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Validation of ISO 6974 for the measurement of the composition of hydrogen-enriched natural gas

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ABSTRACT

Hydrogen gas is considered as one of the means to store electrical energy generated from wind or solar sources. The produced hydrogen gas could be injected into natural gas grids and thus utilised. Currently, most fiscal metering systems for natural gas are not configured for measuring the hydrogen content, notwithstanding that hydrogen is found in some natural gases in low fractions. Neither do the current documentary standards ISO 6974 and ISO 6975 cover hydrogen levels above $0.5 \text{ cmol mol}^{-1}$. To support fiscal metering, measurement standards and validated methods are needed to facilitate accurate composition and energy content measurement. The aim of this work was to develop measurement standards for hydrogen-enriched natural gas with uncertainties for the amount-of-substance fraction hydrogen similar to the analysis of methane and nitrogen in natural gas, as well as to validate ISO 6974 for use in this power-to-gas application. Measurement standards have been developed with state-of-the-art uncertainty for the composition for hydrogen fractions between 3 cmol mol^{-1} and 16 cmol mol^{-1} . A natural gas analyser configured according to ISO 6974-3 was used to confirm the composition of the measurement standards. We conclude that the scope of the current ISO 6974 can be extended to cover natural gas compositions with hydrogen amount-of-substance fractions of up to 20%. The best measurement capability obtained is $0.12\% (k = 2)$, expressed as relative expanded uncertainty.

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Introduction

The expansion of electrical power generation from renewable sources has lead to a number of challenges. One of these challenges is to utilise electrical power that is generated in excess of the instantaneous demand in an efficient way. One of the pathways is to convert this energy into hydrogen gas, which in turn is blended with natural gas and fed into existing gas grids [1]. Several studies have been conducted regarding the health, safety and environmental issues related to the

injection of hydrogen into natural gas grids [2,3]. Based on these studies, injection of up to 20 cmol mol^{-1} of hydrogen into natural gas would be feasible, without significantly increasing the risks associated with gas transport.

Fiscal metering of natural gas in Europe is regulated in EN 1776 [4] and implemented in applicable legislation in the European Union. EN 1776 requires, among others, that the composition of natural gas is measured in accordance with ISO 6974 [5,6] or ISO 6975 [9]. The current scope of both written standards limits their application to natural gases with less

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than 0.5 cmol mol⁻¹ hydrogen. ISO 6975 [9] is far less commonly used for fiscal natural gas composition measurement, and discussions in ISO/TC 193 “Natural gas” are ongoing as to whether this written standard should be brought up-to-date at all. Therefore, ISO 6974 has been selected as the written standard to be validated for blends of hydrogen and natural gas. Two configurations of natural gas analysers are described in this written standard that are suitable for the analysis of hydrogen [7,8]. A natural gas analyser configured in accordance with ISO 6974-3 has been used for the validation.

Metrologically traceable measurement results are required for fiscal metering of natural gas [4,10]. For this purpose, calibration gas mixtures are required that are prepared in accordance with ISO 6142 [11] or characterised for composition in accordance with ISO 6143 [12]. Measurement standards for natural gas with a hydrogen fraction exceeding 3 cmol mol⁻¹ currently do not exist. In the natural gas area, the highest metrological standards are maintained by the national metrology institutes [13]. The equivalence of such measurement standards is assessed in key comparisons which are organised as part of the Mutual Recognition Arrangement of the CIPM [14]. This arrangement gives provisions for the mutual acceptance of certificates of calibrations and measurement standards, which is vital in all sectors relying on measurements and operating across borders. So far, all key comparisons in the natural gas area [15–18] dealt with compositions without hydrogen. The only energy-related measurement standards containing hydrogen that have been subject of a key comparison are standards for refinery gas. In CCQM-K77 [19], a refinery gas mixture was used with a hydrogen fraction of about 7 cmol mol⁻¹. Confirmed best measurement capabilities, expressed as relative expanded uncertainty, range from 0.26% to 0.93%.

The objective of the work described in this paper is to verify whether the framework set by EN 1776 [4] for natural gas composition measurement can be extended to cover blends of hydrogen and natural gas to support fiscal metering for power-to-gas-applications [20,21]. Part of the validation includes the preparation of measurement standards in accordance with ISO 6142 [11] and the use of ISO 6974 [5,6] for the verification of the composition of these measurement standards.

Gas mixture preparation

The gas mixtures needed for the validation of ISO 6974 have been prepared in accordance with ISO 6142-1 [11]. This

method is widely used in the natural gas area and used for high-accuracy measurement and transfer standards. The primary standard gas mixtures (PSMs) maintained by the national metrology institutes are also prepared using this method [13]. For developing and validating analytical methods, multicomponent gas mixtures are required [24]. The composition of the gas mixtures used for this work are shown in Table 1. Only the amount-of-substance fractions of the major components are given in this table. Effects of impurities present in the parent gases have been taken into account while calculating the composition and its associated measurement uncertainty [25]. The matrix mimicking natural gas with hydrocarbons up to the butanes has been kept more or less the same for all mixtures. There is abundant evidence of the good performance of the natural gas analyser and the effects of changes in the matrix composition [16–18].

With the chosen preparation method, small uncertainties are attainable [23]. To preserve the accuracy of the gas mixture preparation, a multistage approach was used. The relative standard uncertainty associated with the amount-of-substance fraction hydrogen ranges from 0.011% to 0.026%. Typical values for the relative standard uncertainty for the fractions of the other components range from 0.005% (methane), 0.009% (carbon dioxide), 0.010% (nitrogen), 0.014% (ethane), 0.018% (propane) to 0.034% (butanes) [25]. In the validation of the method, several mixtures of hydrogen in other matrices were used to evaluate the sensitivity of the method for, e.g., matrix effects. These mixtures have been prepared using the same gravimetric methods.

Equipment

The natural gas analyser (NGA) is configured in accordance with ISO 6974-3 [7]. The GC is from Agilent, 6890 N and configured as follows. The hydrogen is separated on a 3 m Molsieve 13X column and detected using a thermal conductivity detector (TCD). The carrier gas is argon. The sample loop has a volume of 0.5 mL. The second column is a Porapak R, 3 m, 1/8" outer diameter, 80/100 mesh, and is equipped with two detectors: the flame ionisation detector (FID) placed at the exhaust of the TCD. The sampling valve is equipped with a 0.25 mL sample loop. The carrier gas is helium and the column temperature is programmed. The Porapak column is used for the separation of all other components in the gas mixtures. The sample introduction on both columns is done using a multi-position gas valve at ambient pressure.

Table 1 – Compositions of the hydrogen-enriched synthetic natural gas mixtures expressed in amount-of-substance fractions of the abundant components (cmol mol⁻¹).

Component	VSL228632	VSL328630	VSL628453	VSL309545	VSL309454
Hydrogen	3.619	5.460	7.368	10.976	14.913
Carbon dioxide	8.602	8.655	9.262	8.807	8.911
Nitrogen	3.625	5.469	3.928	5.852	7.951
Methane	75.202	71.213	70.352	65.115	58.896
Ethane	5.697	5.903	5.779	5.885	5.937
Propane	3.072	3.124	3.131	3.184	3.212
iso-Butane	0.091	0.087	0.090	0.090	0.090
n-Butane	0.091	0.088	0.090	0.090	0.090

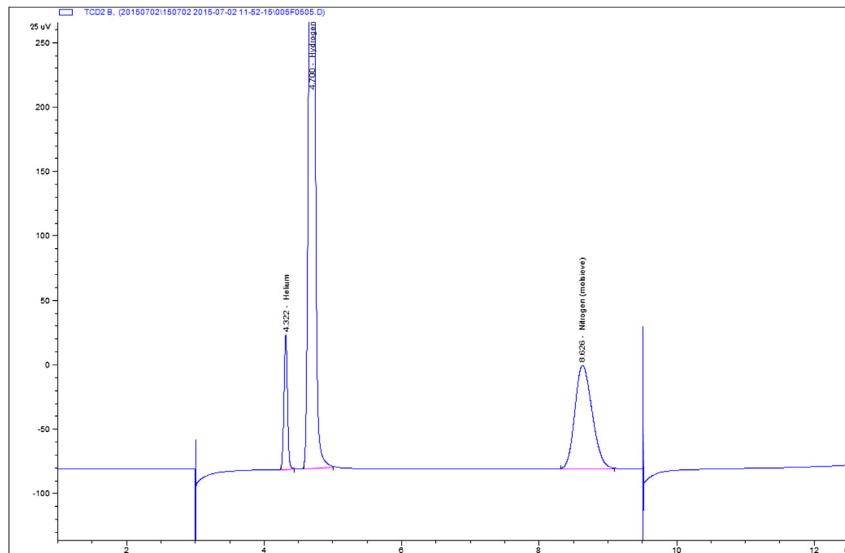


Fig. 1 – Chromatogram of an injection of a synthetic natural gas mixture containing $0.5 \text{ cmol mol}^{-1}$ helium and 3 cmol mol^{-1} hydrogen on the Molsieve 13X column; the chromatogram shows the peaks from helium, hydrogen and nitrogen.

The measurements are compared with those performed on a refinery gas analyser (RGA) used previously for analysing hydrogen in energy gases [19]. The RGA is an Agilent 7890 A and equipped with three channels. The first channel consists of an $25 \text{ m} \times 0.32 \text{ mm} \times 8 \text{ mm}$ aluminium oxide plot S column and an FID. This channel is used to separate and detect the higher hydrocarbons. The second channel consists of an $0.25 \text{ m} \times 1/16''$ HayeSep Q (80/100 mesh) column, an $1 \text{ m} \times 1/16''$ Hayesep N (80/100 mesh) column, and a $2 \text{ m} \times 1/16''$ Molsieve 13X column and is equipped with a TCD. The Molsieve column is used to collect the oxygen, nitrogen, methane and carbon monoxide so that first the carbon dioxide, ethane, ethene, and hydrogen sulphide eluting from the HayeSep N are detected. The higher hydrocarbons are trapped on the HayeSep Q and back flushed. After the last component eluting

from the HayeSep N is detected, the Molsieve is switched online again and the oxygen, nitrogen, methane and carbon monoxide are detected. The third channel consists of a combined HayeSep Q/Molsieve 5A column ($1 \text{ m}/2 \text{ m}, 1/16''$) and is equipped with a TCD. This channel is operated with nitrogen as carrier so that helium and hydrogen can be detected. All other components on this channel are back flushed.

Results

Peak separation and chromatographic performance

A chromatogram from an injection of a low calorific natural gas containing approximately $0.5 \text{ cmol mol}^{-1}$ helium and

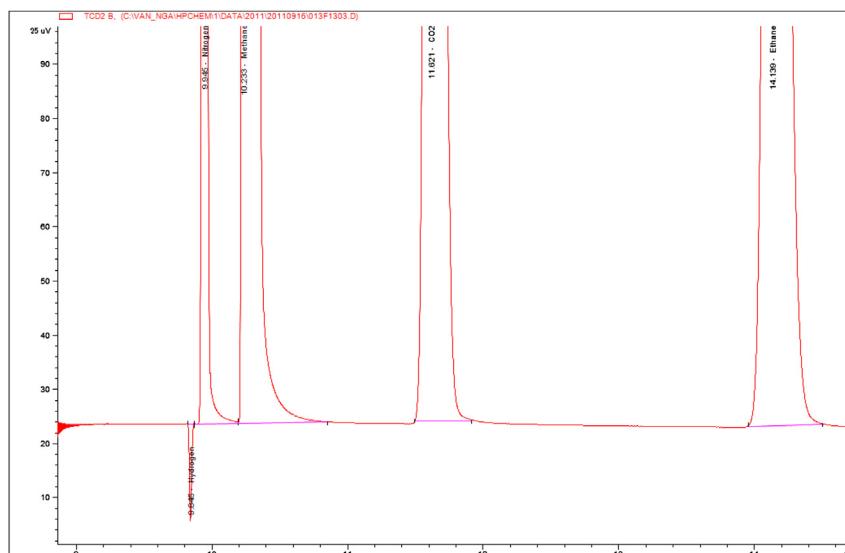
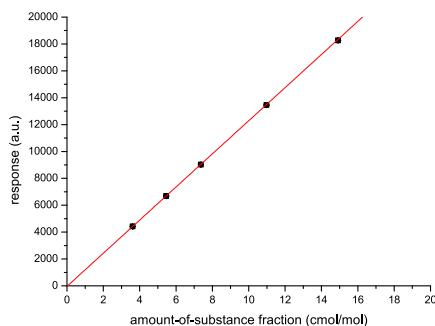


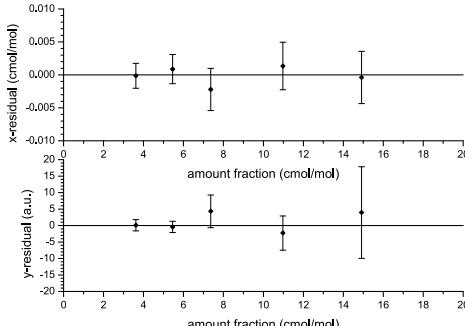
Fig. 2 – Chromatogram of an injection of a synthetic natural gas mixture containing $0.5 \text{ cmol mol}^{-1}$ helium and 3 cmol mol^{-1} hydrogen on the Porapak R column, with a negative peak from hydrogen, followed by nitrogen, methane, carbon dioxide and ethane.

Table 2 – Calibration data natural gas analyser.

Mixture	$x \text{ cmol mol}^{-1}$	$u(x) \text{ cmol mol}^{-1}$	y	$u(y)$	$r \text{ mol cmol}^{-1}$	$u(r) \text{ mol cmol}^{-1}$
VSL228632	3.6189	0.0009	4419.28	0.86	1221.17	0.40
VSL328630	5.4595	0.0011	6684.57	0.85	1224.39	0.29
VSL628453	7.3675	0.0016	9019.88	2.48	1224.28	0.43
VSL309545	10.9760	0.0018	13,456.4	2.59	1225.98	0.31
VSL309454	14.9130	0.0020	18,265.8	6.95	1224.82	0.49



(a) Calibration data and curve on the NGA for hydrogen



(b) Residuals from GDR regression of the hydrogen calibration data

Fig. 3 – Calibration data, function and residuals for hydrogen in natural gas on an NGA configured in accordance with ISO 6974-3 [7]. The uncertainty bars represent 95% coverage intervals.

3 cmol mol^{-1} (see Fig. 1) demonstrates baseline separation of the peaks from helium, hydrogen and nitrogen. The resolution of the helium and hydrogen peaks, computed using the formula in ISO 6975 [9] is 5.6. Oxygen elutes on this column at 6.1 min, so well separated from hydrogen and nitrogen. The peak separation looks better than that shown in figure A.1 of ISO 6974-3 [7]. The presence of hydrogen in a natural gas sample has also an impact on the chromatogram on the Porapak R column (see Fig. 2), as it gives rise to a negative peak just before the nitrogen peak. The resolution between the two peaks is 4.6. The separation of hydrogen from helium (Molecular sieve 13X channel) and nitrogen (Porapak R column) is satisfactory.

Calibration of a GC

The results of calibrating the NGA with a suite of synthetic calibration gas mixtures mimicking hydrogen-enriched natural gas are shown in Table 2 and Fig. 3. The amount-of-substance fraction hydrogen x and its associated standard uncertainty are given, as well as the instrument response (peak area) y , and its associated standard uncertainty. To aid the interpretation, the response factor r , defined as y/x are computed.

From the response factors it can be seen that they gradually change as a function of the amount-of-substance fraction hydrogen. This hints at the need for using a second order polynomial or a straight line with an intercept when calculating a calibration curve using the procedure described in ISO 6143 [12]. The regression method is known as *generalised distance regression*, GDR [23]. Fitting the data confirms the need of a second order polynomial. The fit of

the data satisfies the consistency criteria of ISO 6974-2 [6] for the residuals in x - and y -direction, as shown in Fig. 3. The coefficients are given in Table 3. The calibration function reads as

$$y = a_0 + a_1 x + a_2 x^2$$

The intercept a_0 is significant, as $|a_0| > 2 \cdot u(a_0)$. The coefficient of the quadratic term is just significant, but the contribution of this term is moderate.

The results of measuring the amount-of-substance fraction hydrogen in the suite of gas mixtures on the RGA are shown in Table 4 and Fig. 4.

Just as in the case of the NGA, the response factors increase with increasing amount-of-substance fraction. Also for this instrument, the calibration data can be well fitted by means of a quadratic curve, as shown in Fig. 4. The fit of the data satisfies the consistency criteria of ISO 6974-2 [6] for the residuals. The coefficients of the polynomial are given in Table 5.

The intercept a_0 is insignificant, as $|a_0| < 2 \cdot u(a_0)$. The coefficient of the quadratic term is just significant, but the contribution of this term to the quality of the regression is moderate.

Table 3 – Coefficients of the calibration curve on the NGA.

i	Unit	a_i	$u(a_i)$
0		-38	6
1	mol cmol^{-1}	1233.05	1.86
2	$\text{mol}^2 \text{cmol}^{-2}$	-0.0361	0.0118

Table 4 – Calibration data refinery gas analyser.

Mixture	x cmol mol ⁻¹	$u(x)$ cmol mol ⁻¹	y	$u(y)$	r mol cmol ⁻¹	$u(r)$ mol cmol ⁻¹
VSL228632	3.61890	0.00095	344.14	0.12	95.095	0.041
VSL328630	5.45950	0.00111	520.15	0.12	95.274	0.029
VSL628453	7.36750	0.00160	702.49	0.60	95.349	0.084
VSL309545	10.97600	0.00180	1048.26	0.60	95.505	0.057
VSL309454	14.91300	0.00198	1428.02	0.84	95.757	0.058

Precision and accuracy

The repeatability standard deviation on the RGA ranges from 0.08% to 0.19%. The NGA performs better with a repeatability standard deviation between 0.04% and 0.09%. the number of repeat sample injections was 5 in all cases. These standard deviations have been used to compute the standard uncertainties shown in Tables 2 and 4 by calculating the standard deviation of the mean response, i.e. $u(y) = s/n$ where s denotes the repeatability standard deviation and n the number of repeats. ISO 6974-3 [7] requires the repeatability to be 0.1%. Expressed as a standard deviation, this requirement is 0.35%. Both instruments perform substantially better than the standard requires. The same applies to the repeatability standard deviations of the other components, which are similar to those obtained in the latest key comparisons [16–18].

The calibrated GC was further subjected to a performance evaluation. Using the calibration curve and the parameter values obtained, a variety of hydrogen-containing gas mixtures was analysed. The amount-of-substance fraction hydrogen was calculated using the calibration function and the uncertainty was propagated accordingly using the method described in Refs. [26], which implements the method of ISO 6974 [5,6].

The results of the uncertainty calculation for the NGA are shown in Table 6. The three points at which the uncertainty for the assigned amount-of-substance fraction is calculated are at the low end, middle, and high end of the curve. Based on these results, it can be stated that the analysis of hydrogen in natural gas can be performed with a relative expanded uncertainty of 0.12% using a coverage factor $k = 2$.

The results of the uncertainty calculation for the RGA are shown in Table 7. Based on these results, it can be stated that

Table 5 – Coefficients of the calibration curve on the RGA.

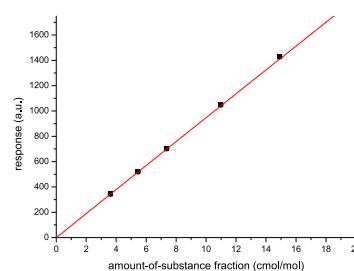
i	Unit	a_i	$u(a_i)$
0		-0.87	0.72
1	mol cmol ⁻¹	95.21	0.22
2	mol ² cmol ⁻²	0.0389	0.0136

the analysis of hydrogen in natural gas can be performed with a relative expanded uncertainty of 0.20%, using a coverage factor $k = 2$.

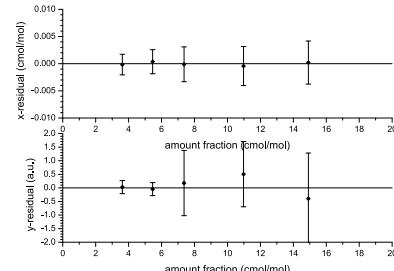
Matrix influence on the analysis of hydrogen

To investigate the influence of the matrix gas, some binary mixtures containing hydrogen have been analysed. The presence of matrix effects may confute the calibration of the analyser, as this part of the standard permits in clause 4.1.2.1 the use of calibration gas mixtures containing helium and hydrogen in a matrix of nitrogen or argon. These are among the matrices investigated (see Table 8). The mixture in methane can be considered as a lean natural gas, a natural gas containing few or no condensable components.

The results of the measurements on the NGA and RGA (Table 9) indicate very good agreement between the measurements on both systems. The uncertainties stated are obtained by propagating the uncertainties associated with the coefficients of the calibration curves and the repeatability of the responses. They do not account for any other effects. E_n is as usual defined as the ratio between the observed difference and its associated expanded uncertainty. The expanded uncertainty is obtained with a coverage factor $k = 2$.



(a) Calibration data and curve on the RGA for hydrogen



(b) Residuals from GDR regression of the hydrogen calibration data

Fig. 4 – Calibration data, function and residuals for hydrogen in natural gas on an RGA. The uncertainty bars represent 95% coverage intervals.

Table 6 – Calculated measurement capabilities for the NGA.

	y	$u(y)$	x cmol cmol $^{-1}$	$u(x)$ cmol cmol $^{-1}$	$u(x)$
Low end	4419.28	0.86	3.6187	0.0013	0.04%
Middle	11,342.54	6.95	9.2547	0.0059	0.06%
High end	18,265.80	6.95	14.9094	0.0076	0.05%

Table 7 – Calculated measurement capabilities for the RGA.

	y	$u(y)$	x cmol cmol $^{-1}$	$u(x)$ cmol cmol $^{-1}$	$u(x)$
Low end	344.14	0.12	3.6185	0.0020	0.05%
Middle	886.08	0.84	9.2809	0.0093	0.10%
High end	1428.02	0.84	14.9173	0.0119	0.08%

The results from the NGA shown in Table 9 indicate that the mixtures in nitrogen (PRM126842) and methane (VSL305164) satisfy the criterion from ISO 6142 [11] that

$$E_n = \frac{|x_{\text{prep}} - x_{\text{meas}}|}{2 \cdot \sqrt{u^2(x_{\text{prep}}) + u^2(x_{\text{meas}})}} \leq 1$$

The mixture in argon (VSL124437) does not satisfy this criterion, which is due to the small standard uncertainty calculated for the measured value x_{meas} . The observed relative difference is 0.05%, so that is still well within the calculated uncertainty from Table 6, which is, after expansion using $k = 2$, 0.12%.

The results from the RGA in Table 9 show slightly better agreement between the values for the measured and calculated amount-of-substance fraction hydrogen, in particular for the mixture in argon.

Further repeats of the experiments described here have indicated that the method reproduces within the stated expanded uncertainties. The reproducibility standard deviation of the entire process is 0.06% for the NGA and 0.10% for the RGA, based on 5 repeat injections of the calibration gas mixtures and the mixtures to be analysed.

Discussion and conclusions

The work presented here demonstrates the suitability of ISO 6974 [5,6] and ISO 6142 [11] for the preparation of calibration gas mixtures and the verification of their composition respectively for natural gas compositions containing between 3 cmol mol $^{-1}$ and 16 cmol mol $^{-1}$. The natural gas analyser configuration described in ISO 6974-3 [7] is suitable for this purpose.

The repeatability standard deviation for hydrogen is well below the requirement stated in ISO 6974-3 [7]. As to the other components, the repeatability standard deviations were similar to those obtained in, e.g., the key comparisons CCQM-K16 [16] and CCQM-K23 [17,18]. These repeatability standard deviations also meet the requirements of this part of ISO 6974.

The calculated measurement capability of 0.12% on the natural gas analyser is slightly better than measurement capabilities of nitrogen and carbon dioxide in natural gas as observed in key comparisons using the same instrument. It is at approximately the same level as those for helium and slightly worse than for methane using the same equipment [17,18]. The cross-validation with mixtures of hydrogen in

Table 8 – Compositional data in amount-of-substance fractions with respect to hydrogen of the mixtures used for assessing the influence of the matrix gas.

Mixture	x cmol cmol $^{-1}$	$u(x)$ cmol cmol $^{-1}$	Matrix gas	Preparation date
VSL124437	3.7993	0.0008	Argon	16-05-2003
PRM126842	5.0022	0.0005	Nitrogen	15-03-2003
VSL305164	9.9900	0.0018	Methane	24-01-2011

Table 9 – Comparison of analysed values on both systems with the preparation data for hydrogen-containing gas mixtures.

Mixture	RGA			NGA		
	x_{meas} cmol cmol $^{-1}$	$u(x_{\text{meas}})$ cmol cmol $^{-1}$	E_n	x_{meas} cmol cmol $^{-1}$	$u(x_{\text{meas}})$ cmol cmol $^{-1}$	E_n
VSL124437	3.7999	0.0020	0.14	3.7939	0.0017	-1.42
PRM126842	4.9959	0.0038	-0.82	4.9980	0.0021	-0.98
VSL305164	9.9876	0.0059	-0.19	9.9869	0.0023	-0.53

argon, methane, and nitrogen shows that the analytical method can be applied to a much wider range of compositions as far as the determination of the amount-of-substance fraction hydrogen is concerned.

Calibration gas mixtures are considered to be certified reference materials (CRMs). CRMs are a kind of measurement standards, and the relevant properties should be stable over a prolonged period of time [27,28]. Hydrogen is a non-reactive component, so any instability is not expected. Given that two of the three mixtures used in the cross-validation were well over 9 years of age at the time of measurement, from the experimental data it can be concluded that there are no stability issues and that these mixtures can be provided with the same stability warranty as is given for similar measurement standards of natural gas. This evidence underpins at the same time the uncertainties for the hydrogen fractions in the calibration gas mixtures stated in Tables 2 and 4.

Based on this work, it can be concluded that the scope of ISO 6974-1 and ISO 6974-2 [5,6] can be extended to cover natural gas compositions with up to approximately 20 cmol mol⁻¹ hydrogen. A suitable configuration for the analysis of natural gas with elevated hydrogen fractions is described, among others, in ISO 6974-3 [7]. By implication, the framework set for fiscal metering by EN 1776 [4] can also be applied to such blends of hydrogen and natural gas. These conclusions are important for the further development of power-to-gas applications on an industrial scale [1].

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