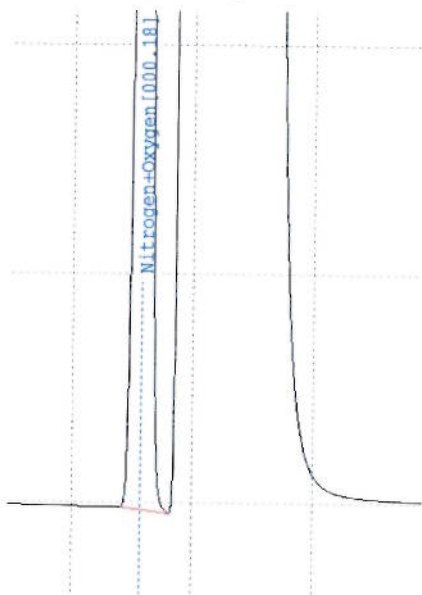Figure 1: Chromatogram on channel 1

Figure 2: Separation between N_2 and CH_4 on channel 1

The chromatogram on channel 2 is shown in figure 3. One of the critical separations is that between n-butane and neo-pentane, see figure 4. By itself, the way that the analyser draws the baseline for n-butane is not a problem, as long as neo-pentane is present at all times (or vice versa). Otherwise, the GC may draw a different baseline (much flatter), resulting in a bias in the n-butane fraction.

N.B. after the testing period BACS has sent another chromatogram with improved integration settings for n-C_4 and neo-C_5, see figure 5. This will reduce any possible bias in the measurement results of n-C_4 and neo-C_5.
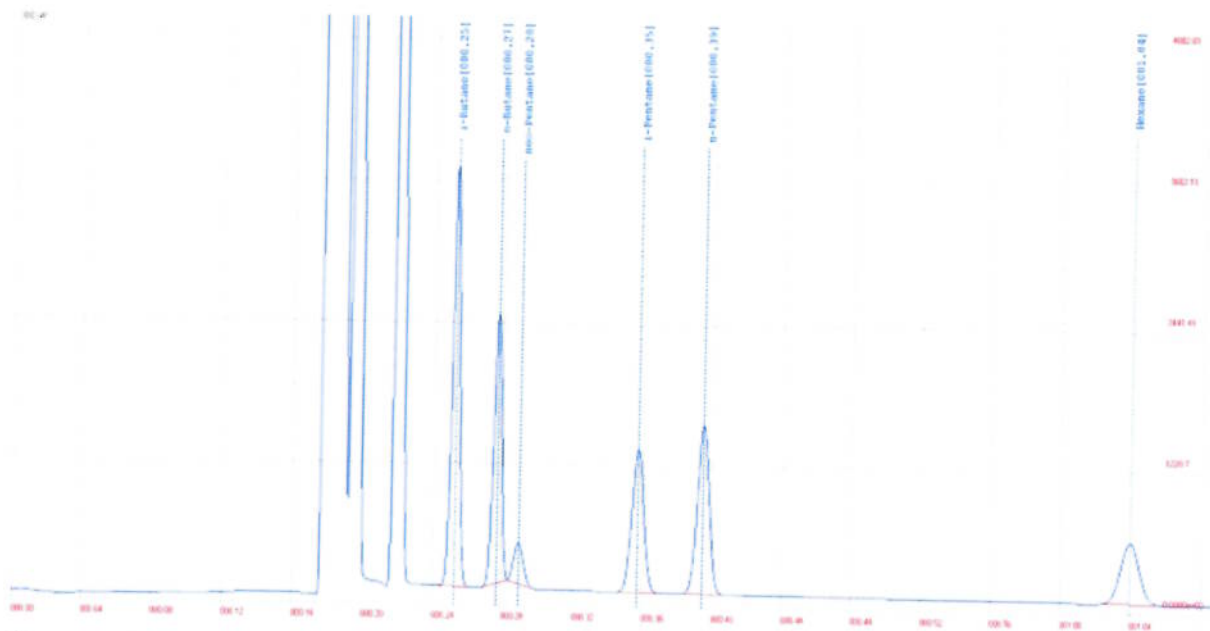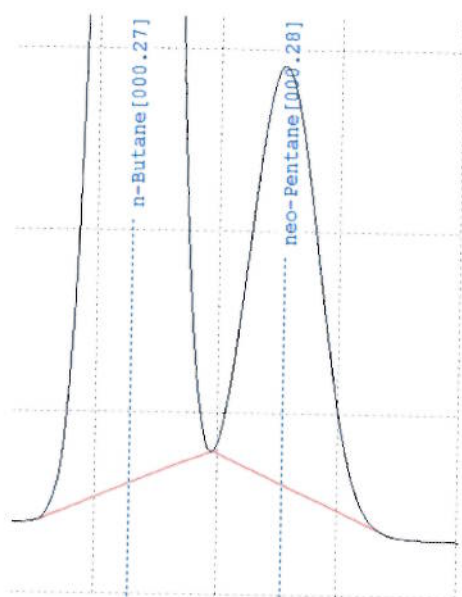
Figure 3: Chromatogram on channel 2

Figure 4: Separation between n-C_4H_{10} and neo-C_5H_{12} on channel 2
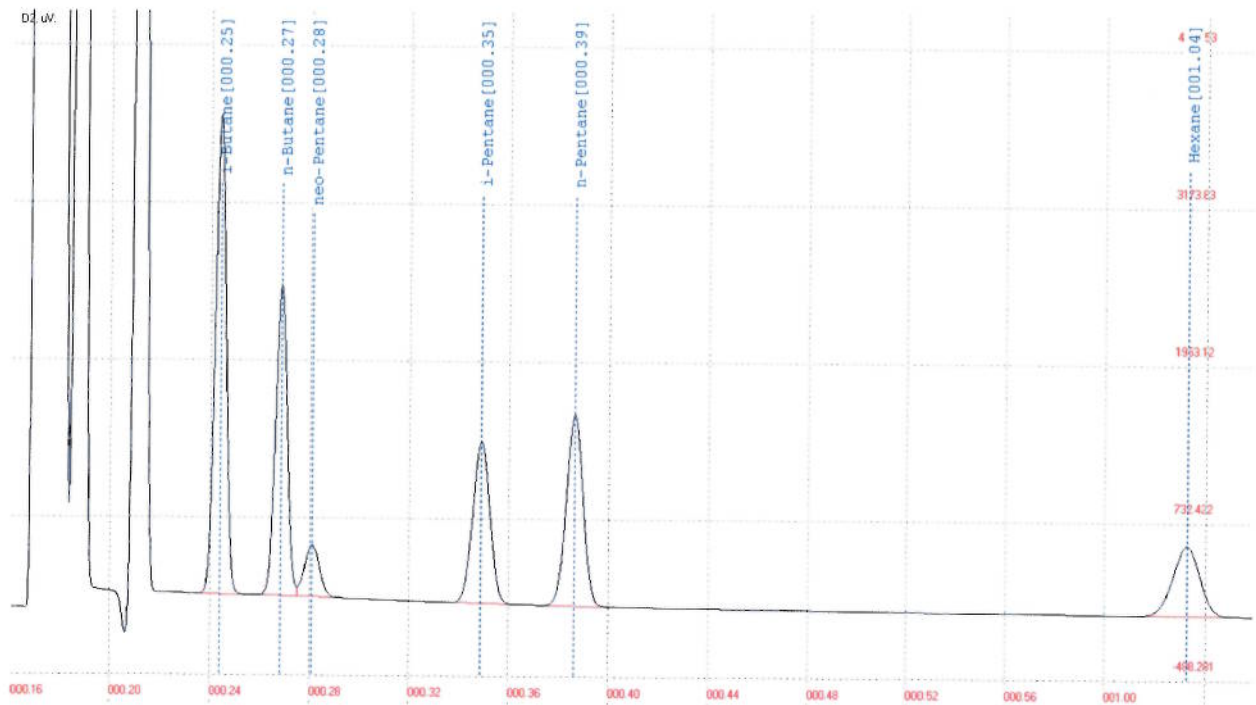
Figure 5: Separation between n-C$_4$H$_{10}$ and neo-C$_5$H$_{12}$ on channel 2 with improved integration settings

Table 4: Resolution between 0.2% N$_2$ and CH$_4$

	1st measurement	2nd measurement	3rd measurement
ω (N$_2$) in seconds	0.09	0.09	0.09
ω (CH$_4$) in seconds	0.38	0.38	0.39
t$_r$ (N$_2$) in seconds	18.26	18.26	18.29
t$_r$ (CH$_4$) in seconds	18.60	18.61	18.65
resolution	0.723	0.745	0.75
average resolution	**0.74**		

Table 5: Resolution between 3.0% N$_2$ and CH$_4$

	1st measurement	2nd measurement	3rd measurement
ω (N$_2$) in seconds	0.10	0.09	0.09
ω (CH$_4$) in seconds	0.37	0.37	0.38
t$_r$ (N$_2$) in seconds	18.29	18.28	18.28
t$_r$ (CH$_4$) in seconds	18.67	18.66	18.67
resolution	0.809	0.826	0.830
average resolution	**0.82**		

Table 6: Resolution between 5.0% N_2 and CH_4

	1st measurement	2nd measurement	3rd measurement
ω (N_2) in seconds	0.11	0.10	0.10
ω (CH_4) in seconds	0.35	0.35	0.36
t_r (N_2) in seconds	18.30	18.27	18.29
t_r (CH_4) in seconds	18.72	18.69	18.71
resolution	0.913	0.933	0.913
average resolution	**0.92**		

Table 7: Resolution between 10.0% N_2 and CH_4

	1st measurement	2nd measurement	3rd measurement
ω (N_2) in seconds	0.10	0.11	0.10
ω (CH_4) in seconds	0.34	0.34	0.35
t_r (N_2) in seconds	18.40	18.41	18.41
t_r (CH_4) in seconds	18.88	18.88	18.89
resolution	1.09	1.04	1.07
average resolution	**1.07**		

Table 8: Resolution between $n\text{-}C_4H_{10}$ and $neo\text{-}C_5H_{12}$

	1st measurement	2nd measurement	3rd measurement
ω ($n\text{-}C_4H_{10}$) in seconds	0.47	0.48	0.49
ω ($neo\text{-}C_5H_{12}$) in seconds	0.61	0.58	0.59
t_r ($n\text{-}C_4H_{10}$) in seconds	27.72	27.72	27.72
t_r ($neo\text{-}C_5H_{12}$) in seconds	28.98	28.98	28.99
resolution	1.167	1.189	1.176
average resolution	**1.18**		

According to ISO 6975 [4] the resolution should not be less than 2, however, this criterion is also not met by comparable analyzer systems. ISO 6974 [12,13] does not mention a criterion for the resolution.

From figure 2 can be seen that a baseline to baseline separation is established between nitrogen and methane. Experience with field analysers for natural gas has learnt that the separation between nitrogen and methane as shown in figure 2 is sufficient for accurate natural gas composition measurement. The choice of a calibration gas mixture with a nitrogen fraction relevant to the natural gas to be measured can help in achieving good accuracy in gas property data (e.g., calorific value, density, Wobbe index).

3.2   Repeatability test

In table 9, the repeatability standard deviation is given from the analysis of the 6 PSMs (see table 3 for the nominal compositions of these mixtures). The repeatability standard deviation is given as coefficient of variation, and arranged in increasing order of the fractions of the components.

The repeatability data are comparable to those obtained with laboratory natural gas analysers and other field analysers. Also the number of stragglers and outliers is consistent with a normal distribution of the data.

Table 9: Repeatability standard deviation (% relative) for all components in the PSMs

Component	Relative standard deviation (%), from lowest to highest fraction					
N_2	0.55	0.07	0.12	0.10	0.07	0.11
CO_2	0.10	0.07	0.06	0.05	0.06	0.09
C_2H_6	0.05	0.07	0.06	0.05	0.07	0.04
C_3H_8	0.45	0.14	0.19	0.20	0.26	0.07
iso-C_4H_{10}	0.13	0.08	0.04	0.04	0.04	0.07
n-C_4H_{10}	0.43	0.06	0.04	0.05	0.04	0.08
iso-C_5H_{12}	0.37	0.17	0.05	0.06	0.15	0.06
n-C_5H_{12}	0.37	0.19	0.06	0.05	0.24	0.07
CH_4	0.021	0.016	0.014	0.009	0.007	0.003

3.3   Reproducibility test

At one of the testing days, the calibration gas (for the composition see table 2) is analyzed several times during the day. From the peak area and the fraction, a response factor is calculated. The standard deviation of the response factors over the day is calculated (table 10).

Table 10: Reproducibility of the response factor for the calibration gas mixture over one day

Component	December 5th 2012 – time of calibration							Standard deviation % relative
	11:18	12:43	14:07	15:34	16:56	18:19	20:16	
Nitrogen	185.16	184.16	184.43	184.66	184.64	184.43	185.27	0.10
Carbon dioxide	152.90	152.19	152.34	152.53	152.54	152.34	152.88	0.15
Ethane	138.49	138.03	138.42	138.36	138.59	138.32	138.19	0.14
Propane	112.30	111.91	112.05	112.00	112.16	112.04	111.90	0.13
n-Butane	82.08	81.47	81.85	81.75	82.07	81.93	81.55	0.29
i-Butane	80.79	80.58	80.74	80.70	80.85	80.77	80.58	0.13
n-Pentane	68.28	67.90	68.11	68.24	68.39	67.87	68.06	0.28
i-Pentane	70.71	70.33	70.54	70.66	70.77	70.31	70.48	0.26

As a rule of thumb, the reproducibility is usually a factor of 2-3 larger than the repeatability standard deviation obtained in proficiency testing for robust methods. Applying this principle to the reproducibility data, it can be concluded that the short-term reproducibility of the analyser is very satisfying.

The same procedure as used for the reproducibility test over one day was used to collected reproducibility data over a one week interval (table 11).

Table 11: reproducibility of the response factor for the calibration gas mixture over one week

Component	December 6th 2012 – December 13th 2012								Standard deviation % relative
	6-12 13:06	7-12 10:00	8-12 10:00	9-12 10:00	10-12 10:00	11-12 10:00	12-12 10:00	13-12 10:00	
Nitrogen	185.16	184.16	184.43	184.66	184.64	184.43	185.27	185.13	0.22
Carbon dioxide	152.90	152.19	152.34	152.53	152.54	152.34	152.88	152.71	0.17
Ethane	140.09	139.41	139.53	139.71	139.73	139.53	140.10	139.95	0.19
Propane	113.26	112.53	112.64	112.97	113.30	112.64	113.77	113.67	0.42
n-Butane	82.13	81.95	82.06	82.14	81.96	82.06	82.57	82.51	0.29
i-Butane	81.01	80.85	80.95	81.02	80.86	80.95	81.45	81.41	0.29
n-Pentane	68.12	67.52	67.61	67.69	67.54	67.61	68.19	68.20	0.45
i-Pentane	70.46	69.96	70.04	70.09	69.93	70.04	70.61	70.53	0.39

Applying the same principle as above, the reproducibility data over a period of a week are still acceptable. It should be noted that in practice these reproducibility figures would be somewhat better because of regular recalibration of the natural gas analyzer.

3.4 Initial calibration and linearity test

3.4.1 Results of linearity test (channel 1)

After initial calibration with the Primary Standard Gas Mixture mentioned in table 3, the following results were obtained from analyzing the 6 validation mixtures and the calibration gas.

N.B. the linearity test has been performed 3 times (3rd, 5th and 11th of December) with comparable results. The figures below are the results of the 11th December measurements.
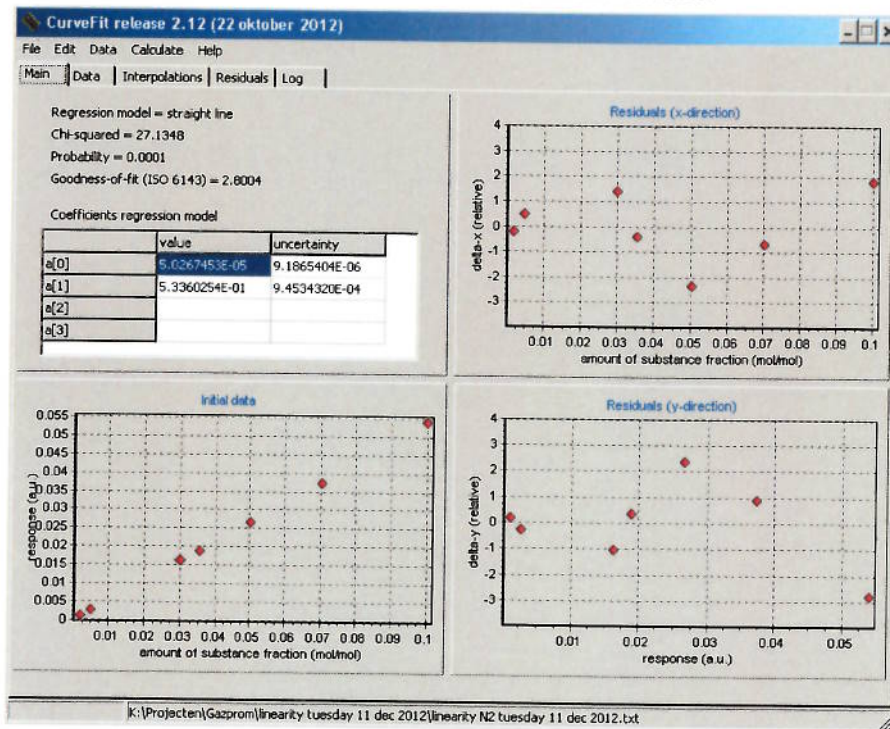

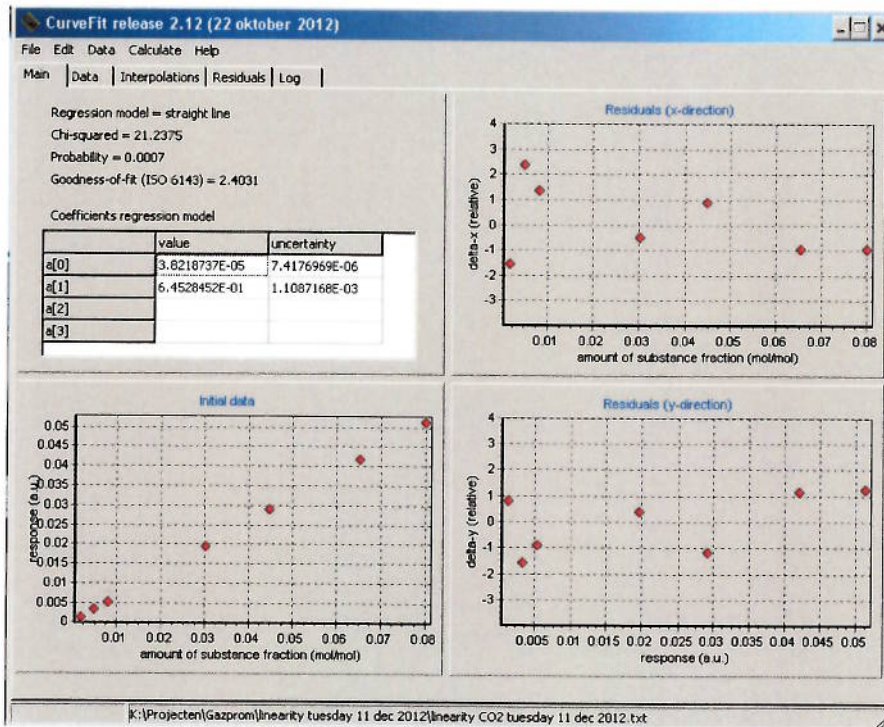Figure 6: Calibration curve for nitrogen: straight line

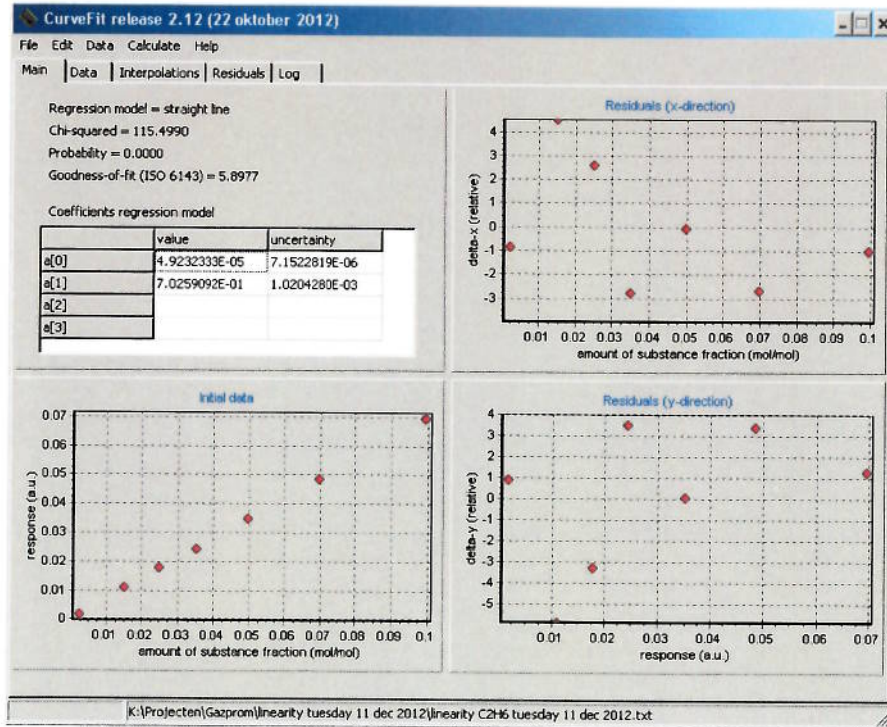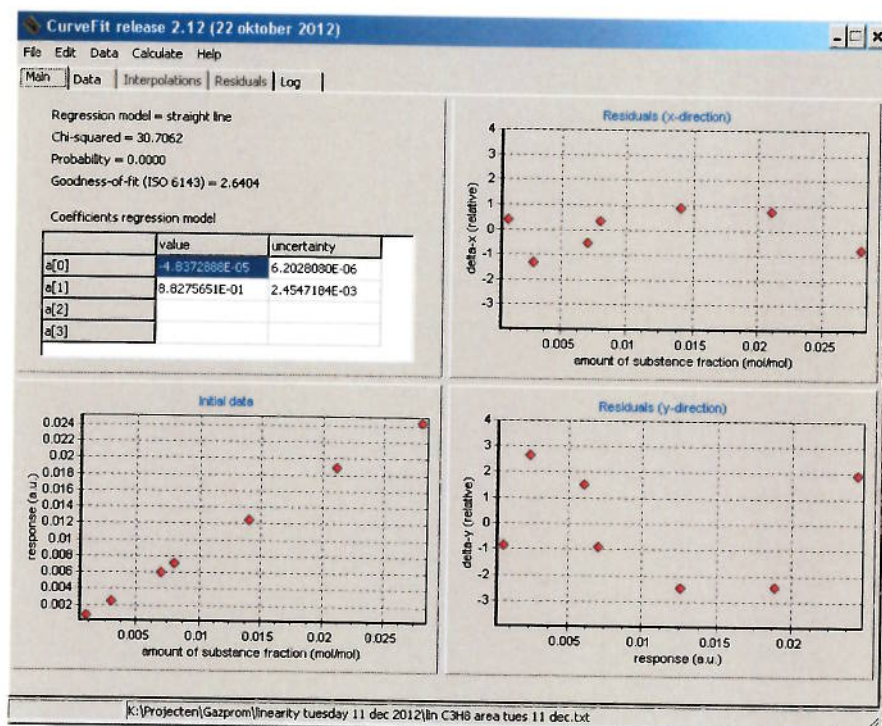**Figure 7: Calibration curve for carbon dioxide: straight line**

Figure 8: Calibration curve for ethane: straight line

Figure 9: Calibration curve for propane: straight line

In figure 6, the results are given of fitting the nitrogen data to a straight line. In the top-left quarter, the selected model is shown ("straight line"). The value of x^2 is just the sum of the squared weighted deviations after fitting. From x^2, a probability can be calculated. If this probability is very small, say, below 0.01, it is unlikely that the model represents the data well. The value of 0.0001 for nitrogen indicates that the fit is not good.

ISO 6143 makes a judgement on the basis of the maximum absolute value of the weighted deviations of the points about the line. According to ISO 6143 [6], this "goodness-of-fit" should be less than 2, meaning that no point deviates more than two times the standard uncertainty in x and y direction from the calibration curve.

At the right-hand side, the relative x- and y-residuals are shown. When the model used for the calibration curve is correct, the residuals should show a random pattern. In the case of nitrogen (figure 6), it is seen that there is some curvature in the data. Fitting the data with a quadratic polynomial would give a better result, but according to the criteria of ISO 6143, it is not necessary to do so.

As can be seen in figures 6-9, not all the residuals in x and y direction are between –2 and 2. The Goodness of Fit (GoF), i.e., the maximum absolute value of the relative residuals, exceeds 2, and the probability (of a good description of the data by the model) is very small. The residuals, GoF and the probability together indicate that a first order curve (straight line) is not a good representation of the results for this broad range of concentrations. Figure 10-13 show the results of a 3rd order polynomial.
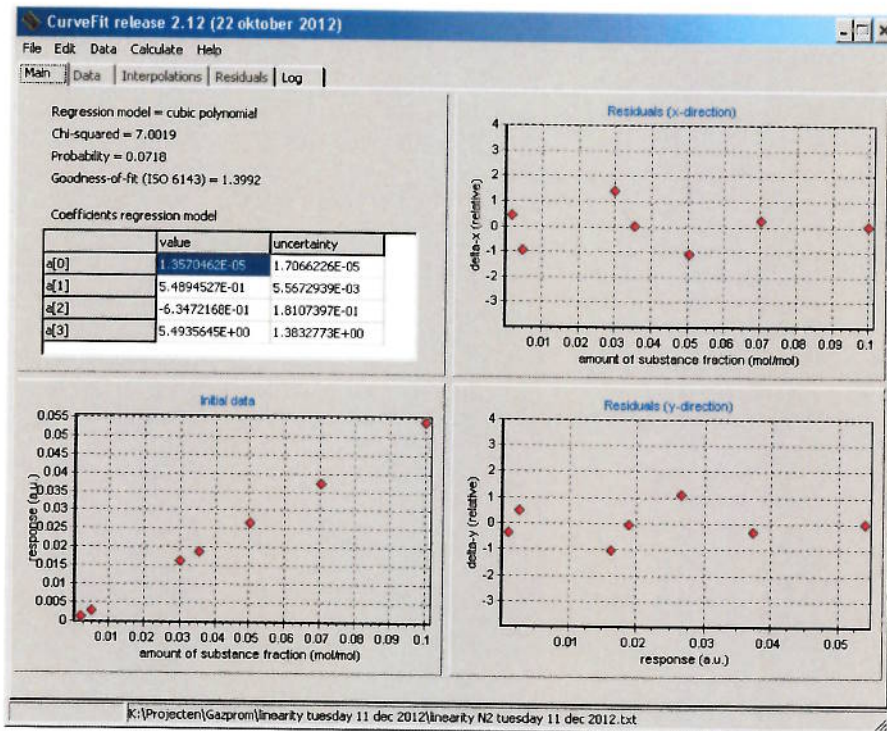
Figure 10: Calibration curve for nitrogen: 3rd order polynomial
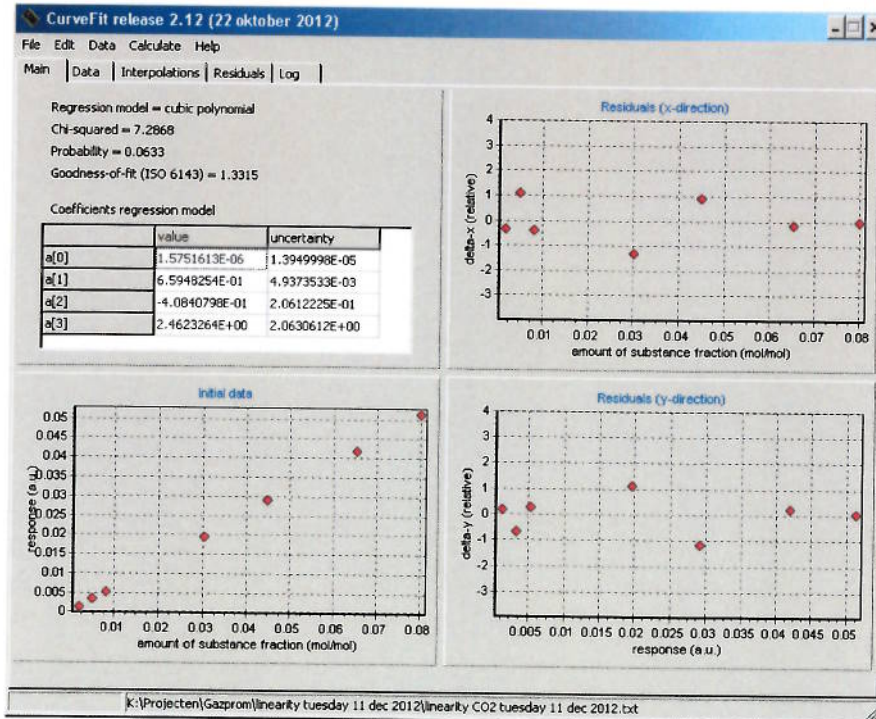
Figure 11: Calibration curve for carbon dioxide: 3rd order polynomial
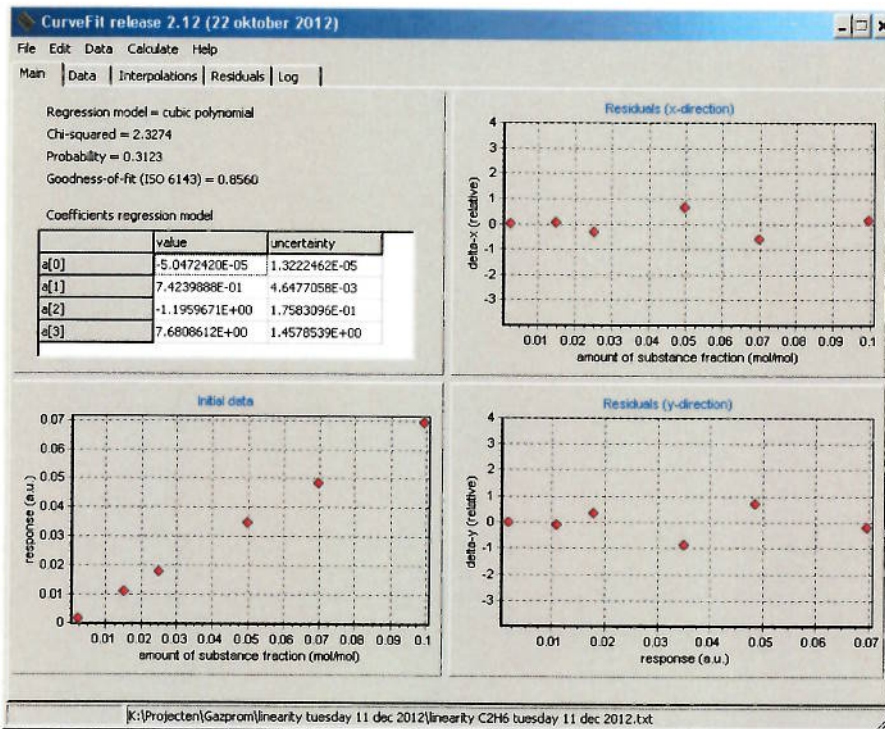
Figure 12: Calibration curve for ethane: 3rd order polynomial
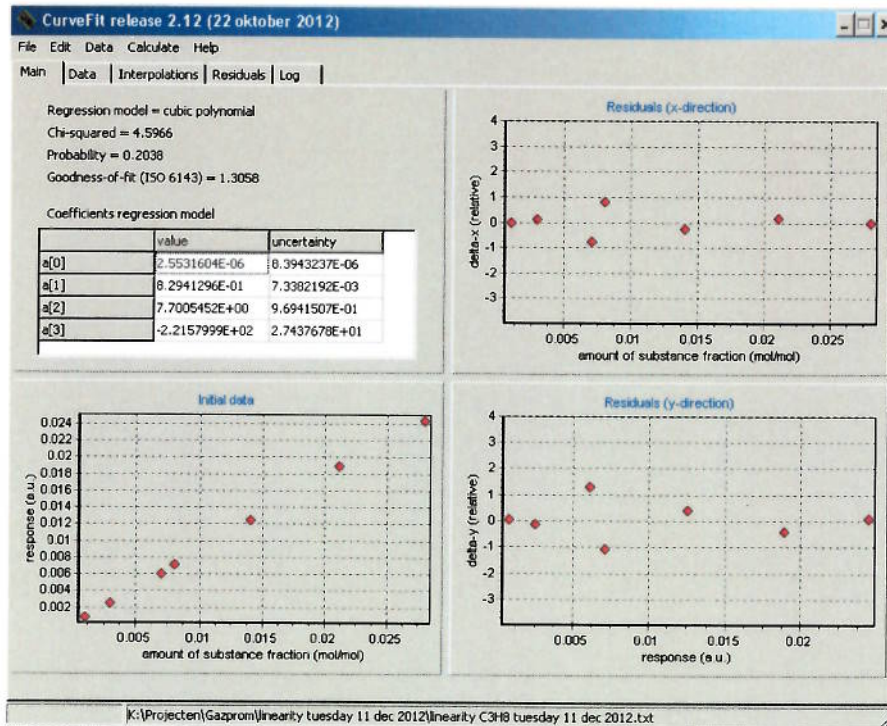
Figure 13: Calibration curve for propane: 3rd order polynomial

For a 3rd order curve, the results for the residuals are within the range of -2 and 2, the GoF is less than 2 and the probability has increased.

3.4.2 Results of linearity test (channel 2)
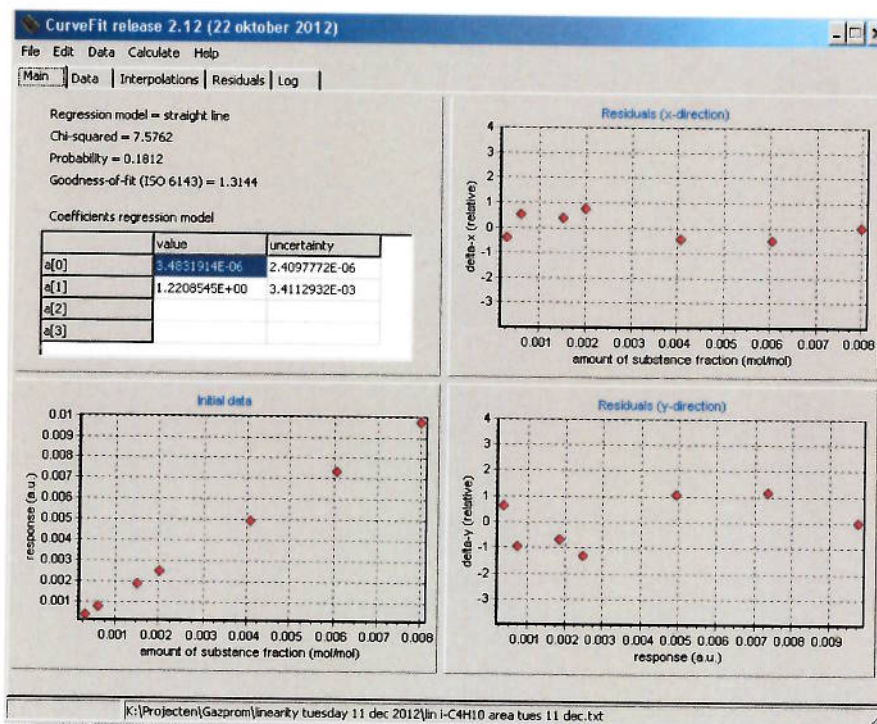
Figure 14: Calibration curve for iso-butane
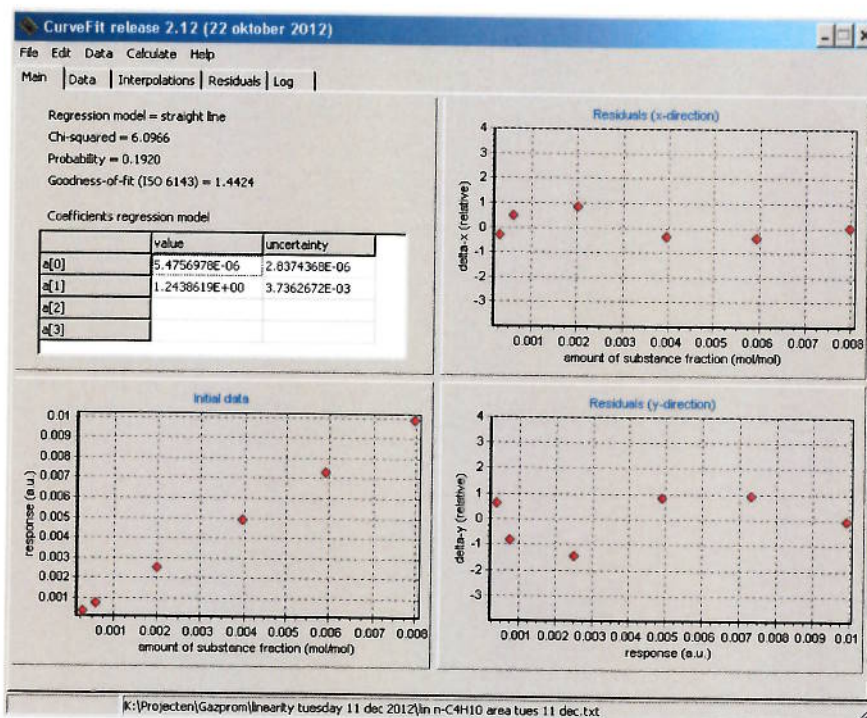
Figure 15: Calibration curve for n-butane
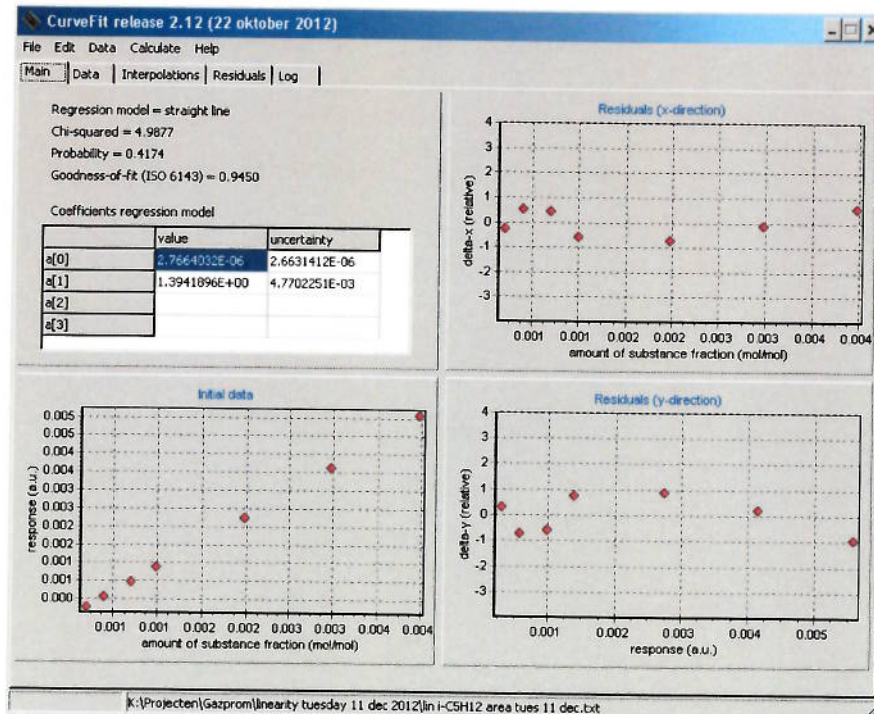
Figure 16: Calibration curve for iso-pentane
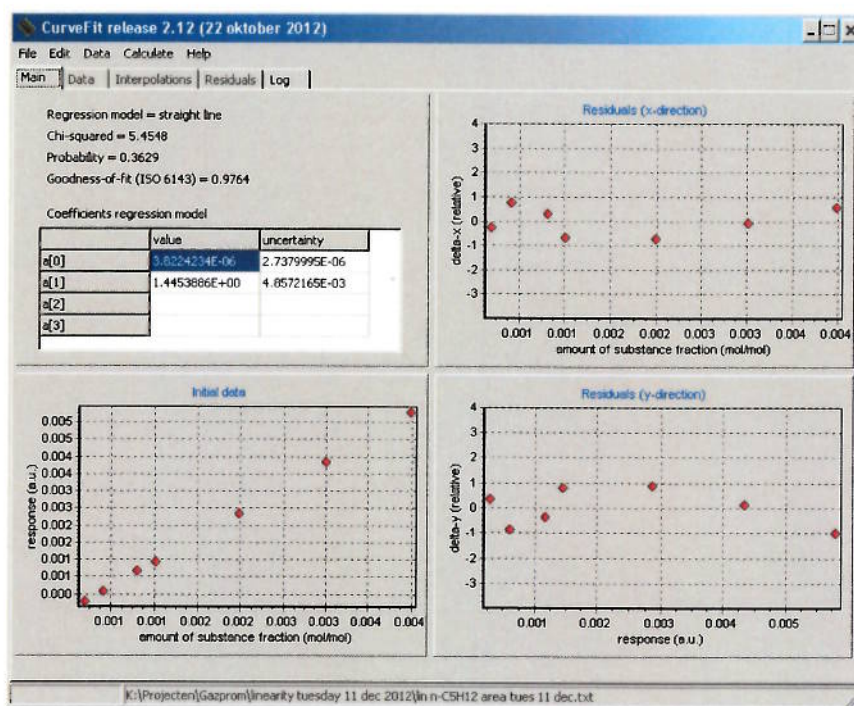
Figure 17: Calibration curve of n-pentane

Results for CH$_4$ calculated "by difference":
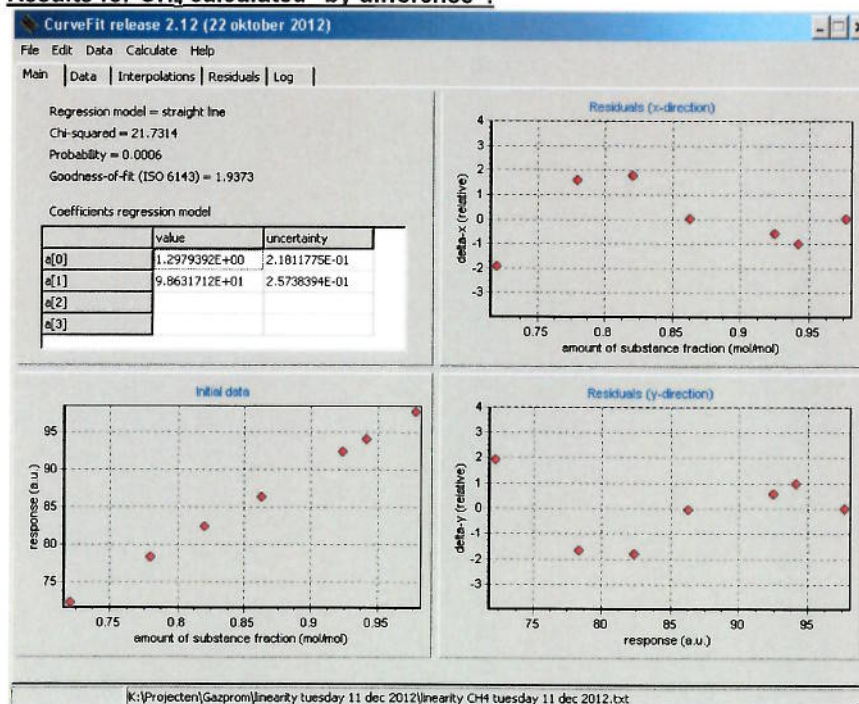
Figure 18: Calibration curve for methane

The results for methane are shown in figure 18. The interpretation of the data is the same as for the other components. The curvature is much less than for nitrogen, and the straight line fit gives a satisfactory description of the dataset.

3.4.3 Discussion of linearity study / curve fitting

The uncertainty in the amount fractions of the validation gas mixtures is given in table 3.

The used uncertainty for the response is a combination of the standard deviation of the 10 injections and an additional uncertainty of 0.25% relative for effects of, e.g., sampling and drift of the system during the period of measurement of the 7 gas mixtures. This additional uncertainty is consistent with the outcome of the reproducibility tests. It is combined with the contribution due to repeatability by means of the law of propagation of uncertainty of the GUM [7]. The combined standard uncertainty associated with the response is quite large when compared to other systems, in particular for methane and ethane. For the components measured with the 2nd channel, the level of uncertainty is very satisfying.

For methane, the uncertainty in the calculated concentration is set on 0.05% relative, in order to see whether it meets the criteria of ISO10723 [2] and GOST 31371 [3].

Further discussion about the uncertainties obtained is given in chapter 4.

For all components analyzed on channel 2, a straight line model is used to describe the relation between concentration and peak area. The residuals show a more or less random spread around zero, so a 1st order line appears to be the right model. For iso-butane, iso-pentane and n-pentane, all residuals are between 2 and −2, and the Goodness of Fit is less than 1. This confirms the validity of the chosen model. Also for the calculated methane concentration a 1st order model gives good results.

For nitrogen, carbon dioxide, ethane and propane, analyzed on channel 1, some of the y-residuals are out of the interval between −2 and 2, and the GoF is greater than 1. Fitting the data with a 3rd order polynomial resolves the issue of a GoF greater than 1, making the fitted model satisfying the consistency criteria of ISO 6143 [6] and ISO 6974-2 [13].

The observed non-linearity for the components on the 1st channel is substantial, when compared to both field analysers as well as laboratory equipment. In most cases, the departure from a straight line through the origin can be modelled satisfactorily by adding a quadratic term to the calibration model. For this analyser, a cubic polynomial is needed. Given the requirement in natural gas standards like GOST 31371 [3] and ISO 6974-2 [13] that a calibration gas mixture should be chosen sufficiently close to the target compositions of the natural gas to be analysed, the observed non-linearity will be of little practical relevance. Most field analysers see a quite constant gas quality, and hence non-linearity effects are only important as far as the choice of the calibration gas mixture is concerned. In situations however where a field analyser sees a wide variety of gas qualities, the non-linearity may add to the overall uncertainty of the analyser.

3.5   Calculations and reference data

3.5.1 Reference data

The six validation gas mixtures have been analyzed by doing 10 repetitive injections. From every first injection, the analyzed composition is used to calculate the superior calorific value on a volume basis (MJ/m^3). The calculated value is compared to the reported GC value. Hereby it should be stated that the GC reports on the basis of real gas conditions, so the value is multiplied by the compressibility factor (z) in order to obtain comparable values.

Table 12: check of reference data: comparison of calculated and reported calorific value

	$H_{S, ideal}$ 25/20 °C (MJ/m^3)		
	calculated based on analyzed composition	reported by GC (= z * Q $_{volume}$)	% difference
mixture # 1	38.373	38.372	-0.002
mixture # 2	35.224	35.223	-0.002
mixture # 3	34.482	34.483	0.001
mixture # 4	35.919	35.920	0.002
mixture # 5	39.470	39.471	0.003
mixture # 6	37.916	37.919	0.008

Only minor differences are observed which are caused by rounding of data. The reference data used by the GC are correct.

3.5.2 Checking the GC performance for the measurement of the calorific value

The calorific value is reported for each of the 10 injections from each individual validation gas mixture. The average reported calorific value is compared to the calculated value based on the gravimetric composition of the gas mixtures.

Table 13: comparison of reported and calculated calorific value based on gravimetry

	$H_{S, ideal}$ 25/20 °C (MJ/m^3)		
	calculated based on gravimetric composition	reported by GC (= z * Q $_{volume}$)	% difference
mixture # 1	38.489	38.390	-0.26
mixture # 2	35.210	35.226	0.04
mixture # 3	34.438	34.485	0.14
mixture # 4	35.914	35.919	0.01
mixture # 5	39.442	39.474	0.08
mixture # 6	37.906	37.919	0.03

With the selected calibration gas mixture composition, the obtained differences are within 0.3% relative. When the calibration gas mixture composition is closer to the line-gas composition (which will be the situation on-site, and which is required in the applicable GOST and ISO standards), the analyzed calorific value will be within 0.2%.

3.6 Stability test, including GC shutdown/restart

3.6.1 Results of stability test

The same natural gas mixture is injected 10 times after a 2 hour time interval during one week.
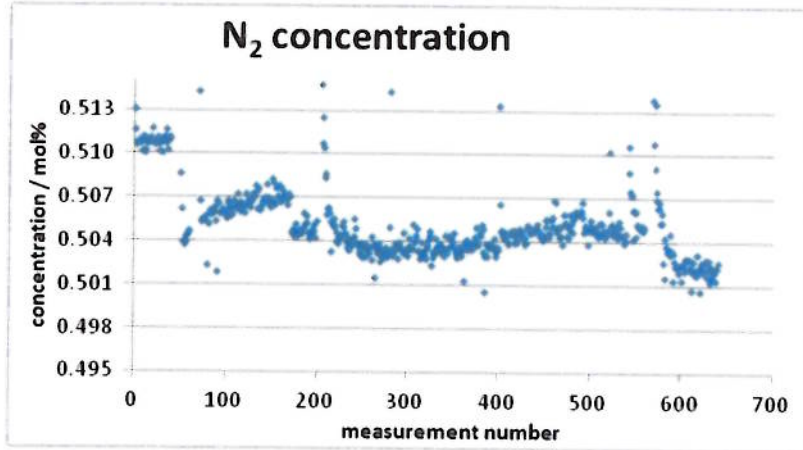

Figure 19: stability of the analyzed N_2 concentration during one week
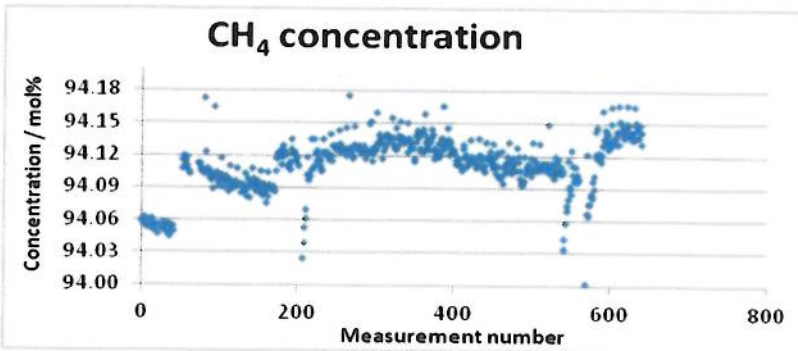

Figure 20: stability of the analyzed CH_4 concentration during one week
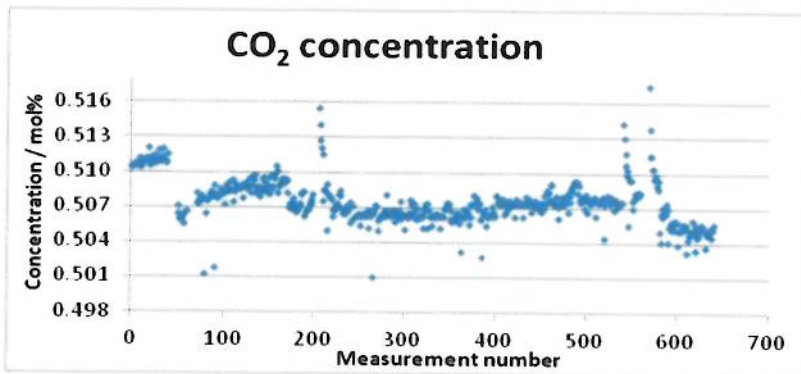
Figure 21: stability of the analyzed CO_2 concentration during one week
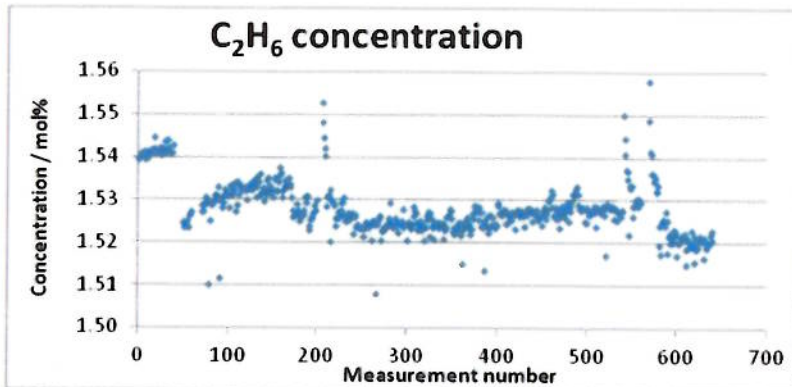
Figure 22: stability of the analyzed C_2H_6 concentration during one week

Figure 23: stability of C_3H_8 the analyzed concentration during one week
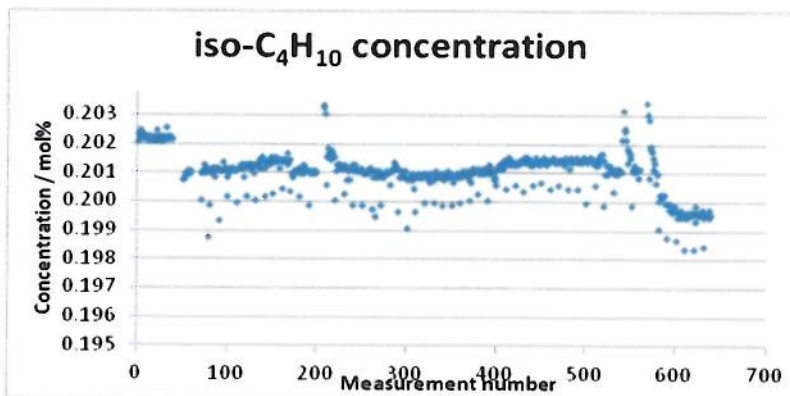
Figure 24: stability of the analyzed iso-C_4H_{10} concentration during one week

Figure 25: stability of the analyzed n-C$_4$H$_{10}$ concentration during one week

Figure 26: stability of the analyzed iso-C$_5$H$_{12}$ concentration during one week

Figure 27: stability of the analyzed n-C$_5$H$_{12}$ concentration during one week
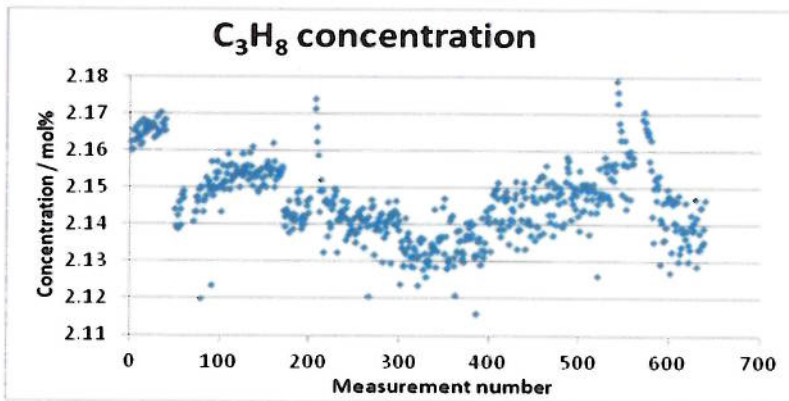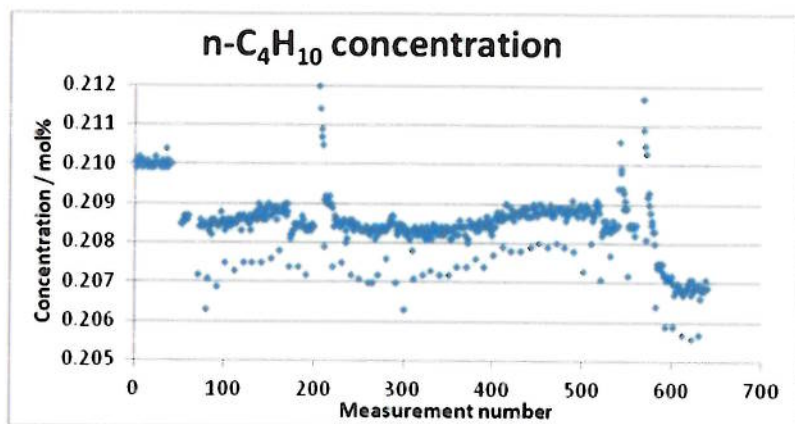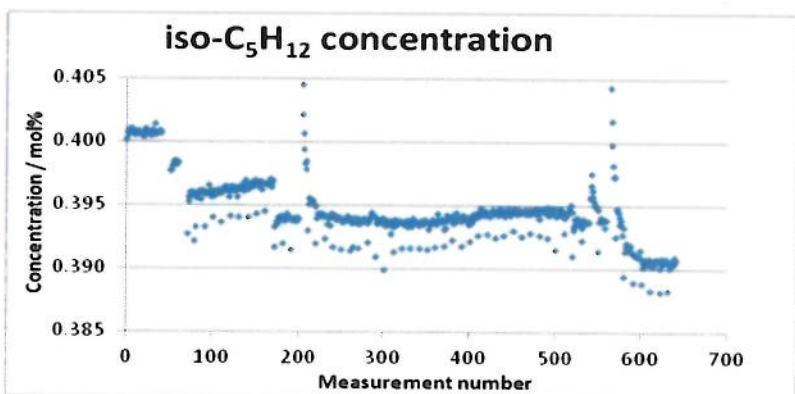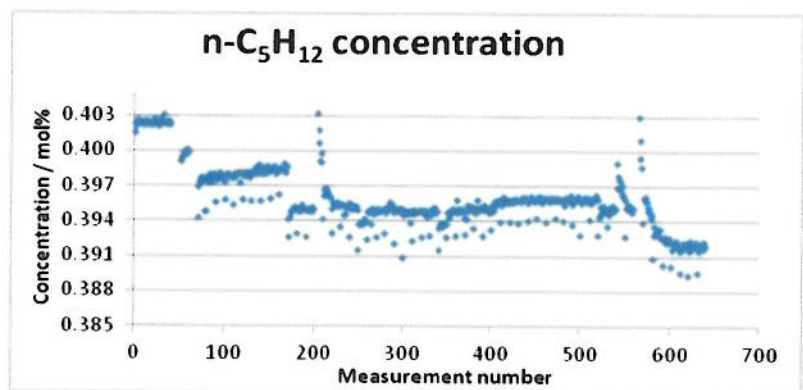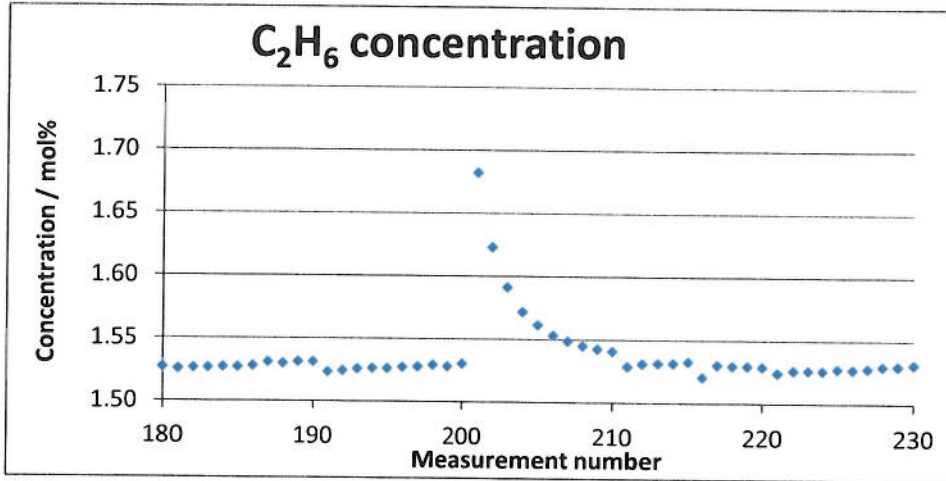
3.6.2 Results of GC shutdown and restart

Figure 28: effect of shutdown and restart after measurement number 200
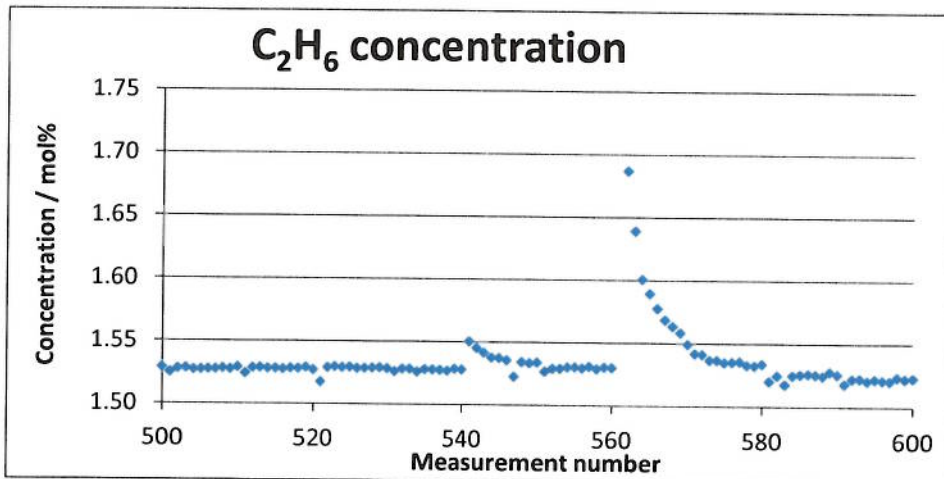
Figure 29: effect of shutdown and restart after measurement number 540 and 560

3.6.3 Discussion of stability testing

From the measurements 180 to 520 shown in figures 18-25, it can be seen that the GC gives stable results within less than 1.0% relative spread over a number of days for channel 1 and less than 0.5% relative spread for channel 2. From this it can be concluded that a calibration interval of one day is sufficient to control drift.

The ambient pressure in the laboratory varied between 99.2 kPa and 102.8 kPa during this stability test, and the change of pressure does not contribute significantly to the results.

The first series of 10 analyses gives different results. The cause of this difference is not further investigated.

In the results for channel 2 it is visible that every 1st analysis from a series of 10 gives lower results. This may be caused by a small leak in the sampling line or sample loop connections in this GC. In the time between the last analysis from a series and the first analysis from the next series (approx. one hour) some air may have leaked in, thus changing the composition of the gas in the sample loop. These analyses have been rejected, so it has no effect on the evaluation of the system. This problem can be fixed, and is not a relevant problem for the GC prototype under test.

3.6.4   Discussion of GC shutdown and restart

As can be seen from figure 28 and 29, the results after a shutdown of more than 15 minutes and restart of the GC are significantly affected. In the above mentioned figures, ethane is taken as an example, but the effect is similar for all components. Critical parameters, such as detector temperature, have to stabilize for representative analyses results. The time between restart and analysis was approximately 15 minutes for the shutdown and restart after measurement 200 and 560. Measurement 541 has been performed approximately 1 hour after the restart. Even in that case it can be seen that measurement number 10 of that cycle is still higher. (However, the obtained data meet the requirements of GOST 31371.7-2008 regarding the allowed divergence between two consistent analyses and the maximum allowed expanded uncertainty of the measurements.) The next cylce of ten measurements gives normal values.

From these tests it can be concluded that after a GC shutdown of more than 15 minutes and restart, up to one hour period of stabilization should be taken into account before the performance of the GC achieves the level required in GOST 31371-2008. During that period an alternative value, such as a default value, or the last values(s) before shutdown, can be used for further calculations.

4 Uncertainty evaluation

Based on the linearity test (section 3.4), the expanded uncertainty of the measurement of the components included in the programme has been determined. The results are shown in table 14. For the range of each component, three points have been calculated: the lower end of the range, the upper end of the range, and the middle. These uncertainties are given in the column "CMC". The calculation method of the CMCs is described in section 2.8 of this report. The maximum uncertainties stated in the GOST 31371 [3] and ISO 10723 [2] are given as well. All uncertainties are given as expanded uncertainty ($k = 2$).

Table 14: Uncertainty from obtained data versus the maximum allowed uncertainty in the GOST and ISO standards

Component	Concentration mol %	Uncertainty (CMC)	U max GOST 31371	Pass / fail GOST 31371	U max ISO 10723	Pass / fail ISO 10723
N_2	0.2	2.0	4.7	Pass	3.1	Pass
	5.0	1.3	4.0	Pass	0.73	Fail
	10.0	0.86	4.0	Pass	0.53	Fail
CO_2	0.2	1.2	6.6	Pass	3.1	Pass
	4.0	1.1	6.0	Pass	0.80	Fail
	8.0	0.80	6.0	Pass	0.59	Fail
C_2H_6	0.25	0.86	4.1	Pass	2.8	Pass
	5.0	1.11	4.0	Pass	0.73	Fail
	10.0	0.77	4.0	Pass	0.53	Fail
C_3H_8	0.1	1.14	6.2	Pass	4.2	Pass
	1.4	1.16	6.0	Pass	1.3	Pass
	2.8	0.98	6.0	Pass	0.94	Pass
iso-C_4H_{10}	0.03	1.5	6.8	Pass	7.3	Pass
	0.4	2.0	6.1	Pass	2.3	Pass
	0.8	1.1	6.0	Pass	1.7	Pass
n-C_4H_{10}	0.03	1.8	6.8	Pass	7.3	Pass
	0.4	2.0	6.1	Pass	2.3	Pass
	0.8	1.2	6.0	Pass	1.7	Pass
iso-C_5H_{12}	0.02	2.1	7.2	Pass	8.7	Pass
	0.2	2.0	6.1	Pass	3.1	Pass
	0.4	1.2	6.1	Pass	2.3	Pass
n-C_5H_{12}	0.02	2.2	7.2	Pass	8.7	Pass
	0.2	2.0	6.1	Pass	3.1	Pass
	0.4	1.2	6.1	Pass	2.3	Pass

Component	Concentration mol %	Uncertainty (CMC)	U max GOST 31371	Pass / fail GOST 31371	U max ISO 10723	Pass / fail ISO 10723
CH_4	72	0.15	0.53	Pass	0.22	Pass
	85	0.13	0.29	Pass	0.20	Pass
	98	0.13	0.05	Fail	0.19	Pass

With the exception of the 98 % methane concentration, all results pass the criteria of the GOST 31371. In order to test this high concentration, a test gas mixture is required with an expanded uncertainty of 0.028% relative for the CH_4 fraction. These mixtures are not available on the market, so meeting this criteria is not possible for any GC.

With respect to the criteria in the ISO 10723 the results for the higher concentrations of N_2, CO_2 and C_2H_6 do not pass the test. The 3rd order curve for the broad selected ranges, together with the obtained standard deviations on channel 1 results in uncertainties that are slightly higher than the advised maximum allowable uncertainty. This issue cannot be resolved by a single point calibration, as the CMCs calculated fully appreciate the non-linearity of the analyser. This approach is equivalent to calibrating the GC with a single calibration gas mixture close to the target amount–of–substance fractions of the components.

For field operation, the issues with the accuracy can be solved by selecting a suitable calibration gas composition close to the line gas composition. The GC is suited for single point calibration, provided that ranges of components are well within one decade and a calibration gas mixture is chosen accordingly, as required in the GOST 31371.6 (2008) and ISO 6974-2 (2002) [3,13] standards.

For methane and the hydrocarbons from propane onwards, the GC operates with a satisfactory uncertainty. For nitrogen, carbon dioxide and ethane, the uncertainty evaluated during the tests is higher than required by ISO 10723. This problem can be overcome by

1. Quantifying the amount–of–substance fraction methane (rather than calculating it by difference);
2. Normalisation of the gas composition data as described in ISO 6976 [11]

The disadvantage of calculating methane by difference is that the fluctuations in the raw amount–of–substance fractions of the measured components enter directly into the uncertainty budget; when using a measured methane fraction followed by normalisation, these effects are largely eliminated and only a small proportion enters into the uncertainty budget.

5   Conclusions

The GC system tested shows good peak separation and repeatability. Also the reproducibility of one day is good, and typically about twice the repeatability of the component at the tested amount–of–substance fraction level. The reproducibility over several days is again typically a factor 2 greater than the reproducibility in one day. The reproducibility over several days is of less relevance, as usually GC systems for natural gas analysis are calibrated each day with a single, well established calibration gas mixture.

For a number of components, the GC system shows appreciable non-linearity for the broad ranges of amount fractions in the validation gas mixtures. This non-linearity can be addressed by a multipoint calibration, but this is not the calibration mode used in the field. Hence, in the field a calibration gas mixture needs be chosen that resembles the gas composition of the natural gas to be analysed. This is by the way a requirement of the GOST 31371.6 (2008) and ISO 6974-2 (2002) standards. With such a choice of a calibration gas mixture, the GC can be operated with satisfactory performance.

The uncertainty associated with the gas composition measurement is satisfactory and meet in most cases the requirements of GOST and ISO standards. Where these criteria are not met, the uncertainty as determined during the tests is good enough for accurate determination of gas properties, such as density (for volume conversion), calorific value and Wobbe index.

After a system shutdown of more than 15 minutes, it takes one hour before the performance of the GC achieves the level required in GOST 31371-2008.

From the performed tests it can be concluded that the on-line Gas Chromatograph, type number KC 50.310-000 from BACS will meet the requirements of GOST 31371, ISO 6974 and ISO 10723 in case an appropriate calibration gas mixture will be used.

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