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Analysis of natural gas — Validation methods for gaseous reference materials

Analyse du gaz naturel — Méthodes de validation pour matériaux de référence gazeux

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

In exceptional circumstances, when a technical committee has collected data of a different kind from that which is normally published as an International Standard ("state of the art", for example), it may decide by a simple majority vote of its participating members to publish a Technical Report. A Technical Report is entirely informative in nature and does not have to be reviewed until the data it provides are considered to be no longer valid or useful.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO/TR 24094 was prepared by Technical Committee ISO/TC 193, *Natural gas*, Subcommittee SC 1, *Analysis of natural gas*.

Analysis of natural gas — Validation methods for gaseous reference materials

1 Scope

This Technical Report describes the validation of the calorific value and density calculated from current practice natural gas analysis by statistical comparison with values obtained by measurement using a reference calorimeter and a density balance.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 6142, *Gas analysis — Preparation of calibration gas mixtures — Gravimetric method*

ISO 6974-1, *Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 1: Guidelines for tailored analysis*

ISO 6974-2, *Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 2: Measuring-system characteristics and statistics for processing of data*

ISO 6974-3, *Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 3: Determination of hydrogen, helium, oxygen, nitrogen, carbon dioxide and hydrocarbons up to C8 using two packed columns*

ISO 6974-4, *Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 4: Determination of nitrogen, carbon dioxide and C1 to C5 and C6+ hydrocarbons for a laboratory and on-line measuring system using two columns*

ISO 6974-5, *Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 5: Determination of nitrogen, carbon dioxide and C1 to C5 and C6+ hydrocarbons for a laboratory and on-line process application using three columns*

ISO 6974-6, *Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 6: Determination of hydrogen, helium, oxygen, nitrogen, carbon dioxide and C1 to C8 hydrocarbons using three capillary columns*

ISO 6976, *Natural gas — Calculation of calorific values, density, relative density and Wobbe index from composition*

Guide to the expression of uncertainty in measurement (*GUM*), BIPM/IEC/IFCC/ISO/IUPAC/IUPAP/OIML, 1995

3   Development of the validation methods

The validation methods for gaseous reference materials (VAMGAS) project was established by a group of European gas companies as an approach to confirming the practices used in natural gas analysis and physical property calculations.

The VAMGAS project proposed comparing the calorific value and density calculated from the current practices for natural gas analyses with values obtained by measurement using a reference calorimeter (located at the Ofgas, UK laboratory) and density balance (located at the Ruhrgas, Germany laboratory). Robust statistical comparisons allowed an assessment of the validity of the practices.

The natural gas analysis practice covered by the VAMGAS project can be divided into the following steps:

— The gravimetric preparation of gas mixtures used as calibrants in the analysis of natural gas in accordance with ISO 6142. At the highest level, these mixtures are categorized as primary reference gas mixtures (PRMs) and are available from national institutes such as Bundesanstalt fur Materialforschung und -prüfung (BAM) of Germany and Nederlands Meetinstituut (NMi) of the Netherlands.

— The analysis of natural gas by gas chromatographic methods, such as those given is ISO 6974 (all parts). This is a multiple part International Standard that provides a number of different approaches to the gas chromatographic analysis of natural gas. ISO 6974-2 describes the processing of calibration and analytical data to determine the uncertainties on sample component concentrations that are required for the calculation of uncertainties on calculated physical property values of the sample gas.

— The calculation of the values of physical properties from the results of the gas chromatographic analyses as described in ISO 6976.

The VAMGAS project was divided in two parts:

a)   Part 1: comparison of the calorific values and densities of two PRMs calculated from the gravimetric preparation data against the values obtained from the reference calorimeter and density balance (see Figure 1);

b)   Part 2: gas chromatography intercomparison exercise, in which calorific values and densities calculated from the analyses of two natural gases (with bracketing calibration using PRMs) were compared to the values obtained from the reference calorimeter and density balance (see Figure 2).

The two separate exercises would enable problems arising from either the gravimetric preparation or the gas chromatographic analyses to be identified.

The participants in the VAMGAS project were Ruhrgas AG (Germany and project co-ordinator), Gasunie (the Netherlands), Gaz de France (France), BAM (Germany), NMi (the Netherlands) and Ofgem (previously Ofgas, the UK). In addition, a total of 18 laboratories participated in the gas chromatography intercomparison.
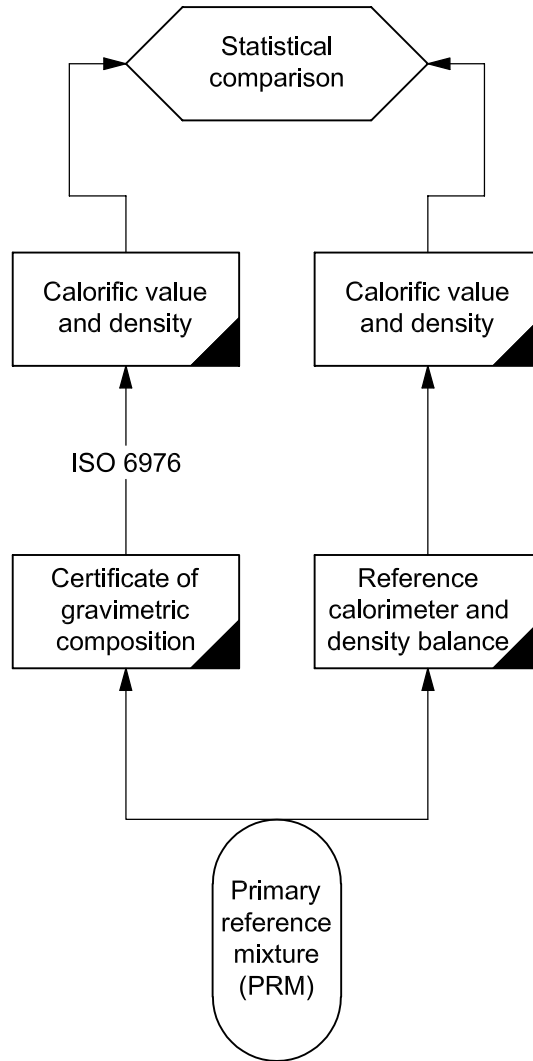
The technical report from the VAMGAS is given in Annex A.

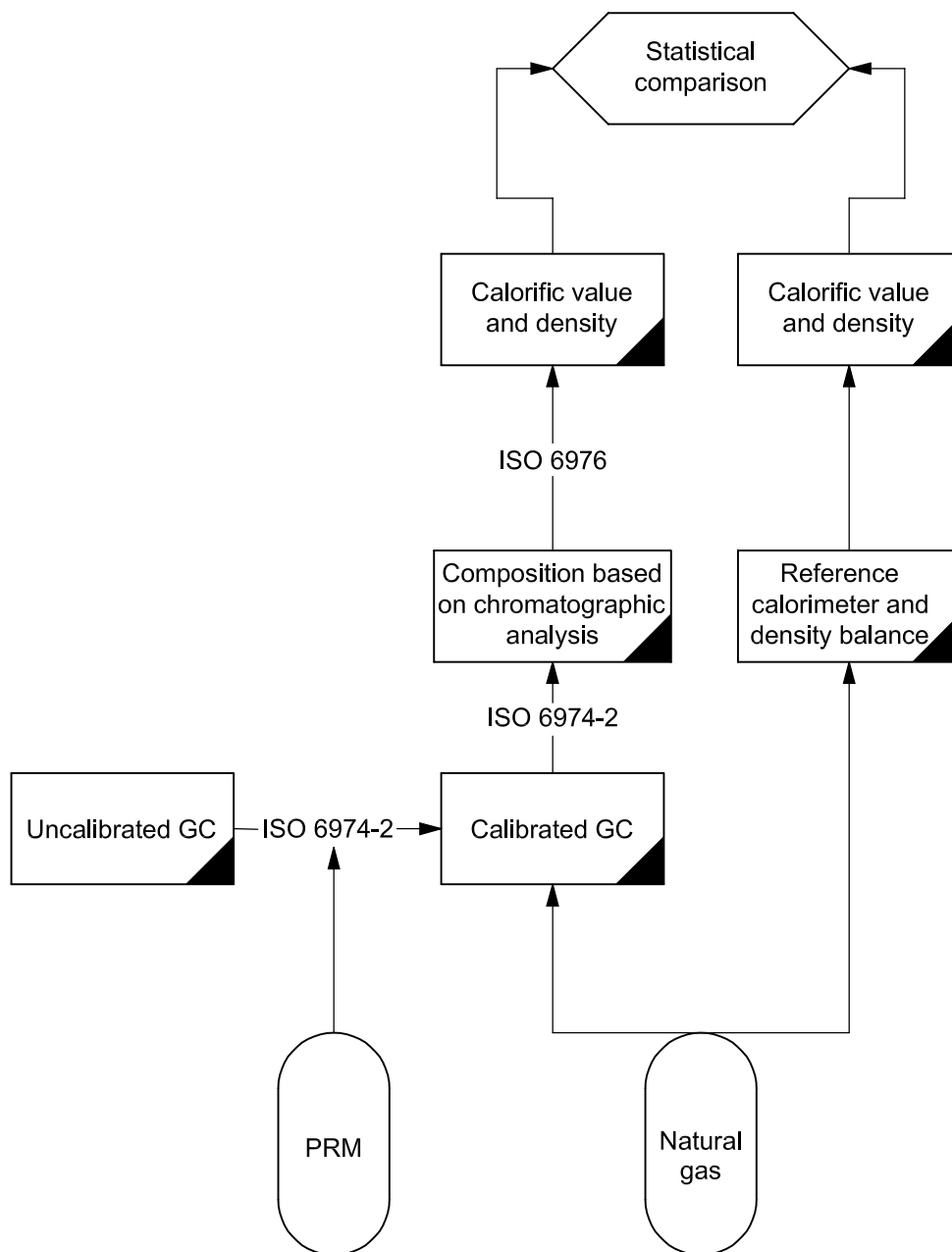Figure 1 — Schematic concept of part 1 of the VAMGAS project

Figure 2 — Schematic concept of part 2 of the VAMGAS project

4   Results of the VAMGAS project

The project report provides results on two sets of comparisons.

a)   The results of the exercise using the PRMs showed statistical agreement between the calorific values and densities calculated from the gravimetric preparation data and the values of these physical properties obtained from direct measurement using reference instruments.

b)   The results of the gas chromatographic intercomparison showed statistical agreement between the calorific values and densities calculated from gas chromatographic analyses, carried out using PRMs as calibrants, and the values of these physical properties obtained from direct measurements using reference instruments.

It can be concluded that the VAMGAS project has validated the current systems of natural gas analyses and calculation of physical property data involving the previously mentioned ISO International Standards. As a result, all parties in the supply and use of natural gas, whether supplier or consumer, can have confidence in these. The current ISO International Standards for calibration gas preparation and natural gas analysis, if carefully applied, give values of calorific value and density that are in agreement with values that were independently determined by reference measurements. This also includes the tabulated values in ISO 6976, which are used in calculations of thermal energy for billing/fiscal transfer purposes.

The VAMGAS project was carried out as an integrated project to study the complete system of natural gas analysis involving the gravimetric preparation of calibration gas mixtures, the gas chromatographic analysis and calculation of physical properties. Reference measurements of the physical properties were applied during the VAMGAS project as a means of assessing the system. It is stressed that readers take account of the whole project; and it is totally wrong to take isolated parts and results of the project and use these for other purposes in the belief that the project results justify such an approach.

For example, in the first part of the project comparison was made between the physical property values calculated from the gravimetric preparation data of the PRMs and the values obtained from the reference measurements. It is important not to use the results from this part of the project to justify using reference measurements of a physical property to validate the composition of a prepared natural gas mixture. There are three reasons.

—   The VAMGAS project was not designed to investigate the applicability, or otherwise, of such a procedure. The VAMGAS project was designed to investigate whether or not a cylinder of gas designated as a PRM can provide gas of the composition given on the certificate attached to that cylinder.

—   In the preparation of the PRMs, the national institutes have rigorous procedures including a system of validating the mixture composition by gas chromatographic analysis to give confidence in the composition of the gas mixture.

—   Whereas it is true that a gas mixture of known composition has an unique calorific value or density, the same is not true of the reverse relationship: a specific calorific value or density does not have a corresponding unique gas composition; in fact a calorific value or density can result from an almost infinite number of different gas compositions. Hence, it is not technically feasible to validate gas mixture compositions using measurements of a physical property. As a simple illustration, consider the manufacture of a multi-component mixture containing both isomers of butane. If, by mistake, the same isomer was added twice then the resulting mixture would have the same calorific value and density as the required mixture but the composition would be incorrect. Measurements of the calorific value or density would appear to validate the mixture composition when it was, in fact, in error.

Annex A
(informative)

Report on the validation methods for gaseous reference materials

A.1 General

A.1.1 Summary

In the first part of the project, 12 primary reference gas mixtures were produced by BAM and NMi. As regards composition, the gas mixtures produced were similar to type L Groningen gas and type H North Sea gas.

The superior calorific value, H_s, molar mass, M, and density at normal conditions of the mixtures were calculated from the component concentrations specified by the producers. The calculated data were then compared with the results of direct measurements of physical properties. The methods used for direct measurement of physical properties were reference calorimetry[1] and precision densitometry[2]. Statistically significant agreement was found between the calculated data and the measurements.

Table A.1 — Comparison of experimental (M_{exp}) and calculated (M_{calc}) values of the molar mass for different PRMs [a]

Gas mixture	Type of gas	M_{exp} g/mol	M_{calc} g/mol	Relative difference %
BAM 9605 4933	L	18,564 3	18,564 6	0,002
NMi 0602E	L	18,542 7	18,543 0	0,002
BAM 9605 4902	H	18,793 1	18,796 6	0,018
NMi 9497C	H	18,946 5	18,946 9	0,002
[a] Calculations are made in accordance with ISO 6976.				

In the second stage, 20 natural gas samples was taken from the natural gas transmission system of Ruhrgas AG. These samples included both type L Groningen gas and type H North Sea gas. Gas samples were taken in batches, so that the compressed gas cylinders filled with each of the two types were of identical composition. The homogeneity of the batches, i.e. the agreement between the compositions of the samples in the various gas cylinders, was verified using the precision densitometer. The stability of the gas samples during sampling was also tested.

Table A.2 — Comparison of experimental (ρ_{exp}) and calculated (ρ_{calc}) values of the gas density at standard conditions for different PRMs [a]

Gas mixture	Type of gas	ρ_{exp} kg/m^3	ρ_{calc} kg/m^3	Relative difference %
BAM 9605 4933	L	0,773 19	0,773 19	—
NMi 0602E	L	0,772 29	0,772 38	0,012
BAM 9605 4902	H	0,783 24	0,783 41	0,022
NMi 9497C	H	0,789 67	0,789 72	0,006
[a] Calculations are made in accordance with ISO 6976.				

Table A.3 — Comparison of experimental (CV_{exp}) and calculated (CV_{calc}) values of the superior calorific value for different PRMs [a]

Gas mixture	Type of gas	CV_{exp} MJ/kg	CV_{calc} MJ/kg	Relative difference %
BAM 9605 4933	L	44,061	44,068	0,015
NMi 0603E	L	44,222	44,220	0,006
BAM 9605 4902	H	51,896	51,887	0,017
NMi 9498C	H	51,910	51,895	0,03
[a] Calculations are made in accordance with ISO 6976.				

Table A.4 — Expanded uncertainties (95 % confidence interval) **of the experimental reference values and the calculated physical properties**

Parameter	Gas mixture	
	Type H relative %	Type L relative %
Calculated density	0,01	0,01
Measured density	0,015	0,015
Calculated molar mass	0,007	0,007
Measured molar mass	0,015	0,015
Calculated calorific value	0,1	0,1
Measured calorific value	0,035	0,035

For these gas samples, primary reference gas mixtures were once again produced. The composition of these primary reference gas mixtures was selected so that they could be used for "bracketing calibration". These gas mixtures were used in a round-robin test series with a total of 18 participants from nine European countries (see A.2.8.2). The test program was designed to ensure that the repeatability and comparability of the results obtained by each individual participant could be determined by statistical methods with a view to allowing an assessment of the uncertainty of all the individual results. Analytical results were transmitted as raw data for uniform evaluation. Once again, the superior calorific value, molar mass and density at normal conditions were calculated in accordance with ISO 6976.

The results of the round-robin test series are summarized in Table A.5:

Table A.5 — Comparison of the values of the physical properties calculated from the mean of the 18 participating laboratories with the values obtained from direct measurement by the reference methods

Parameter	Type of gas	Mean of the laboratories	Reference method	Relative difference %
Calorific value, MJ/kg	H	52,561	52,563	0,003
	L	44,701	44,688	0,027
Molar mass, kg/kmol	H	18,115	18,122	0,036
	L	18,604	18,612	0,045
Density, kg/m^3	H	0,7549	0,7551	0,034
	L	0,7748	0,7752	0,048

A.1.2 Background

Chemical composition analysis represents a special case in the field of metrology as it is not possible to ensure traceability to the SI unit "mole". The objective is to avoid this problem by creating PRMs. PRMs represent the best possible realization of the composition of a material. The primary reference gas mixtures used in this project were produced by gravimetry, by successively weighing the individual pure components.

However, the significance of PRMs for chemical composition analysis is disputed because of the difficulty of estimating cost, which is unsatisfactory for general use, and the often confusing terminology employed. In this context, "traceability" means no more and no less than the statement of a result with documented uncertainty. It is important not to confuse this quality target with the minimization of measurement error.

In view of the associated advantages, traceability is of very considerable importance for the European natural gas industry, which operates a highly complex pipeline system with a comparatively large number of gas compositions. Traceability becomes even more significant in the framework of the liberalized market. As the value of gas supplied to a customer is calculated from the superior calorific value and volume flow measured, measurement uncertainties have considerable financial impact.

This is why European gas companies have assumed the role of pioneers in this field, a role which is evident from their participation in the ISO TC/193 and ISO TC/158 International Standards committees working on traceability in natural gas analysis and gas analysis in general. Metrological institutes are also paying increased attention to this requirement of their customers.

NOTE   The participants in this joint research project under the leadership of Ruhrgas AG of Germany were Gasunie of The Netherlands, Gaz de France of France, Nederlands Meetinstituut of The Netherlands, Bundesanstalt für Materialforschung und -prüfung of Germany and Ofgem (previously: Ofgas) of the United Kingdom.

A.2 Material and methods

A.2.1 Primary reference gas mixtures

Primary reference gas mixtures (PRMs) are prepared by a gravimetric procedure as described in ISO 6142 and are verified using the Dutch (NMi) or German (BAM) national primary standard gas mixtures (PSMs). PRMs prepared by this method show the highest accuracy of gas standards and can be used as calibration gases by the industry and calibration laboratories.

The production of a primary calibration gas mixture consists of a number of stages:

a)   purity analysis of the starting components (pure gases) by FTIR, GC and MS methods;

b)   gravimetric preparation of the gas mixture in passivated cylinders;

c)   validation of the mixture using analytical methods to ensure that no errors have occurred during the preparation process;

d)   issue of the certificate.

A.2.1.1   Purity analysis of the starting components

The gases from which the mixture is prepared should be of known high purity and should preferably not be contaminated by any of the other component gases that are to be part of the final mixture. The most accurate method for determining purity is to quantify the impurities and to calculate the purity on a molar basis by difference (purity is equal to 100 % minus the impurities). If high-purity starting gases are used, this means that it is important that the concentrations of impurities be determined to at least the 10×10^{-9} to $1\,000 \times 10^{-9}$ mole fraction level in fairly pure gases. High-resolution Fourier transformation spectrophotometers equipped with a gas cell of 100 m optical path length and several gas chromatographic methods (such as GC-MS, GC-ECD, GC-DID) are available for carrying out these analyses.

Component purity and the associated uncertainty are estimated on the basis of estimates of impurity levels and the uncertainty associated with these values. All the data obtained in this purity analysis are used in the final calculation of the composition of the gas mixture prepared.

A.2.1.2   Gravimetric preparation of gas mixtures

For the preparation of a calibration gas mixture (see Figure A.1), a pre-treated aluminium cylinder with a mass of approximately 8 kg is used. The cylinder is evacuated overnight using a turbo-molecular pump to achieve a vacuum of about 10^{-6} mbar. The gas remaining in the cylinder is usually the same as the matrix gas and, therefore, makes a negligible contribution to the uncertainty in the composition of the final mixture.

Using a quadrupole mass spectrometer attached to the vacuum system, it is possible to analyse the composition of the gas remaining in the evacuated cylinder. This is especially important when gas mixtures with very low concentrations (nannolitres per litre levels) are prepared. In such cases, traces of moisture or oxygen can cause instability of the final mixture.

The various high-purity gases are transferred to the sample cylinder in such a way that no (extra) impurities are added from the materials used. For this purpose, a special assembly of electro-polished tubing, valves, pressure and vacuum gauges and turbo molecular vacuum pumps with metal membranes is used.

To clean the system, the tubing connecting the sample cylinder to the starting cylinder is evacuated and subsequently pressurized with the gas to be filled in. Experiments have shown that it is sufficient to repeat this procedure eight times in order to remove all the contaminants present in the system. Since the system does not include a compressor, the actual (vapour) pressure of the starting gases is used to pressurize the system. If a refinery gas or natural gas mixture is prepared, the first component to be introduced to the cylinder is, therefore, that with the lowest (vapour) pressure. Among other things, a compressor is not used, in order to avoid possible contamination of the system with oil vapour or metal particles. For the same reason, the vacuum system used consists of an oil-free membrane pre-vacuum pump in combination with a turbo-molecular pump. After the tubing has been cleaned, an amount of the "pure" gas is added to the sample cylinder in a controlled way using a fine metering valve. The amount of gas added to the sample cylinder is monitored by placing the sample cylinder on a top weighing balance during the filling process.

This way of adding components to the cylinder allows considerable flexibility for the preparation of all kinds of gas mixtures and results in very good target precision.

The precise mass of the gas introduced into the cylinder is determined by weighing the cylinder before and after introduction of the component and comparing the weight of the sample cylinder several times with the weight of a reference cylinder (in accordance with the Borda weighing scheme). Using a reference cylinder, corrections for zero drift of the balance used, and influences of changing atmospheric conditions (temperature, atmospheric pressure and humidity changes, which can cause a change in buoyancy) are minimized. The mass comparison is performed on a 10 kg mass comparator with a resolution of 1 mg by calibrated mass pieces. The typical uncertainty of mass determination is about 1,5 mg.

The traceability of gas composition to the SI system is ensured by using mass pieces directly calibrated against the Dutch national standard of the kilogram.

After the mass determination of the first component, the sample cylinder is connected to the filling station again for the introduction of the second component. This sequence of adding components and weighing of the cylinder is repeated until all the components required have been introduced to the sample cylinder. The introduction of large quantities of gas (e.g. matrix gas) to a cylinder results in a rise in the temperature of that cylinder. As the difference in temperature between the sample cylinder and the reference cylinder has an influence on weighing, it is necessary to observe a cool-down period. After the final component has been added to the cylinder and the final weighing operation has been completed, the gas mixture, which now has a pressure of about 10 MPa to 12 MPa (100 bar to 120 bar), is homogenized by rolling the cylinder for a few hours.

The exact mixture composition and the associated uncertainties can be calculated from the data of the purity analysis of the starting gases and the results of weighing. Typical uncertainties for minor components in the mixture are of the order of 0,03 % (relative to the concentration). For components with high concentrations, even lower uncertainties can be achieved.

14

100 bar

7

8

13

15

2

3

6

9

5.8-3

10

1

4

11

7

5

+/-

12

16
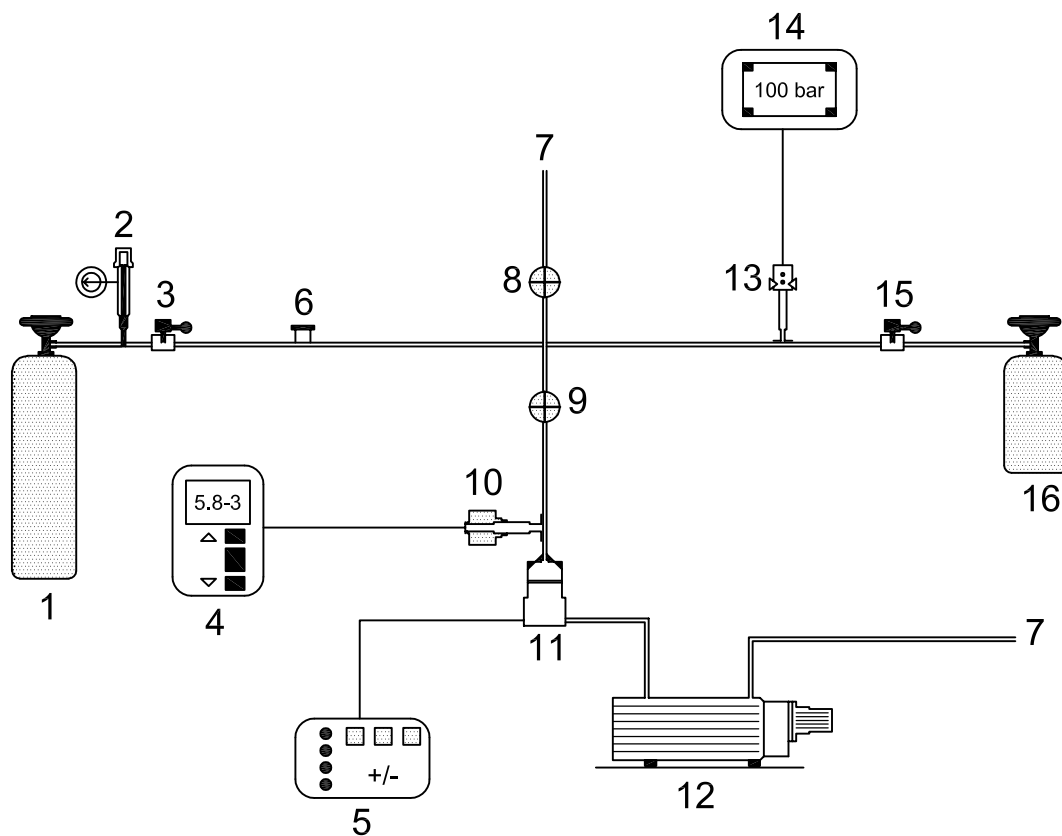
Key

1 standing cylinder
2 needle valve and manometer
3 valve A
4 vacuum indicator
5 power supply
6 filter
7 vent
8 valve C
9 valve D
10 vacuum sensor
11 turbopump
12 vacuum pump
13 pressure sensor
14 pressure indicator
15 valve B
16 sample cylinder

═════ Tubing

───── Electrical connections

Figure A.1 — Diagram of the gas filling station used for the preparation of PRMs

A.2.1.3 Validation of the gas mixture

Although the entire preparation procedure is defined and all uncertainty sources are identified and quantified, the composition of the final mixture is verified to ensure that no errors have occurred during the preparation process.

After the introduction of each component to the cylinder, the pressure of the cylinder is recorded and compared with the calculated (predicted) pressure. However, this is a very rough method, which gives only a preliminary indication of the reliability of mixture preparation.

A more accurate method for the validation of the gas mixture composition is the analysis of the mixture. For analysis, a suitable analyser is selected and calibrated in the range of interest using primary standard gas mixtures containing the same components as the mixture to be verified.

With appropriate PSMs for the calibration of the analyser, calibration curves can be calculated for each component. The analysed concentration of a component in the freshly prepared mixture is determined using the mathematical formula of a calibration curve and compared with the gravimetric concentration. If the difference between these two values is larger than the uncertainties associated with these values, the gas mixture is rejected and the entire preparation and verification cycle must be repeated

A.2.1.4 Issue of a certificate

After verification of the gravimetric data by analysis, the gas mixture is approved as a PRM and a certificate is issued. This certificate includes information for the user of the calibration gas mixture such as the concentrations and associated uncertainties, period of expected stability, information about side connections, cylinder pressure, etc.

This certificate can also be used for demonstrating to accreditation organizations and trading partners that the results of the measurements are traceable to accepted International Standards and are, therefore, accurate and comparable with other measurements.

A.2.2 Preparation of compressed natural gas samples

A.2.2.1 Objective

The objective was to produce two sets of cylinders filled with compressed natural gas samples (min. 6 × type L-gas and 6 × type H-gas) with identical compositions for use in the VAMGAS interlaboratory comparison.

11 type L and 11 type H natural gas samples were taken from the Ruhrgas pipeline system. The cylinders were pressurized using an oil-free compressor. The sample gas was filtered through a molecular sieve filter followed by a particulate filter to remove any residual moisture. To prevent contamination of the sample cylinders with higher hydrocarbons and mineral oil, the cleanliness of the sampling system and the natural gas stream were checked before sampling by performing extended hydrocarbon analyses up to C_{40}. The condensation behaviour of the natural gas samples was calculated on the basis of the combined natural gas and higher hydrocarbon analysis to ensure that no condensation occurred inside the cylinder.

A.2.2.2 Cylinder preparation

The 10 l aluminium cylinders [Luxfer[1)]] equipped with stainless steel valves were purchased from Messer-Griesheim[2)]. The cylinders were cleaned, heat-treated and filled with dry nitrogen upon delivery. The cylinder contents were initially homogenized by rolling and heating for 6 h each and afterwards checked for residual moisture by a routine Karl-Fischer method. Moisture was always found to be below the detection limit of 0,01 mg/m^3 in the gas phase. The cylinders were evacuated to $< 0,1$ Pa (10^{-3} mbar) (Leybold Thermovac)

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1) Luxfer is an example of a suitable product available commercially. This information is given for the convenience of users of this part of this International Standard and does not constitute an endorsement by ISO of this product.

2) Messer-Griesheim is an example of a suitable supplier. This information is given for the convenience of users of this part of this International Standard and does not constitute an endorsement by ISO.

using a vacuum pump [VacuuBrand $RZ8$[3)]; $p < 4 \times 10^{-2}$ Pa (4×10^{-4} mbar)]. Back diffusion of oil from the vacuum pump was prevented by a trap cooled by liquid nitrogen. During evacuation, the cylinders were heated to 60 °C by a jacket heater [Isopad[4)]]. For matrix conditioning, the cylinders were filled with high-purity methane (Messer Griesheim) up to a pressure of approximately 200 kPa (2 bar), homogenized, heated and evacuated again. Afterwards, the cylinders were shipped to the sampling site. Sampling was performed within five days after evacuation.

A.2.2.3   Sampling system and method

The main component of the sampling system, which was assembled in-house, was an oil-free high-pressure compressor [Desgranges & Huot[5)], $p_{max} = 50$ MPa (500 bar)], which was used to increase the cylinder pressure by [10 MPa to 12 MPa (100 bar to 120 bar)] above pipeline pressure [4 MPa to 6 MPa (40 bar to 60 bar)].

The gas cylinders were connected to a closed loop made of pre-cleaned stainless steel tubing using Swagelock[6)] tees. Purpose-built cylinder connectors with flush lines [Hage[7)]], which protruded into the interior of the cylinder valves, allowed this dead volume to be flushed with sample gas. The gas was sampled through two large-volume high-pressure filters. The first filter was filled with 1,5 kg of molecular sieve 3A [Fluka[8)]], the second was used as a particulate filter [Headline[9)] filters efficiency $> 99,9$ % for particulates $> 0,1$ µm]. Flexible tubing with Minimess[10)] connectors was used to connect the sampling system to the sampling station and the cylinder arrangement.

The sampling system, all connecting lines and the cylinder valves were extensively flushed with sample gas. After a leak check had been performed, the valve connecting the cylinder arrangement to the sampling system was closed and the cylinder valves were opened. The valve was opened slowly and the cylinders were pressurized by slowly increasing the back-pressure of the sampling system. When the pipeline pressure was reached, the pressure booster was started up automatically. The final pressure was set to 10 MPa (100 bar). The entire sampling procedure took approximately eight hours.

The cylinders were homogenized twice after sampling, by heating and rolling.

A.2.2.4   Sampling sites

Sampling sites were located at Dorsten (type L gas from the Groningen field) and Krummhörn (type H gas from the Ekofisk field). Both sites are located in Germany. The sampling system was connected to sampling units that are also used for custody transfer measurements. These units are, therefore, continuously flushed with fresh gas and can be considered clean.

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3)   VacuuBrand RZ8 is an example of a suitable product available commercially. This information is given for the convenience of users of this part of this International Standard and does not constitute an endorsement by ISO of this product.

4)   Isopad is an example of a suitable product available commercially. This information is given for the convenience of users of this part of this International Standard and does not constitute an endorsement by ISO of this product.

5)   The Desgranges & Huot compressor is an example of a suitable product available commercially. This information is given for the convenience of users of this part of this International Standard and does not constitute an endorsement by ISO of this product.

6)   Swagelock is an example of a suitable product available commercially. This information is given for the convenience of users of this part of this International Standard and does not constitute an endorsement by ISO of this product.

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9)   Headline is an example of a suitable supplier. This information is given for the convenience of users of this part of this International Standard and does not constitute an endorsement by ISO.

10) Minimess is an example of a suitable product available commercially. This information is given for the convenience of users of this part of this International Standard and does not constitute an endorsement by ISO of this product.

A.2.2.5   Additional quality assurance measures

The natural gas streams were checked for higher hydrocarbons using analytical methods developed by the Ruhrgas laboratory. The cleanliness of the sampling system was also ensured by this method.

The analysis method involves the use of a stainless steel trap (80 cm × 1,2 cm OD) filled with 40 g dehydrated silica gel 50 Å (200 mesh to 500 mesh). Hydrocarbons above C_{10} are quantitatively trapped on the solid sorbent. Breakthrough volumes were shown to be > 1,2 m^3(N). Approximately 400 l (N) of natural gas were sampled. The trapped components were eluted using 400 ml of a mixture of CH_2Cl_2 and pentane (60:40 by volume). The eluate was then concentrated to 10 ml and analysed by GC/FID. The detection limit of the method is 0,001 mg/m^3 (N) per component. Hydrocarbons up to C_{40} can be detected.

A routine natural gas analysis for components up to C_{10} was also performed on this occasion. The results of the natural gas analysis and the higher hydrocarbon analysis up to C_{14} were combined for calculating the phase behaviour of the natural gas stream. The calculation was performed using the Hysim[11] commercial software package. A modified Soave-Redlich-Kwong equation of state was selected for calculation. The calculated phase envelope of the type H gas is shown in Figure A.2.

The tests were performed before sampling in order to ensure that the sampling cylinders were not contaminated with oil and no liquid phase was formed inside the cylinder.
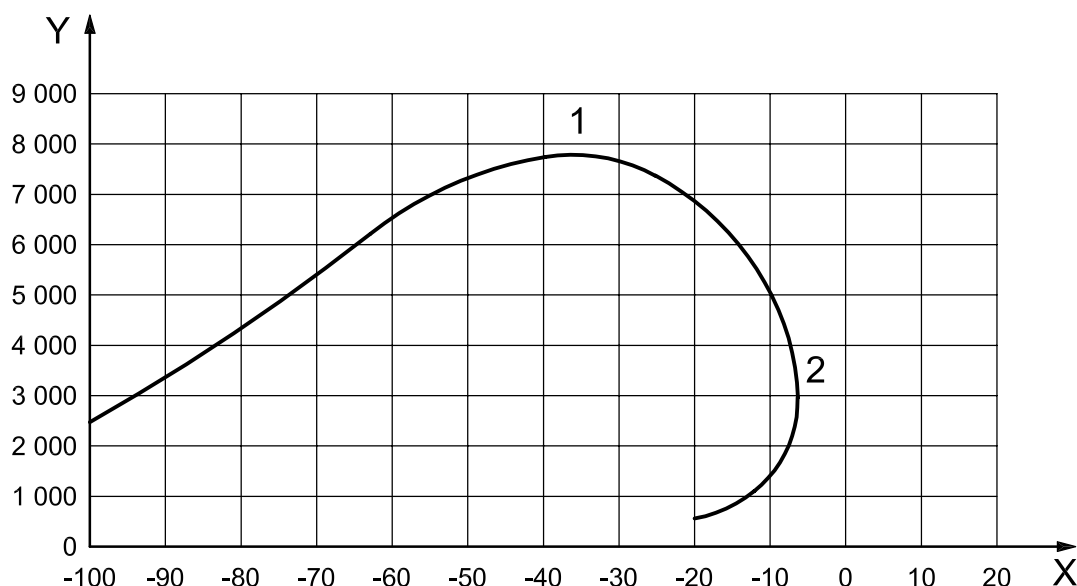
Key

X   temperature, expressed in degrees Celsius

Y   pressure, expressed in kilopascals

1   cricondenbar

2   cricondentherm

NOTE   Higher hydrocarbon content up to C_{14} are included in the calculation.

**Figure A.2 — Phase envelope of the type H natural gas samples calculated
by a Soave-Redlich-Kwong equation of state**

11) Hysim is an example of a suitable product available commercially. This information is given for the convenience of users of this part of this International Standard and does not constitute an endorsement by ISO of this product.

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A.2.2.6   Certification of the cylinders

One cylinder of each sample batch was investigated by precision densitometry. The procedure corresponded exactly to the procedure followed when measuring the reference gases. 16 single measurements were performed for each gas and fitted to the virial equation (Equation A.2). The uncertainty of the fit was not increased compared with the reference gases, a good indication of mixture homogeneity.

The measurement results are listed in Table A.6.

Table A.6 — Measurement results from the density balance for the natural gas samples

Sample	Molar mass g/mol	Density [at 20 °C, 101,325 kPa (1,013 25 bar)]
Type L gas, cylinder 3590	1,612	0,775 2
Type H gas, cylinder 3592	18,122	0,755 1

A.2.2.7   Homogeneity and stability tests

Homogeneity tests were first performed by routine GC analysis. All cylinders were analysed twice under repeatability conditions. The analysis runs were performed uncalibrated (only a check sample was analysed together with the samples), since the task was to detect differences between the sample cylinders and there was insufficient time for calibration runs (11 cylinders had to be analysed on the same day). The statistical analysis indicated no detectable differences between the cylinders.

For six cylinders of each batch, the gas density was then measured by precision densitometry at approximately 1,5 MPa (15 bar) and 3 MPa (30 bar), with four individual measurement points per cylinder. The measurements show satisfactory agreement to within ± 0,003 %.

Sample stability testing was performed by repeating the densitometric measurements after approximately six months storage. The results of these repeated tests were the same as those obtained during the first analysis.

Finally one of the cylinders of each batch was completely consumed and gas density was determined at different pressure levels. This test also gave no indication of any change in gas composition. It can, therefore, be assumed that the natural gas samples are stable.

A.2.3   Reference calorimeter

A.2.3.1   Design

The reference calorimeter at the Technical Directorate of the Office of Gas Supply (Ofgas) was designed to be the primary standard for determining the heat of combustion of natural gas samples. The instrument is based on that used by Pittam and Pilcher at the University of Manchester in the late 1960s for studying the heat of combustion of methane and other hydrocarbons[1], [2]. This instrument was, in turn, based on that built by Rossini at the National Bureau of Standards in the USA in the early 1930s for studying the heat of formation of water[3] and the heats of combustion of methane and carbon monoxide[4]. The Ofgas reference calorimeter was constructed and refined by Mr C. Lythall. The experiment produces a superior heat of combustion in kilojoules per gram, at a constant pressure, for combustion at 25 °C.

There have been three major changes from the designs of previous workers:

a)   The sample of gas burnt is weighed directly.

b)   The experiment is controlled and data are collected automatically by computer.

c)   Measurements are made at a faster rate.

A.2.3.2 Calorimeter Theory

The objective of the Ofgas reference calorimeter is to measure the quantity of energy liberated in the complete combustion of a hydrocarbon fuel gas. This is achieved by allowing the energy liberated in the reaction to be transferred to a well-stirred liquid, in a calorimeter, and measuring its temperature rise. Multiplying this temperature rise by the energy equivalent of the calorimeter gives the amount of energy liberated in the reaction. The energy equivalent is the energy required to raise the temperature of the calorimeter by one degree Celsius at the same mean temperature as the combustion experiment. It is determined by electrical calibration experiments.

An ideal calorimeter would be thermally isolated from its environment so that the temperature change observed is due solely to the reaction. As complete isolation from the environment is not possible in practice, a calorimeter is usually surrounded by a thermostatically controlled jacket and allowance is made for the various energy sources and sinks. The reference calorimeter is designed as an isoperibolic instrument.

There are three external influences and they are all sources of energy:

a)   the water stirrer;

b)   the self-heating of the temperature-measuring device;

c)   energy flowing from the jacket to the calorimeter as a result of the temperature difference.

Figure A.3 shows a temperature versus time curve for a typical experiment (combustion or calibration). Data collection starts at a predetermined temperature. The temperature of the calorimeter is allowed to rise, due to the influences mentioned above, for 750 s. This is the pre-period. At time, t_b, the main period begins as either combustion is initiated or the calibration heater is switched on. During the main period, which continues for 1 030 s, the temperature quickly rises by about 3 °C.
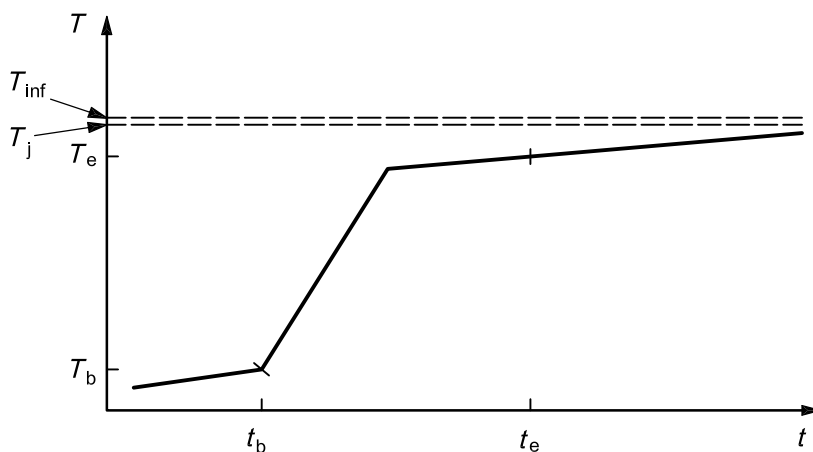
NOTE   The calorimeter is of an isoperibolic type, which means that the temperature is allowed to rise as a result of the ambient temperature. Refer to the text for details.

Figure A.3 — Temperature vs. time plot of a typical experiment conducted using the Ofgas reference calorimeter

At the end of the heat input the main period continues for an extra 1 020 s, to time t_e, to allow the calorimeter to equilibrate. The post-period then begins. During this period, which continues for 1 780 s, the temperature rise is again solely due to external influences.

The temperature rise observed during the main period is due to the energy liberated from the reaction and the energy from the three external influences. This temperature rise is corrected by use of the pre- and post-period data to eliminate the temperature rise caused by external influences.

The rate of change of temperature of the calorimeter during the pre- and post-period is given by Equation (A.1):

$$\frac{\mathrm{d}T}{\mathrm{d}t} = u + k\left(T_{\mathrm{j}} - T\right) \tag{A.1}$$

where

T is the temperature of the calorimeter;

T_{j} is the jacket temperature;

u is a constant power input due to the stirrer and the thermometer;

k is the cooling constant due to thermal leakage from the jacket derived from Newton's law of cooling.

If left for a long time, the calorimeter will reach a temperature, T_{inf}, above the jacket temperature. At this point, $\mathrm{d}T/\mathrm{d}t = 0$ and from Equation (A.1) $T_{\mathrm{j}} = T_{\mathrm{inf}} - u/k$. Substituting for T_{j} in Equation (A.1) gives Equation (A.2):

$$\frac{\mathrm{d}T}{\mathrm{d}t} = k\left(T_{\mathrm{inf}} - T\right). \tag{A.2}$$

Integrating Equation (A.2) gives Equation (A.3):

$$T = T_{\mathrm{inf}} - \left(T_{\mathrm{inf}} - T_0\right)\exp\left(-kt\right). \tag{A.3}$$

where $T = T_0$ at $t = 0$ is not the same for the pre- and post-period.

The temperature versus time data for the pre-and post-periods is initially fitted to Equation (A.2) using a linear regression. With T_{f} and T_{a} as the mid-point temperatures of the pre- and post-periods and using g_{f} and g_{a} to denote the equivalent dT/dt, T_{inf} can be eliminated from Equation (A.2) to give Equations (A.4) and (A.5):

$$k = \frac{g_{\mathrm{f}} - g_{\mathrm{a}}}{T_{\mathrm{a}} - T_{\mathrm{f}}} \tag{A.4}$$

and

$$T_{\mathrm{inf}} = \frac{g_{\mathrm{f}}T_{\mathrm{a}} - g_{\mathrm{a}}T_{\mathrm{f}}}{g_{\mathrm{f}} - g_{\mathrm{a}}}. \tag{A.5}$$

With these values of k and T_{inf}, the data are now fitted to Equation (A.3), using a linear regression of temperature versus $\exp(-kt)$, for both the pre- and post-periods. This gives accurate values for T_{inf} and T_0. The values of T_{inf} for both periods are expected to be the same. With these new values, the temperatures T_{b} and T_{e} at times t_{b} and t_{e}, i.e. the beginning and the end of the main heating period, can be interpolated using Equation (A.3).

The corrected temperature rise is now found by subtracting T_{ex}, due to the external energy sources, from the temperature rise $(T_{\mathrm{e}} - T_{\mathrm{b}})$. This correction is evaluated using an integrated form of Equation (A.2), as given in Equations (A.6) and (A.7):

$$T_{\mathrm{ex}} = k\int_{t_{\mathrm{b}}}^{t_{\mathrm{e}}} \left(T_{\mathrm{inf}} - T\right)\mathrm{d}t \tag{A.6}$$

$$\therefore T_{\mathrm{ex}} = k\left(T_{\mathrm{inf}} - T_{\mathrm{m}}\right)\left(t_{\mathrm{e}} - t_{\mathrm{b}}\right) \tag{A.7}$$

where T_m is the mid-point temperature of the main period, equal to Equation (A.8):

$$T_m = \frac{1}{(t_e - t_b)} \int_{t_b}^{t_e} T \, dt \qquad (A.8)$$

T_m is determined by numerical integration of the temperature-versus-time data using the trapezium rule; it is not necessarily equal to $(T_b + T_e)/2$.

There are several energy sources or sinks in a gas-burning calorimeter for which it is not necessary to correct. These can be either quantified or eliminated. To quantify them, it is necessary to measure them. To eliminate them, it is necessary to make them constant from run to run. To eliminate the constant factors, a short run is performed during which gas is burnt for about 80 s instead of 16 min. The energy input and mass of gas used in the short run are subtracted from the equivalent values for the long gas run, thus eliminating the external effects.

A calorimeter can be calibrated to determine the energy equivalent in one of two ways:

a)   by burning a gas of known heat of combustion (e.g. hydrogen);

b)   by electrical heating.

Each method has advantages and disadvantages. The reference calorimeter is calibrated electrically, as this is traceable to national standards. The rate of energy input during the calibration is determined by the voltage and the current flowing through the heater. The same rate of energy input is achieved during gas combustion by selecting an appropriate gas flow rate.

A.2.4 Construction and operation

A.2.4.1   Basic structure

The reference calorimeter is shown in Figure A.4. It consists of two nested cans with an air gap between them. The inner can is filled with distilled water and contains a glass reaction vessel with heat exchanger, a calibration heater, a constant-speed stirrer and a platinum resistance thermometer (Tinsley). A recess is included for the insertion of a cold finger to bring the calorimeter to its starting temperature. The cold finger is removed and the recess plugged when the calorimeter is in use. Where components pass through the lid of the inner can, they are sealed with O-rings and silicon rubber to prevent water loss.

The inner can is mounted on three plastic joints, on the base of the outer can, keeping a uniform distance between the two. The outer can is closed at the top by a hollow lid and is immersed to just above the bottom of the lid in a thermostatically controlled bath of water. This water is pumped through the hollow lid, thus keeping a constant temperature environment around the inner can.

The outer bath is temperature-controlled at about 27,3 °C. There is constant background cooling from a coil supplied with a 10 °C water and antifreeze mixture. Power is supplied to the bath heater from an Automatic Systems Laboratories (ASL) Series 3000 precision temperature controller [12] connected to an ASL F17 resistance bridge [13] and a platinum resistance thermometer. This system keeps the bath temperature stable to $\pm$ 0,001 °C during a run.

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12) The ASL Series 3000 precision temperature controller is an example of a suitable product available commercially. This information is given for the convenience of users of this part of this International Standard and does not constitute an endorsement by ISO of this product.

13) The ASL F17 resistance bridge is an example of a suitable product available commercially. This information is given for the convenience of users of this part of this International Standard and does not constitute an endorsement by ISO of this product.
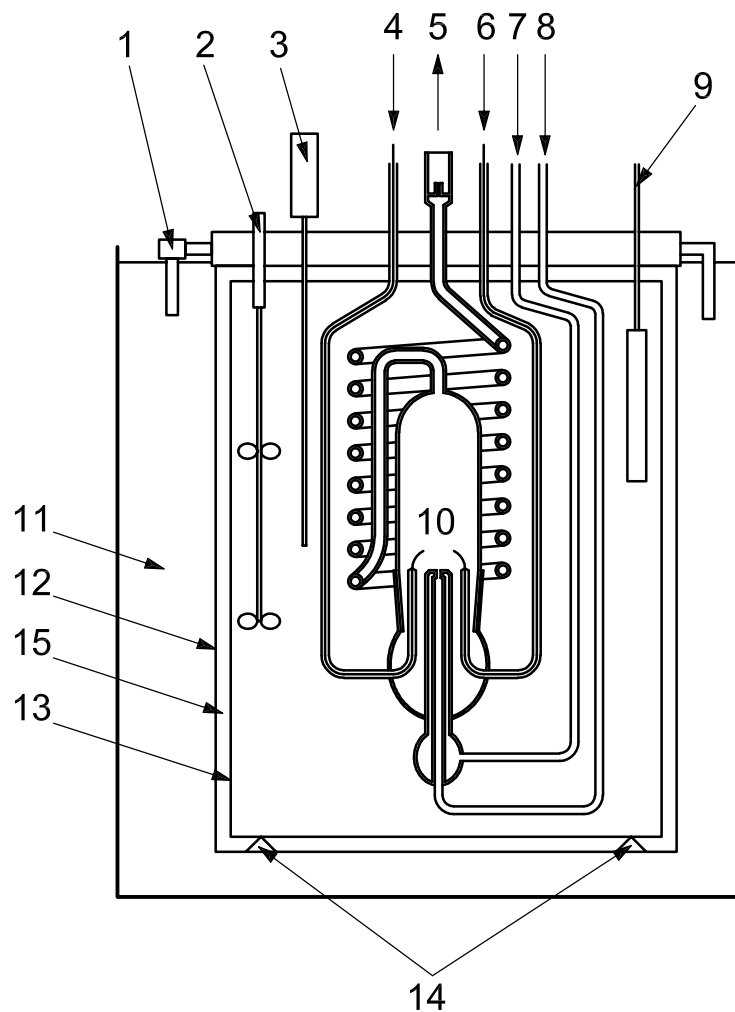
Key

1 lid pump
2 stirrer
3 platinum thermometer
4 oxygen
5 exhaust
6 spark voltage
7 oxygen plus argon
8 fuel
9 calibration heater
10 spark gap
11 outer bath
12 outer can
13 inner can
14 foot
15 air gap

NOTE   The calorimeter is based on the calorimeter developed by Rossini.

Figure A.4 — Schematic drawing of the burner/heat exchanger of the Ofgas reference calorimeter

A.2.4.2 Temperature measurement and data collection

The platinum resistance thermometer feeds one side of an ASL F18 resistance bridge with a Tinsley 25 Ω standard resistor (type 5685) balancing the other side. Resistance ratio readings are recorded every 3 s. The 25 Ω standard resistor is immersed in an oil-filled bath controlled to 20 °C. The temperature of the resistor is measured and is stable to better than 0,1 °C. The temperature is used to calculate the value of the 25 Ω resistor from its calibration curve.

Calorimeter control and data collection are carried out by a Cube EuroBeeb[14] running Real Time Basic. This is an event-driven language with event timings accurate to better than 0,002 s. The EuroBeeb has IEEE488, RS232 and digital I/O interfaces. At the end of a run, the data are passed to a PC for processing.

A.2.5 Gas runs

A.2.5.1 Overview

The sample gas is combusted inside the glass reaction vessel submerged in the water in the inner can. Ultra-high-purity oxygen is mixed with argon and then fed to the burner, through one arm of the vessel. Here it mixes with the fuel gas, supplied along a second arm. The argon acts as a moderator to lift the flame off the tip, preventing decomposition of the sample, heat transfer up the arm and carbon build-up on the tip. A second feed from the oxygen supply goes to the base of the reaction vessel through a third arm to provide an oxygen-rich atmosphere.

Two platinum electrodes act as a spark gap just above the tip of the burner. A series of 20 kV pulses to ignite the gas are supplied from a car ignition coil and fed to the electrodes along wires situated inside two of the arms of the reaction vessel.

A.2.5.2 Gas sample

A 250 ml cylinder is filled to a pressure of 1,4 MPa (14 bar) with the sample gas. The mass of the cylinder is about 190 g and about 1 g of gas is burnt during a run. The cylinder is weighed before and after each run on a Mettler AT201 balance[15] which reads to 10^{-5} g. To allow for buoyancy changes, which can be quite sizeable, a dummy cylinder of identical external volume is weighed at the same time. A change in the mass of the dummy is applied as a correction to the mass of gas used.

The cylinder is connected to one arm of the reaction vessel via an ultra-fine flow needle valve. Near the end of the pre-period, the computer opens two valves to start oxygen and argon flow. 60 s later, on a signal from the computer, the operator manually opens the valve on the cylinder. A series of sparks to ignite the gas is initiated by the computer at the same time. Once ignition has occurred, the operator continuously adjusts the needle valve to maintain a constant flow rate. The flow rate is set to give the same rate of temperature rise as during the calibration runs.

At the end of gas combustion, the operator turns off the sample gas and the computer switches on a flow of argon to purge the needle valve and fuel line to ensure that all the gas leaving the cylinder is burnt. 30 seconds later all gases are switched off and the equipment is allowed to continue to the end of the post-period. The cylinder is removed and reweighed.

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14) Cube EuroBeeb is an example of a suitable product available commercially. This information is given for the convenience of users of this part of this International Standard and does not constitute an endorsement by ISO of this product.

15) The Mettler AT201 balance is an example of a suitable product available commercially. This information is given for the convenience of users of this part of this International Standard and does not constitute an endorsement by ISO of this product.

A.2.5.3   Reaction products

The hot combustion gases flow out of the reaction vessel through the heat exchanger and give their energy to the water, leaving the calorimeter at the prevailing calorimeter temperature. The gases then pass into a chain of three water absorption tubes and an electronic carbon monoxide monitor.

The carbon monoxide monitor is used to check for incomplete combustion. Test runs are conducted to find the correct flow rates for argon and primary and secondary oxygen, to reduce the CO level as much as possible, while still being able to ignite the gas.

The water absorption tubes contain magnesium perchlorate. These are weighed on the Mettler balance against a dummy tube to correct for buoyancy changes. When magnesium perchlorate absorbs water, it expands in volume by 0,6 cm^3/g of water absorbed. This expansion displaces an equivalent volume of oxygen from within the tubes, resulting in an apparent loss of mass. This loss is calculated and applied as a correction to the mass of water. Newly filled tubes are conditioned for 12 h prior to use by passing dry oxygen through them.

A.2.5.4   Water leaving the calorimeter

Most of the water produced during combustion condenses and remains in the reaction vessel in liquid form. However, about 10 % of the water is carried out of the vessel as a vapour during the combustion period. This water represents about 470 J as its heat of condensation is not given up (2 441,78 $J·g^{-1}$). At the end of the run, the output arm from the reaction vessel is flushed with oxygen for 20 min to transfer all traces of water in this arm to the water absorption tubes. This also ensures that the absorption tubes are filled with oxygen as they were when first weighed. The tubes are then removed and weighed and a correction is applied to the energy balance.

A.2.5.5   Water remaining in the calorimeter

The water absorption tubes are reconnected to the outlet of the reaction vessel and oxygen is used to flush out the remaining water overnight. This water represents an increase in the energy equivalent of the calorimeter. It is corrected for by adding half the heat capacity (4,18 $J·g^{-1}$ $°C^{-1}$) of the mass of water times the temperature rise. It represents about 12 J.

A.2.6 Gas corrections

A.2.6.1   Introduction

The temperatures of the oxygen, argon and fuel gas are usually different from the mid-point of the reaction. This represents an energy source or sink for the experiment that needs to be corrected for. The duration of the gas flows is timed using the pulse counter and the off-air frequency standard. This time and the measured flow rates of the gases give the total volume of gas fed into the calorimeter during the run. The gases are assumed to be at room temperature so the total source or sink of energy is calculated using the molar heat capacities of the various gases (methane, 35,64 $J·mol^{-1}$ $°C^{-1}$, oxygen, 29,37 $J·mol^{-1}$ $°C^{-1}$ and argon, 20,79 $J·mol^{-1}$ $°C^{-1}$). The closer the room temperature is to the mid-point of the reaction the smaller is the correction. For this reason, the room is kept at 25 °C. This correction may be up to ± 20 J depending on the temperatures.

A.2.6.2   Correction to standard pressure

The reaction takes place at the prevailing atmospheric pressure plus the excess pressure in the reaction vessel. These pressures are measured during the run and the Van't Hoff equation is used to correct the result to a standard pressure of 101,325 kPa:

$$q = nRT \ln\left(\frac{p}{101,325}\right)$$

(A.9)

where

q is the energy to be added to the experiment;

p is the total pressure in the reaction vessel;

R is the gas constant;

T is the absolute temperature;

n is the number of moles decrease in gas volume.

The energy correction can be up to $\pm$ 80 J.

A.2.6.3   Other energy corrections

A small correction is required for the water vapour left in the reaction vessel after the second flushing. The volume of vapour represents 7 J of energy not given up by condensing. This correction varies slightly with temperature and pressure but mostly cancels itself out between long and short runs.

There are two other corrections to be considered:

a)   energy from the spark;

b)   effects due to incomplete combustion at ignition and extinction.

These two factors can be quantified by performing runs where no gas is burnt and measuring the temperature rise. On the reference calorimeter, these factors are corrected for by conducting a short gas run where gas is burnt for about 80 s. It is expected that the mass of gas that is lost at ignition and extinction, and the energy input due to the spark are the same for long and short runs. If the energy liberated and the mass of gas burnt in the short run (E_s and m_s, respectively) are subtracted from the energy and mass for the long run (E_l and m_l, respectively), the result should then be due to just the gas burnt, i.e. heat of combustion is equal to $(E_l - _s)/(m_l - m_s)$. Only long and short runs within a few days of each other are used together for calculating the heat of combustion. This prevents any variations in sparking conditions from affecting the results.

A.2.6.4   Electrical clibration

A 50 Ω heater was constructed by winding resistance wire around a small hollow cylinder. This is connected to a stabilized 50 V power supply via a Tinsley 1 Ω standard resistor (type 1659)[16]. A Solatron type 7065 microprocessor voltmeter[17] switches every three seconds between measuring the voltage across the 50 Ω heater and the 1 Ω resistor. The voltage across the 1 Ω resistor gives the current flowing in the circuit. To stabilize the temperature of the 1 Ω resistor, it is removed from its case and suspended in the oil in the same bath as the 25 Ω resistor. Its temperature is measured and is stable to better than 0,1 °C. The value of the 1 Ω resistor is calculated from its temperature coefficient. When heating is not required, a dummy 50 Ω heater is switched into the circuit to stabilize the power supply and the 1 Ω resistor

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16) Tinsley 1 Ω standard resistor (type 1659) is an example of a suitable product available commercially. This information is given for the convenience of users of this part of this International Standard and does not constitute an endorsement by ISO of this product.

17) Solatron type 7065 Microprocessor Voltmeter is an example of a suitable product available commercially. This information is given for the convenience of users of this part of this International Standard and does not constitute an endorsement by ISO of this product.

The duration of the heating period is measured by a Malden 8816 pulse counter[18] fed from a Quartzlock 2A off-air frequency standard (Dartington Frequency Standards). The Quartzlock gives a 10 MHz signal phase locked to the BBC Radio 4 transmissions on 198 kHz.

The product of time, voltage and current gives the energy input into the calorimeter. The corrected temperature rise then gives an energy equivalent for the calorimeter in J/K. Calibration runs are fully automatic, once started, and up to four runs can be performed in a day. Several runs are averaged to produce long and short energy equivalents for use in the long and short gas runs.

A.2.7 Gas density apparatus

The measurements were performed with the high-accuracy gas-density apparatus at Ruhrgas AG in Dorsten, which was developed by Kleinrahm and Wagner of Bochum University. It uses the "two-sinker method," which is a compensation method based on the Archimedes buoyancy principle. A detailed description of the apparatus is given by Pieperbeck *et al*. (1991). Instead of the usual single sinker, the apparatus uses two specially matched sinkers as shown in Figure A.5. One is a hollow sphere (S) and the other is a solid ring (R). The two sinkers have approximately the same mass and the same surface area and are made of the same stainless steel material with gold-plated surface; however, there is a considerable difference in volume ($V_S \approx 106,8$ cm^3 and $V_R \approx 15,6$ cm^3).

Each of the sinkers is put on a sinker support or is lifted from it, the support being connected to a microbalance by a thin wire via a magnetic suspension coupling. To measure the density of a gas in the cell, the sinkers are alternately placed on the sinker support or lifted from it and the resulting differential buoyancy force $\Delta F = \Delta m \cdot g$ acting on the sinkers is measured by a semimicro-balance positioned above the coupling.

The density can be determined from the Equation (A.10):

$$\rho = \frac{\Delta m - \Delta m_{\text{vac}}}{\Delta V(T,p)} \cdot \left(1 - \frac{\rho_{\text{air}}}{\rho_{\text{w}}}\right) \tag{A.10}$$

where

ρ is the density;

Δm is the difference between ring mass and sphere mass ($m_R - m_S$) in the test gas, determined as the average of 30 single measurements ($m_R \approx m_S \approx 123,4$ g);

Δm_{vac} is the residual difference of sinker masses ($m_R - m_S$)$_{\text{vac}}$ measured in evacuated cell;

$\Delta V(T,p)$ is the difference in sinker volumes ($V_S - V_R$) at temperature T and pressure p;

ρ_{air} is the density of air during calibration of the balance;

ρ_{w} is the density of calibration mass used in the balance ($\rho_{\text{w}} = 8\,000$ kg/m^3).

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18) Malden 8816 pulse counter is an example of a suitable product available commercially. This information is given for the convenience of users of this part of this International Standard and does not constitute an endorsement by ISO of this product.
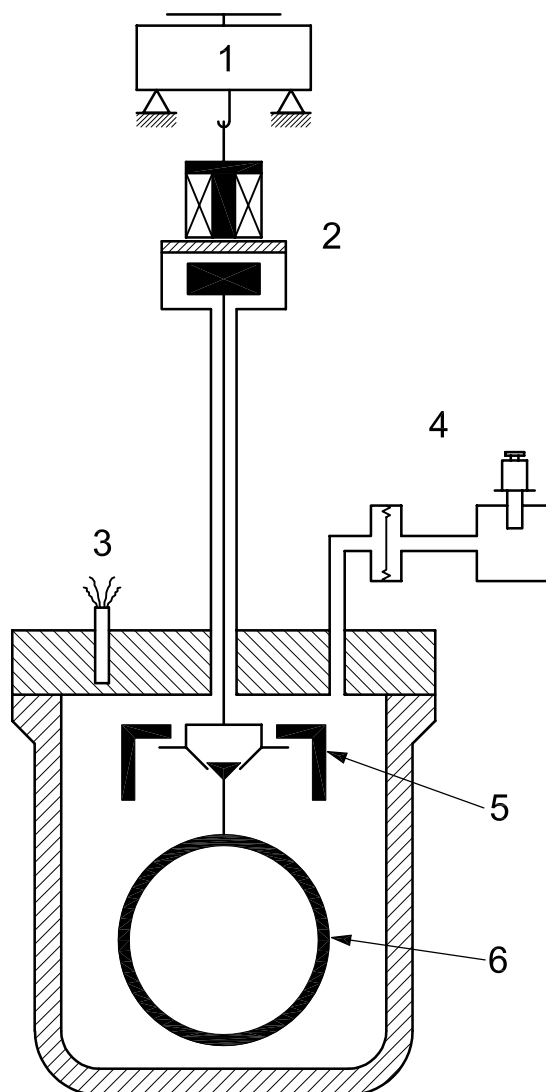
Key

1   microbalance
2   magnetic suspension coupling
3   platinum thermometer, 25 Ω
4   pressure measurement
5   solid-ring sinker
6   hollow-sphere sinker

Figure A.5 — Schematic drawing of the gas density apparatus

A.2.7.1   Determination of the molar mass from density measurements

For the determination of the molar mass of the gas mixtures investigated in this project, the density of each gas sample was measured on the 293,15 K isotherm in the density range from 5 kg/m^3 to 50 kg/m^3 in steps of 5 kg/m^3 or 10 kg/m^3, or in the pressure range from 0,5 MPa to 6 MPa in steps of 0,5 MPa or 1 MPa. Each point was measured twice.

The procedure for determining the molar mass from the density measurements has already been described by Guo *et al*. (1995) [6].

The molar mass, M, is related to the density, ρ, through the definition of the compression factor Z as given in Equation (A.11):

$$Z = \frac{p \cdot M}{\rho \cdot R \cdot T}$$ (A.11)

where

p is the pressure;

T is the temperature ($T = 293{,}15$ K);

R is the molar gas constant [$R = (8{,}1451 \pm 0{,}002\ 1)$ J/(mol·K)].

The compression factor can be expressed in terms of the density by a virial equation truncated after the third virial coefficient C, as given in Equation (A.12):

$$Z_{\text{vir}} = 1 + B \cdot \rho + C \cdot \rho^2$$ (A.12)

The values for the molar mass, M, the second virial coefficient, B, and the third virial coefficient, C, are fitted simultaneously to the measured p, ρ, and T values by minimizing the root mean square of the deviation $(Z - Z_{\text{vir}})/Z_{\text{vir}}$.

In order to determine the density or the compression factor for a given set of M, B and C values at a given pressure on the 293 K isotherm, Equations (A.11) and (A.12) may be solved iteratively. In this way, values for the density ρ_{ref} and the compression factor Z_{ref} may also be obtained for the reference conditions $p_{\text{ref}} = 0{,}101\ 325$ MPa and $T_{\text{ref}} = 293{,}15$ K.

A.2.7.2   Gas chromatography

Gas chromatography is currently the most widely used method for determining the physical properties of natural gases, such as superior calorific value and density at standard conditions. Gas chromatographs are used both in the field for custody transfer measurements and in the laboratory for quality assurance purposes.

Gas chromatographs are mainly separate units equipped with several columns, column switching equipment and in some cases several column ovens. Only molecular sieve columns are used for the separation of inert gases and methane. Lower hydrocarbons are separated using polymer columns (e.g. Porapak, Poraplot, Hayesep[19]). For higher hydrocarbons, a non-polar fluid (methyl silicon, DC-200, etc.) is normally used. There seems to be a tendency away from packed columns towards proprietary capillary columns.

Only TCD (thermal conductivity detectors) and FID (flame ionization detectors) are used as detectors.

A number of high-performance analysers are described in parts 3 to 6 of ISO 6974.

A.2.7.3   ISO 6974 (all parts) and ISO 6976

ISO 6974-2 describes a multi-point calibration method, preferably with seven-point calibration, for determining systematic non-linearities in the calibration curves of the individual separated components and for defining an optimized calibration function in each case. This allows the uncertainties of the calibration curves to be determined and the composition of an analysed gas to be stated with a defined uncertainty.

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19) Porapak, Poraplot, Hayesep are examples of a suitable products available commercially. This information is given for the convenience of users of this part of this International Standard and does not constitute an endorsement by ISO of these products.

In view of the complexity of calibration in accordance with ISO 6974 (all parts), simpler calibration procedures using a few calibration gases with compositions selected to approximate to those of the gases to be analysed are often used in laboratory practice.

Superior calorific value and density at normal conditions are now almost always calculated from gas analysis results using the method laid down in ISO 6976 which defines a calculation procedure (mixing rules) for the calculation of superior calorific value, density, relative density and Wobbe number from the gas composition. ISO 6976 also includes a table of the physical properties of the various pure substances contained in natural gas.

A.2.8 Round-robin tests

A.2.8.1 Background

The round-robin tests were intended to validate the process of natural gas analysis by gas chromatography by state-of-the-art methods in combination with the calculation of physical data in accordance with ISO 6976.

The tests cover a combination of PRMs and natural gases. The basic principle is as follows: the analyser is calibrated with the PRMs with a defined uncertainty and the natural gases are then analysed. The physical properties superior calorific value, molar mass and density are then calculated from the composition analysis and compared with the reference measurements.

The purpose of this process validation exercise is to investigate the current weaknesses of gas chromatography, i.e. the relatively high uncertainty of the superior calorific values tabulated in ISO 6976 and the relative response factors (Kaiser factors) for the evaluation of higher hydrocarbons.

A.2.8.2 Organisation of the round-robin tests

The laboratories participating in the tests are listed in Table A.7.

NOTE   In order to conduct the round-robin program within a relatively tight time schedule with 18 participating laboratories, the participants were subdivided into six groups of three laboratories each. A separate set of samples was produced for each group, allowing several laboratories to conduct tests at the same time. Each set included four primary reference gas samples and two natural gas samples. The PRMs were produced with reference to the natural gases in order to allow "bracketing calibration". "Bracketing calibration" is a special calibration procedure in which the component concentrations in the two calibration gases are slightly above and slightly below, respectively, the component concentrations in the gas to be analysed. This ensures calibration functions which are especially precise in the analysis range of the gas to be analysed.

A.2.8.3 Questionnaire for round-robin tests

Laboratories wishing to participate were requested to complete a questionnaire on the measurement systems, calibration procedures and quality assurance methods to be used for the round-robin tests. The purpose of this questionnaire was to assess the qualifications of the laboratories concerned in the field of natural gas analysis.

The extent of the calibration procedures applied and the generally very high quality of the calibration gases used indicate that quality assurance in connection with the results obtained is of prime importance for all the laboratories participating. Some of the participants have accreditation or a quality system in accordance with ISO 9001. The analysis systems used are highly varied, constituting a representative cross section of the systems and equipment available. This ensures that the results of the VAMGAS round-robin test are suitable for achieving the target of general validation of the method.

Table A.7 — Laboratories participating in the round-robin test

Company	Address
BEB	Riethorst 12 D-20659 HANNOVER
BGTech	Ashby Road, Loughborough UK-LEICESTERSHIRE LE11 3 GR D
Bundesanstalt für Materialforschung und - prüfung	Unter den Eichen 87 D-12205 BERLIN
DONG	Agern Allee 24 - 26 DK-2970 HORNSHOLM
Distrigas	Digue du Canal 102 B-1070 BRUSSELS
EffecTech Ltd.	Tullygay House, Great Glen UK-LEICESTERSHIRE LE 8 9GF
ENAGAS	Apdo. 354 E-50080 ZARAGOZA
Expro North Sea Ltd.	Cremeyl Road 2 - 4 UK-READING, BERKSHIRE
Gasag Berliner Gaswerke	Ringstrasse D-12105 BERLIN
Gaz de France DR/DRX/QDG	BP 33 F-93211 ST-DENIS LA PLEINE CEDEX
NAM	Postbus 28000 NL-9400 HH ASSEN
Nederlandse Gasunie N. V.	Postbus 19 NL-9700 MA GRONINGEN
Ofgem	3 Tigers Road, Wigston UK-LEICESTERSHIRE LE18 4 UX
Ruhrgas AG	Halterner Straße 125 D-46284 DORSTEN
Saybolt Nederland B. V.	P.O. Box 151 NL-3000 AD ROTTERDAM
SGS Redwood B. V.	P.O. Box 200 NL-3200 AE SPIJKENISSE
SNAM	V. le De Gasperi 2 I-20097 SAN DONATO MILANESE
Statoil	Box 308 N-5508 HAUGESUND
Thyssengas GmbH	Postfach 11 05 62 D-47145 DUISBURG

A.2.8.4   Round-robin test program

A.2.8.4.1   Defined program

All the participants were requested to conduct the round-robin tests in accordance with the best methods available to them. On the other hand, the sequence in which the gases were analysed was fixed. This program was intended to allow an assessment of the repeatability of the measurement systems used. The form of the test reports was also fixed. The reports included both the evaluated, calibrated results and all the raw data (peak areas). The participants were not allowed to change any part of the analytical system during the analytical series.

The defined program included a total of eight test days, which were completed within four weeks (including shipment). During transportation, the ambient temperature of each cylinder was monitored by electronic temperature loggers to assure that no condensation occurred.

A.2.8.4.2   Repeatability of analysis system

The objective was to determine the repeatability of each substance analysed on each individual analytical system. The test procedure included four test days for this purpose. On each measurement day, each gas was analysed five to seven times in succession. In order to ensure an adequate volume of data for statistical analysis, laboratories not capable of performing more than five analyses per day repeated the missing analyses on two additional test days.

In addition, each participant was required to calibrate his/her gas chromatograph each day using his/her own calibration method, which had already been described in the questionnaire. Both the calibrated, non-normalized result for each constituent analysed and the raw data (peak surfaces) were reported. The measurement programme was proposed as follows:

⎯ day 1:   type H PRM;

⎯ day 2:   type L PRM;

⎯ day 3:   type H natural gas;

⎯ day 4:   type L natural gas.

A.2.8.4.3   Determination of superior calorific value and gas density with defined uncertainty

The objective of this second part of the round-robin test program was to determine the superior calorific value and density of the natural gas samples with a defined uncertainty. Four test days were included for this purpose. Type H and type L gases were analysed in a defined sequence over a period of two days each.

The sequence required was as follows:

    PRM 1 – natural gas – PRM 2 – natural gas – PRM 1 – natural gas – PRM 2.

On each test day, the natural gas was analysed three times and each of the related calibration gases was analysed twice.

As in the first part of the program, each participant was required to use its own calibration method and to report both the calibrated results and the raw data.

A.3 Results and discussion

A.3.1 Stability and handling of gas mixtures

A.3.1.1 Possible physico-chemical influences

Gas mixtures produced by gravimetric methods in accordance with ISO 6142 may reach a relative uncertainty of < 0,001 % for their main components. This figure only reflects the uncertainty of the gravimetric method. In the past, it was not possible to verify the composition of these gas mixtures with equivalent uncertainty to that reached in the production process. Because there were fears of a possible change in gas composition, many producers, therefore, stated uncertainty figures which were one to two orders of magnitude higher in their certificates.

For this reason, the VAMGAS project included a fundamental investigation of the stability of contained gas mixtures. The following possible physico-chemical influences were investigated:

— surface activity of the aluminium cylinder;

— homogeneous and heterogeneous gas reactions;

— contamination or changes in composition due to leakage;

— condensation and demixing effects at large sampling rates.

A.3.1.2 Standard cylinder treatment

It is mandatory to fabricate pressure cylinders from high-strength aluminium alloys for safety reasons. Alloying elements and impurities, however, tend to concentrate on the surface of the material, increasing the surface activity. Especially zinc, manganese and copper are said to have detrimental catalytic effects on the active components of a contained gas mixture. In this project, cylinders manufactured from aluminium alloy 6061 were used. This alloy contains some copper, but concentrations of manganese and zinc are both very low.

The surface properties of the finished cylinder are determined by an aluminium oxide surface layer. This oxide layer is built up during oxidizing heat treatment, which is routinely applied to each cylinder. The treatment process consists of a tempering and an ageing stage in order to remove residual stress from the material and increase its mechanical stability. This treatment increases the thickness of the natural oxide layer to 40 nm to 50 nm and crystallizes the formerly porous oxide layer, exposing a surface roughness of 0,35 µm to 0,5 µm. In addition, most organic contaminants are volatilized by oxidation.

The aluminium oxide surface layer achieved by the standard treatment is already sufficiently inactive to natural-gas-like mixtures. Catalytic activity at room temperature is restricted to the (fast) isotope scrambling of hydrogen/deuterium. Skeletal rearrangements of reactive hydrocarbons (containing a double bond) are energetically feasible only at higher temperatures. Rearrangement reactions of saturated hydrocarbons are not reported except at higher temperatures in the presence of noble metal catalysts.

A major prerequisite for the stability of a contained gas mixture is the careful removal of adsorbed moisture from the wall. For this purpose, the cylinder is normally repeatedly heated, evacuated and re-filled with dry nitrogen. Water exhibits a very high affinity for the alumina surface, with an enthalpy of adsorption of about 50 kJ/mol. Various adsorption sites are exhibited with greatly varying activities. The desorption kinetics of water from alumina are complex. About 20 % of the surface adsorption sites are so strong that the adsorbed water is released only at temperatures above the melting point of the aluminium alloy. These H_2O-occupied sites play an active role in the isotope exchange of hydrogen.

A.3.1.3   Advanced cylinder treatment methods

Advanced cylinder treatment methods are known to enhance the surface morphology and cleanliness of the inner cylinder surface and to reduce its catalytic activity. It is not necessary to apply such costly techniques to a cylinder that is intended to contain a natural-gas-like mixture. The details of the treatment procedures are kept confidential by their owners. The generally available information on the treatment methods is listed in the document "Physico-Chemical Interferences on Contained Gas Mixtures". The treatment methods result in the replacement of the crystalline aluminium oxide layer by an amorphous, glassy layer of components containing either oxygen or fluorine.

Cylinders which have been pre-treated by advanced methods are commercially available from Scott Specialty Gases[20] (see Table A.8).

Table A.8 — Scott Aculife™ treatment procedures[21]

Parameter	Scott Aculife™ procedure number			
	III	IV	V	VI
Surface morphology				
Chemical polishing	—	—	X	—
Electropolishing	—	—	—	—
Moisture content				
Heat treatment	X	X	X	X
Evacuation	X	X	X	X
Surface reactivity				
Chemical vapour deposition (CVD)	—	X	X	X
Matrix conditioning	—	—	—	—
Surface cleanliness				
Acid etch	—	X	—	X
Degreasing	—	—	—	X
Sub- / supercritical fluid cleaning (SFC)	—	—	—	X

A.3.1.4   Gas phase reactions

Energetically feasible gas phase reactions involve oxygen as the reactant. None of these reactions are sufficiently fast to influence the composition measurably over a reasonably short time scale (years). The induction times for hydrocarbon oxidation reactions at room temperature are given in Table A.9.

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20) Scott Specialty Gases is an example of a suitable supplier. This information is given for the convenience of users of this part of this International Standard and does not constitute an endorsement by ISO.

21) Scott Aculife is an example of a suitable process available commercially. This information is given for the convenience of users of this part of this International Standard and does not constitute an endorsement by ISO.

Table A.9 — Induction times of hydrocarbon oxidation reactions

Compound	Induction time [a] s
Methane, CH_4	$1,7 \times 10^{34}$
Ethane, C_2H_6	$2,5 \times 10^{30}$
Propene, C_3H_6	4×10^{22}
Toluene, $C_6H_5CH_3$	$1,2 \times 10^{23}$
NOTE For comparison, the estimated age of the universe is 6×10^{17} s.	
[a] Conditions: 300 K and an oxygen partial pressure assumed to be 10,1 kPa (1 010 mbar).	

A.3.1.5   Heterogeneous reactions

Methane is an extremely stable compound and very harsh conditions are necessary to attack the molecule. Methane activation is observed at relatively low temperatures only in the presence of super-acid catalysts (e.g. zeolites, HF/SbF_5) and some soft electrophilic metal catalysts [e.g. Hg(II), Pt(II,IV), Pd(II)]. Without a suitable reactant, the electrophilic and super-acid attack leads to isotope scrambling of hydrogen atoms. Isotope scrambling, thus, does not affect the composition of a hydrocarbon gas mixture. Any coupling or exchange reactions are thermodynamically not feasible because of the high thermodynamic stability of methane. Again the presence of strong oxidants, including activated molecular oxygen, is a prerequisite for functionalization.

Heterogeneous oxidation and coupling reactions are in the focus of current research. The best available heterogeneous catalysts, however, still require high temperatures ($> 650\ °C$) for a significant reaction yield. The reaction always involves an activated form of surface oxygen that is capable of abstracting a hydrogen atom from CH_4, presumably by homolytic C-H bond fission. The activated forms of surface oxygen may either be O^- or O_2^{-2}, from the oxidative attack results a surface OH^- ion, which condenses, via proton migration, to form H_2O, a surface oxide ion and a vacancy.

In this sense, surface activity is a function of redox-active metals in the surface oxygen layer. With respect to the stability of contained hydrocarbon gas mixtures, changes in the gas composition can be expected, only if molecular oxygen is present at a high level, the gas mixture also contains unsaturated hydrocarbons, the cylinder is heated above 150 °C with its gas filling and the cylinder has a highly impure surface (with Li, Na, Cl, Ba, Mn, W and/or La present).

Of course, gas mixtures having reactive components (e.g. H_2S, COS, NO_x) are by far more susceptible to surface activity.

A.3.1.6   Leakage

Molecular mass transport mechanisms (Knudsen diffusion and activated diffusion) can have an impact on the composition of gas mixtures. These mechanisms exhibit a selectivity that is dependent, in the first order, on the square root of the molecular mass of a component. The prerequisite for the occurrence of molecular transport is a pore dimension which is small compared to the mean free path, λ, of a gas molecule [$\lambda \sim 4\ \mu m$ for an ideal gas at 100 kPa (1 bar)].

Molecular transport mechanisms occur only at low and medium pressures (up to ~ 2 bar) for pore diameters in the low nanometre range. At higher pressures, leakage is due only to laminar flow.

A.3.1.7   Condensation

Condensation can occur when the contents of a cylinder are sampled at high flow conditions, e. g. when the cylinder valve is opened in order to flush a valve or an attached gas line. At very high flow rates, the sampling of a gas mixture may be considered adiabatic and low temperatures ($\Delta T \sim -150\ °C$) occur in the valve nozzle,

leading to the formation of droplets of condensable components. These droplets are transported at lower rates than the gaseous components and the condensable components are therefore concentrated inside the cylinder. For this reason, it is recommended that the lines be evacuated in order to remove the contained air and that the system be flushed with the gas only at low flow rates.

A.3.1.8 Rules for handling precision gas mixtures

From the statements made above, it is clear that a change in the composition of the gas mixture can be caused by incorrect handling, even if clean gas cylinders without leakage are used. For the VAMGAS project, rules for the proper handling of gas mixtures were, therefore, stated in a document that was distributed to all the laboratories participating and all the participants in the round-robin tests.

It is important to prevent contamination of the gas during the purging of piping and valves. It is also essential to ensure that gas is not taken from the cylinders at high flow rates. In the case of high flow rates, it is necessary to take special precautions (such as heating the cylinders). It is necessary that the gas mixtures be stored at room temperature. If the hydrocarbon dew point of the mixture is relatively high as a result of the presence of condensing components such as propane and butane, it is necessary that the gas be stored at a temperature which is at least 10 °C to 15 °C above the hydrocarbon dew point.

A.3.2 Comparison between calculated and experimental data

A.3.2.1 Methods

A z-test was used to assess agreement between the calculated and experimental data.

The z-test checks whether two results are identical taking into account their respective variances. The z-test is defined as given in Equation (A.13):

$$z_{\text{test}} = \frac{\left|\hat{H}_1 - \hat{H}_2\right|}{\sqrt{u^2\left(\hat{H}_1\right) + u^2\left(\hat{H}_2\right)}}$$

(A.13)

where

$\hat{H}_1$, $\hat{H}_2$ are the properties under test;

$\mu(H)$ is the standard uncertainty of property H.

If the value z_{test} is below the critical level of 1,96 (95 % confidence interval), the two values H_1 and H_2 are considered statistically identical. Otherwise, if $z_{\text{test}} > 1,96$, the two values are not considered to be identical for statistical purposes.

For this procedure, the variances of both the calculated values and the experimental data must be known. For this reason, the VAMGAS project included comprehensive error investigations, with determination of the uncertainties of both the experimental data and the calculated values. The procedure used entailed a re-evaluation of the uncertainties of the tabulated values (see ISO 6976).

A.3.2.2 Superior calorific value

Table A.10 shows a comparison of the experimental and calculated superior calorific values on a mass basis and their respective uncertainty values.

**Table A.10 — Comparison of experimental (reference method) and
calculated calorific values for the PRMs**

Gas mixture	Calorific values				Relative difference %	z_{test} **value**
	Experimental		Calculated			
	CV_{exp} MJ/kg	$\mu(CV_{exp})$	CV_{calc} MJ/kg	$\mu(CV_{calc})$		
BAM 9605 4933	44,061	0,015	44,068	0,048	0,015	0,13
BAM 9605 4902	51,896	0,018	51,887	0,049	0,017	0,17
NMi 9498C	51,910	0,018	51,895	0,048	0,03	0,3
NMi 0603E	44,222	0,015	44,220	0,048	0,006	0,05

The uncertainty of the experimental values was 0,034 % (relative), and that of the values calculated (in accordance with ISO 6976) was about 0,1 % (relative) (95 % confidence interval). The agreement between the experimental and calculated superior calorific values was very good and the z values calculated were below the critical level of 1,96. There was no statistically significant difference between the values determined by tests and calculations.

A.3.2.3 Molar mass/gas density

Tables A.11 and A.12 show comparisons of the experimental and calculated values of molar mass and gas density at normal conditions.

**Table A.11 — Comparison of experimental (reference method) and
calculated molar mass for the PRMs**

Gas mixture	Molar mass				Relative difference %	z_{test} **value**
	Experimental		Calculated			
	M_{exp} g/mol	$\mu(M_{exp})$	M_{calc} g/mol	$\mu(M_{calc})$		
BAM-L 9605 4933	18,564 3	0,003 7	18,564 6	0,001 0	0,002	0,08
BAM-H 9605 4902	18,793 1	0,003 8	18,796 6	0,001 0	0,018	0,89
NMi-H 9497C	18,946 5	0,003 8	18,946 9	0,000 9	0,002	0,10
NMi-L 0602E	18,542 7	0,003 7	18,543 0	0,000 9	0,002	0,48

**Table A.12 — Comparison of experimental (reference method) and
calculated density for the PRMs**

Gas mixture	Density				Relative difference %	z_{test} **value**
	Experimental		Calculated			
	ρ kg/m^3	$\mu(\rho)$	ρ kg/m^3	$\mu(\rho)$		
BAM-L 9605 4933	0,77319	0,00015	0,77319	0,00005	0,001	0,01
BAM-H 9605 4902	0,78324	0,00016	0,78341	0,00006	0,022	1,00
NMi-H 9497C	0,78967	0,00016	0,78972	0,00005	0,006	0,30
NMi-L 0602E	0,77229	0,00015	0,77238	0,00005	0,012	0,57

With only 0,002 % difference between the experimental and calculated values, agreement was excellent for three gases. In one case (BAM-H 9605 4902), agreement was less good but the result of the z-test does not indicate any statistically significant difference between the two values.

### A.3.3 Comparison of direct and indirect methods by an interlaboratory comparison

A.3.3.1 Introduction

All the inter-comparison evaluations and statistical calculations were performed by Gasunie. Considering that the inter-comparison included 18 participants, each reporting more than 1 000 individual results, one can estimate the tremendous effort required for processing the data.

A brief description of the method used is given in 3.3.2 to 3.3.9.

A.3.3.2 Bracketing calibration

Bracketing calibration is exemplified by Figure A.6. The reference gases are used for calibration and their component concentrations are selected to be slightly above and slightly below the sample concentration. Ordinarily, least squares regression is used to determine the calibration coefficients, their variances and covariances.
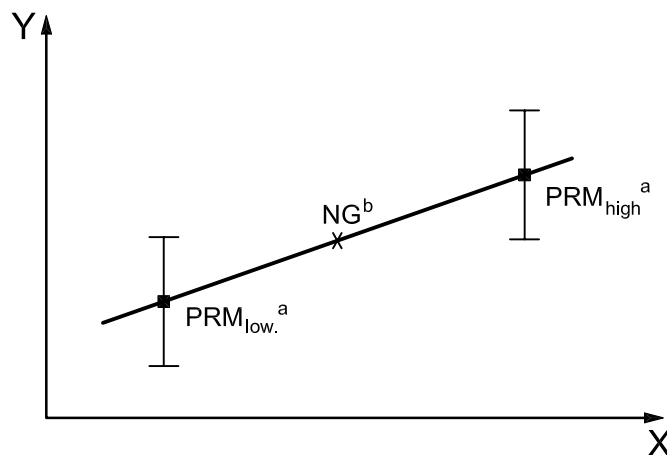
Key

X   concentration

Y   peak area

[a]   Primary reference mixture, in duplicate.

[b]   Natural gas, in triplicate.

Figure A.6 — Bracketing calibration example

Bracketing calibration was applied to all directly calibrated components, i.e. methane, nitrogen and the hydrocarbons up to $n\text{-}C_5$.

In each case, the raw data reported by the participants were processed in order to ensure that calculations were performed by the same method.

A.3.3.3 Relative response factors

The indirect components, i. e. those that were directly calibrated, were evaluated using relative response factors in accordance with Equation (A.14):

$$x_{i,\text{indirect}} = A_{i,\text{indirect}} \times \left(\frac{x_\text{b}}{A_\text{b}} \right) \times R_{i,\text{f}} \qquad\qquad (A.14)$$

where

$x_{i,\text{indirect}}$ concentration of the indirect component;

$A_{i,\text{indirect}}$ peak area of the indirect component;

x_b concentration of the bridge component;

A_b peak area of the bridge component;

$R_{i,\text{f}}$ relative response factor.

The relative response factors were set to their theoretical values using a formula developed by Kaiser, as given in Equation (A.15):

$$R_{i,\text{f}} = \frac{n_\text{b} \times M_{i,\text{indirect}}}{n_{i,\text{indirect}} \times M_\text{b}} \qquad\qquad (A.15)$$

where

$M_{i,\text{indirect}}, M_\text{b}$ are the molar masses of the indirect and bridge components, respectively;

$n_{i,\text{indirect}}, n_\text{b}$ are the number of carbon atoms in the respective components.

A.3.3.4 Evaluation of component groups

Depending on the design of the gas chromatograph, several of the components of the natural gas samples are not separated. Critical components in this category include 2,3-dimethylbutane/2-methylpentane/3-methylpentane and cyclopentane/2,2-dimethyl butane. Gas chromatographs with column backflushing do not separate components above a certain chain length at all. Furthermore, the number of the isomers of hydrocarbons above C_5 is too high to allow reporting of each individual component.

In these cases, "pseudo-components" were reported; these were evaluated in a special way. Assumptions concerning the average number of carbon atoms of the pseudo-components, their enthalpy, density and molar mass were made on the basis of the results of the four laboratories that had reported all the individual components.

A.3.3.5 Detection of outliers

A Grubbs test for the detection of outliers was performed for the calculated physical properties. Two outliers were detected and removed from the data set before determining the mean values and the uncertainty of the mean for calorific value, density and molar mass.

A.3.3.6 Results

The individual results of the participating laboratories are given in Figures A.7 to A.12. With respect to the desired method validation, however, the mean of the laboratories is of prime interest. The values are summarized in Table A.13.

Table A.13 — Comparison of calorific value, molar mass and gas density of the mean of the laboratories and the results from the reference measurements

Parameter	Type of gas	Mean of the laboratories	Reference method	Relative difference %
Calorific value, MJ/kg	H	52,561	52,563	0,003
	L	44,701	44,688	0,027
Molar mass, kg/kmol	H	18,115	18,122	0,036
	L	18,604	18,612	0,045
Density, kg/m^3	H	0,7549	0,7551	0,034
	L	0,7748	0,7752	0,048

A.3.3.7 Calorific value

The calorific value, calculated as the mean of the participating laboratories, was compared to the reference value by a z-test. Agreement was within 0,003 % for the type H natural gas and within approximately 0,03 % for type L gas. A z-test demonstrated that the mean of the laboratories was statistically equal (within 95 % confidence interval) to the reference. It is noteworthy that both the uncertainty of the results of the individual laboratories and the lack of agreement with the reference value is higher for type L gas than for type H gas due to the larger amount of nitrogen.

A.3.3.8 Gas density

The gas density derived from gas chromatography is also in statistically proven agreement with the reference measurements. The agreement of the average of the laboratories is within 0,04 % for L gas and 0,05 % for H gas.

A.3.3.9 Molar mass

Agreement with the reference values is essentially on the same level as for the gas density. For type L gas, the values agree within 0,03 %; for type H gas, the agreement is 0,05 %.

The uncertainty for the individual laboratories, however, is very small compared to the inter-laboratory variance. For this reason, the molar mass derived from composition analysis is statistically not equal to the reference value, if the uncertainty estimate is based upon the uncertainties of the individual laboratories. If the uncertainty estimate is based upon the inter-laboratory variance, the z-test gives statistical agreement for type H gas, but not for type L gas.

It can, therefore, be concluded that an uncertainty estimate that is based upon the repeatability of the measurements most probably underestimates the real uncertainty of composition analysis.

A small but nevertheless notable bias of 0,044 % can be detected between gas chromatography and reference densitometry, with the value of the reference method being higher than the gas chromatographic value.
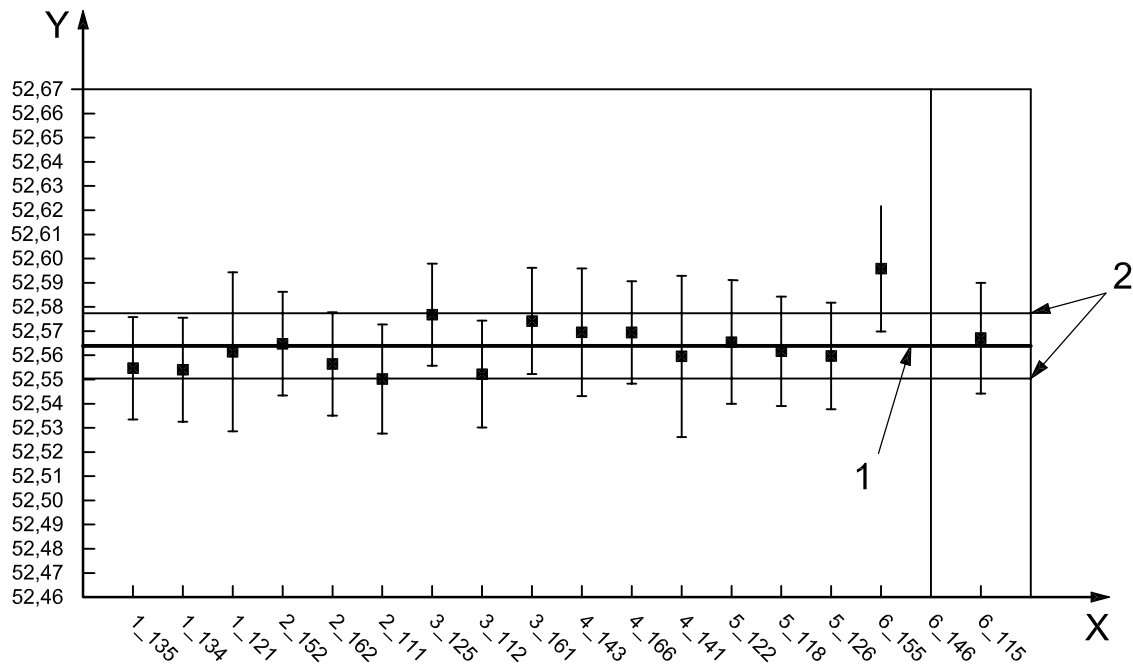
A possible reason for this bias can be that the concentrations of the minor components are underestimated in the gas analysis. One contribution is certainly due to components that are below the detection limit of the respective methods. Components that are not detected as a result of normalization are evaluated like the matrix gas, i.e. methane. The molar mass calculated from gas chromatography is likely, therefore, always be lower than the true value.

The natural gas samples contain hydrocarbons above C_{10}, which are normally near or below the detection limit of the GC system. As these components have a large molar mass, they contribute to the molar mass of the gas sample even at low concentrations. These higher hydrocarbons were quantified in the natural gas samples by the Ruhrgas laboratory using the method described previously. The analysis results are given in

Table A.14. These values give rise to the assumption that approximately 50 % of the detected bias of 0,04 %, i.e. 40 ppm, are due to the C_{10+} fraction. On the other hand, the contribution of the higher hydrocarbons to the calorific value is certainly negligible on the uncertainty scale considered, as the variation of calorific value on a mass basis with hydrocarbon chain length is very small. With respect to the gas density, these biased component uncertainties are obscured by the higher uncertainty level of the calculated density values.

Table A.14 — Component concentrations of the C_{10+} fraction of the natural gas samples as determined by a special analysis technique

Component	Type H natural gas mol/mol $\times 10^6$	Type L natural gas mol/mol $\times 10^6$
C_{10}	1,55	4,71
C_{11}	0,19	1,49
C_{12}	0,03	0,49
C_{13}	< 0,01	0,09
C_{14}	< 0,01	0,01
C_{15}	< 0,01	0,01

Key

X   laboratory number

Y   calorific value, CV, expressed in megajoules per kilogram (scale $\pm$ 0,2 %)

1   result of the reference method: CV_{ref} = (52,563 0 $\pm$ 0,0134) MJ/kg

2   confidence interval

■   average of single-laboratory results

⌶   confidence interval of single-laboratory results

Figure A.7 — Comparison of the results of the individual laboratories with the result of the reference method for the calorific value of the type H natural gas
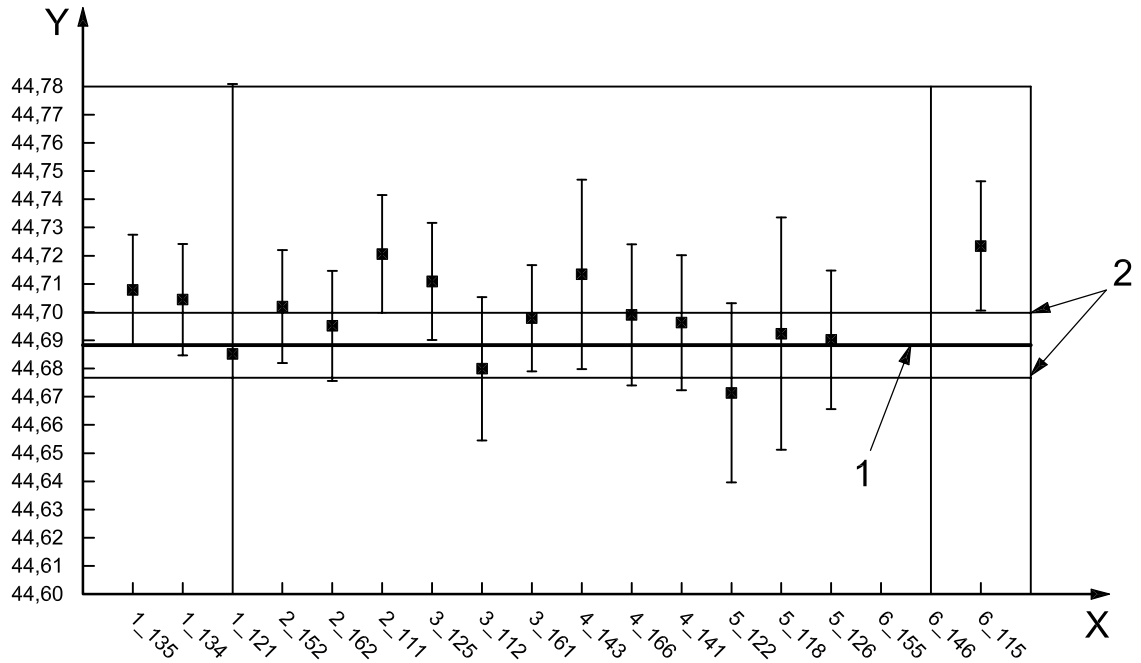
Key

X   laboratory number
Y   calorific value, CV, expressed in megajoules per kilogram (scale $\pm$ 0,2 %)

1   result of the reference method: $CV_{ref} = (44,688\ 3 \pm 0,012\ 1)$ MJ/kg
2   confidence interval

■   average of single-laboratory results
Ι   confidence interval of single-laboratory results

Figure A.8 — Comparison of the results of the individual laboratories with the result of the reference method for the calorific value of the type L natural gas
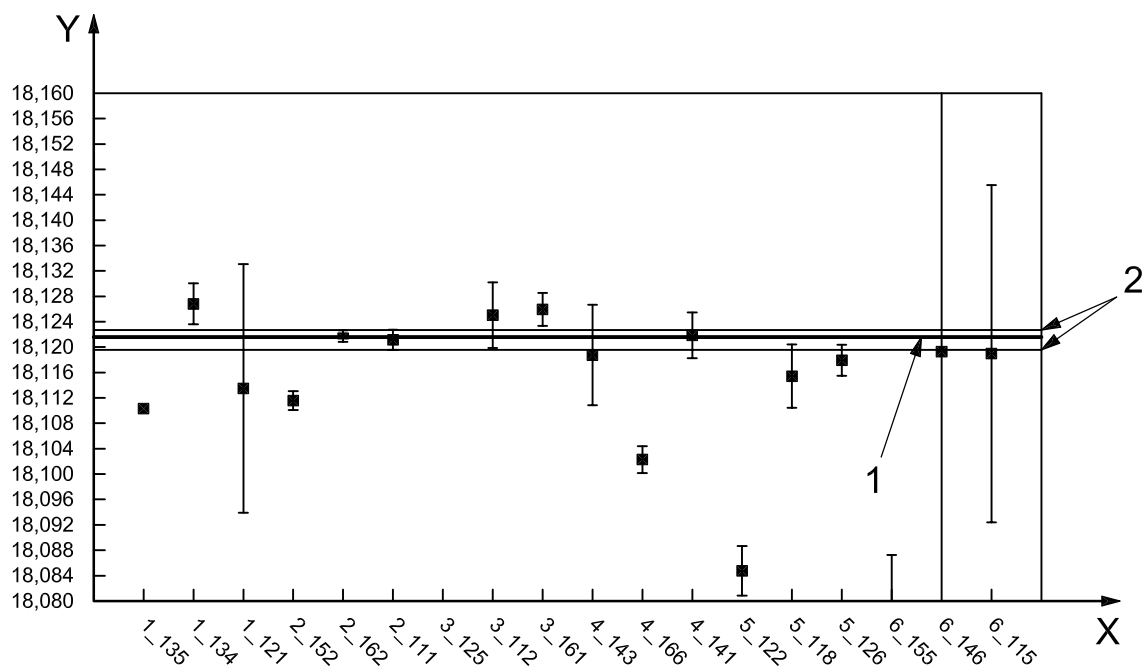
Key

X laboratory number

Y molar mass, M, expressed in kilograms per kilomole (scale $\pm$ 0,2 %)

1 result of the reference method: $M_{ref} = (18,121\ 7 \pm 0,001\ 8)$ kg/kmol

2 confidence interval

■ average of single-laboratory results

Ⅰ confidence interval of single-laboratory results

Figure A.9 — Comparison of the results of the individual laboratories with the result of the reference method for the molar mass of the type H natural gas
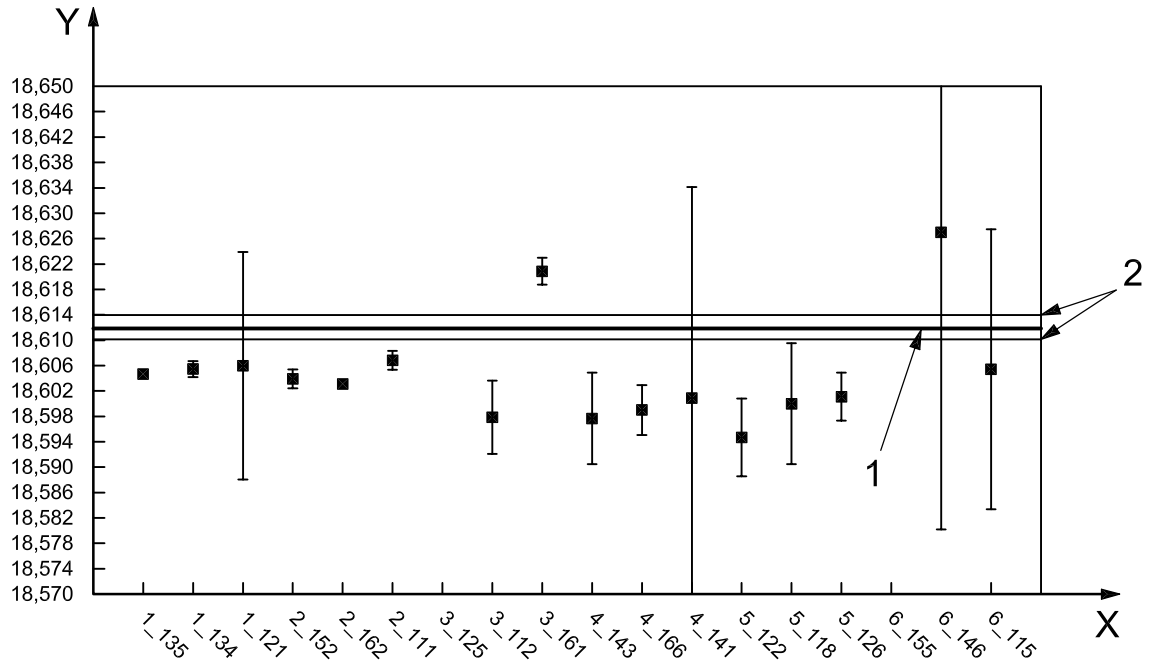
Key

X laboratory number

Y molar mass, M, expressed in kilograms per kilomole (scale $\pm$ 0,2 %)

1 result of the reference method: $M_{ref} = (18{,}611\ 8 \pm 0{,}001\ 9)$ kg/kmol

2 confidence interval

■ average of single-laboratory results

⌶ confidence interval of single-laboratory results

Figure A.10 — Comparison of the results of the individual laboratories with the result of the reference method for the molar mass of the type L natural gas
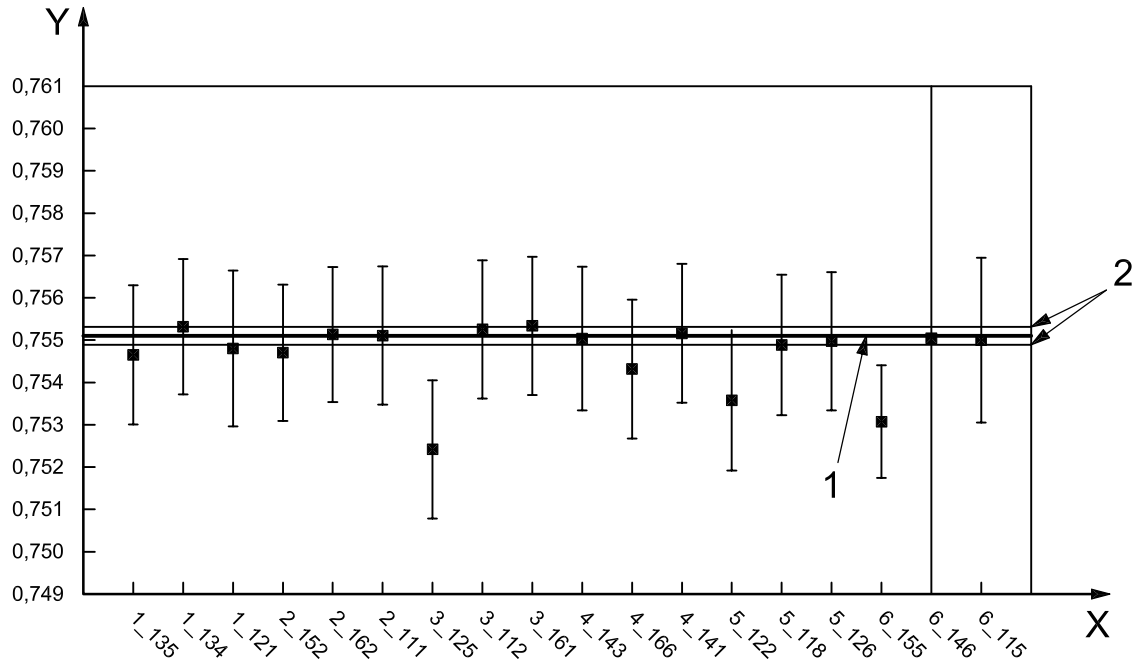
Key

X   laboratory number

Y   density, D, expressed in kilogram per cubic metre (scale $\pm$ 0,8 %)

1   result of the reference method: $D_{ref} = (0,755\ 11 \pm 0,000\ 2)$ kg/m^3 at $T = 293,15$ K and $p = 101,325\ 1$ kPa)

2   confidence interval

■   average of single-laboratory results

⌶   confidence interval of single-laboratory results

Figure A.11 — Comparison of the results of the individual laboratories with the result of the reference method for the density of the type H natural gas
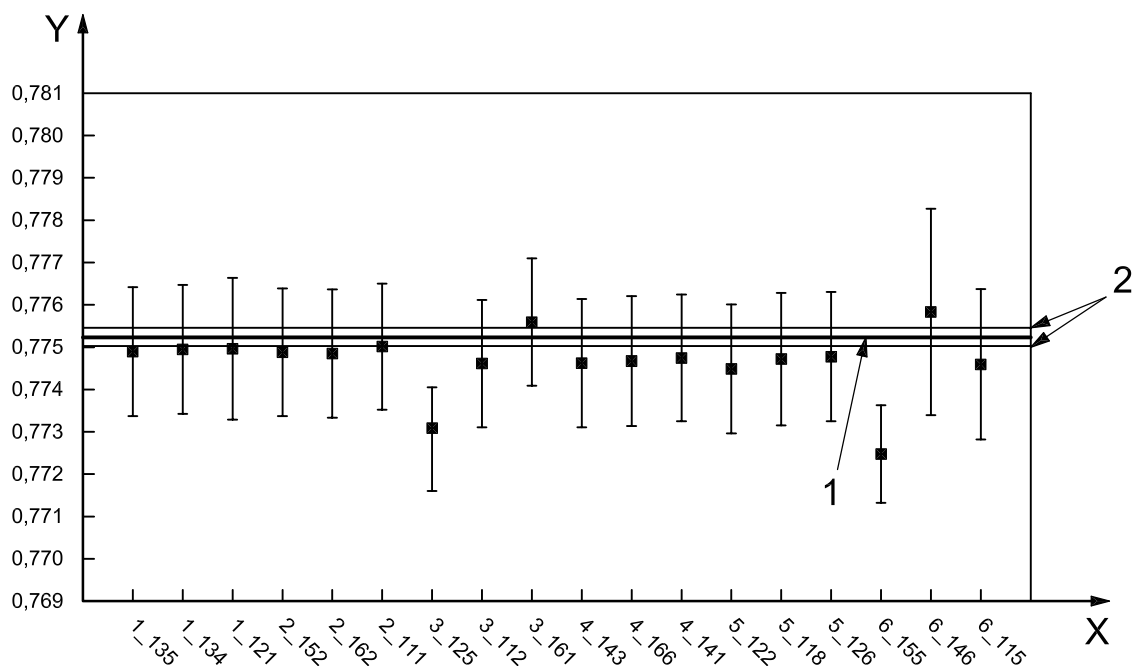
Key

X   laboratory number

Y   density, D, expressed in kilogram per cubic metre (scale $\pm$ 0,8 %)

1   result of the reference method: $D_{ref} = (0{,}755\ 21 \pm 0{,}000\ 2)$ kg/m^3 at $T = 293{,}15$ K and $p = 101{,}325\ 1$ kPa

2   confidence interval

■   average of single-laboratory results

⌶   confidence interval of single-laboratory results

Figure A.12 — Comparison of the results of the individual laboratories with the result of the reference method for the density of the type L natural gas

A.3.4 Uncertainty sources

In this report, "traceability" is used to mean the statement of a measurement result together with the associated uncertainty. On this basis, the necessity to pay considerable attention to the contribution made by each individual method used to the overall uncertainty level is clear. In Annex A, only the results of the uncertainty calculations are summarized.

A.3.4.1 Gas composition, gravimetric preparation and calculated physical properties

The uncertainties of the calculated physical properties of the PRMs were calculated using strict error-propagation rules, starting from the gravimetric preparation process and taking the uncertainties of the tabulated values into account. It was necessary to re-evaluate the uncertainties of the tabulated values with respect to ISO 6976, as the confidence intervals were not stated in some cases.

The overall uncertainties of the different properties are shown in Table A.15. Figure A.13 shows the different contributions to the overall uncertainties. With respect to the composition uncertainty, the contributions of the individual components of the gas mixture are given in Figure A.14. However, as a result of the very low uncertainty of the gravimetric preparation process, the contribution of the uncertainty in composition to the overall uncertainty is relatively small (see Figure A.13). In Figure A.13, the uncertainty of the calorific value is dominated by the uncertainty of the calorific value of methane.

Table A.15 — Composition uncertainties of PRMs manufactured by NMi

Relative standard uncertainty of typical H-gas and L-gas given by NMi		
Component	H-gas %	L-gas %
Methane, CH_4	0,001	0,001
Carbon dioxide, CO_2	0,005	0,006
Ethane, C_2H_6	0,006	0,009
Propane, C_3H_8	0,011	0,010
n-butane, n-C_4H_{10}	0,012	0,010
i-butane, iso-C_4H_{10}	0,012	0,011
n-pentane, n-C_5H_{12}	0,025	—
Nitrogen, N_2	0,014	0,005

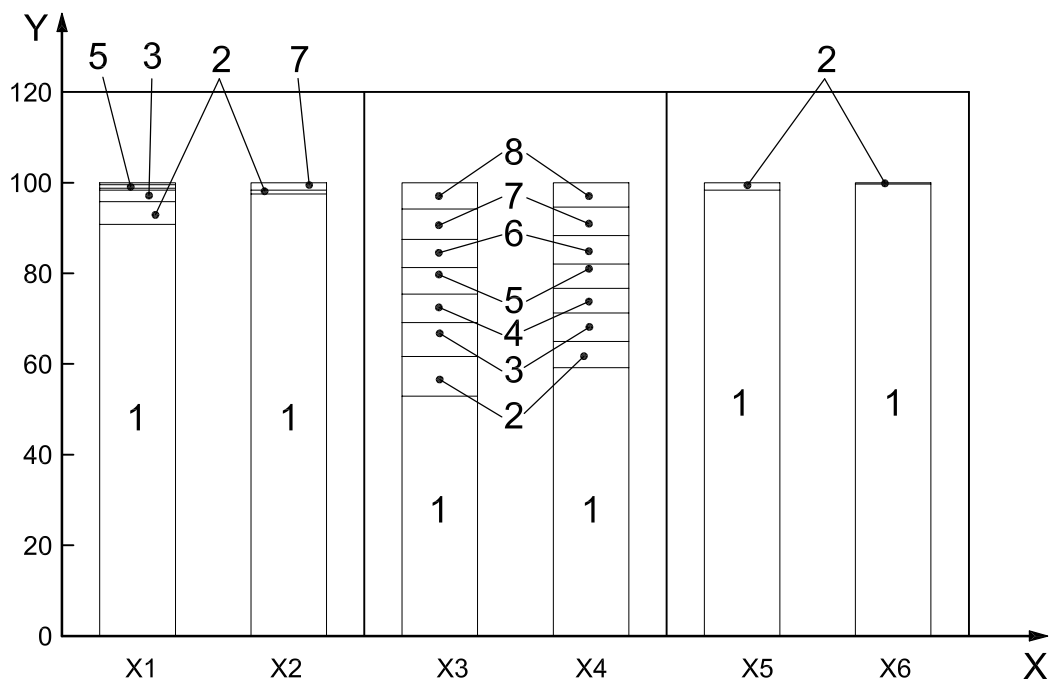
Key
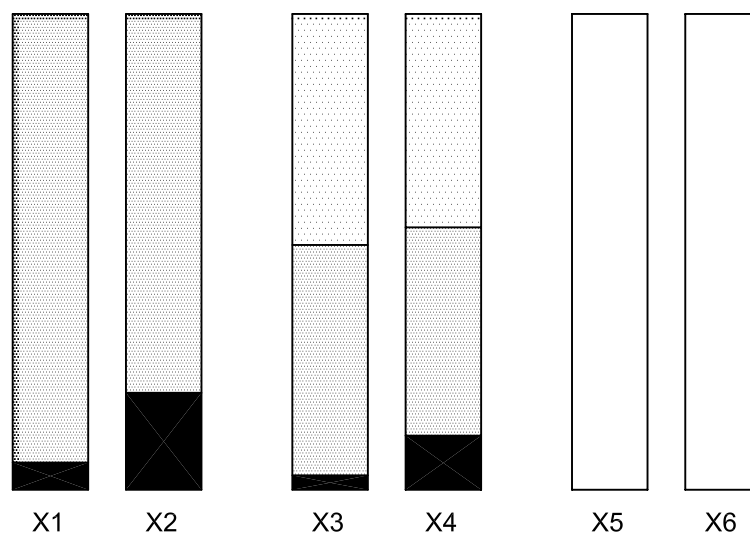
X1 molar mass of H-gas

X2 molar mass of L-gas

X3 density of H-gas

X4 density of L-gas

X5 calorific value of H-gas

X6 calorific value of L-gas

x_i, composition

M_i, molar mass

R, gas constant

H, enthalply on a mass basis

Figure A.13 — Assessment of the uncertainty contributions to the calculated physical properties

Key

X1 molar mass of H-gas

X2 molar mass of L-gas

X3 density of H-gas

X4 density of L-gas

X5 enthalply, mass of H-gas

X6 enthalply, mass of L-gas

Y relative contribution, %

1 CH_4

2 C_2H_4

3 C_3H_8

4 i-C_4H_{10}

5 n-C_4H_{10}

6 n-C_5H_{12}

7 N_2

8 CO_2

Figure A.14 — Assessment of the source of uncertainty of calculated physical properties

A.3.4.2 Densitometry

As the uncertainty assessment of the densitometer is rather complex, only the results for a 95 % confidence interval are given here. The expanded uncertainty of a single density measurement is $\leqslant 0,02$ % (relative) for $\rho \geqslant 2$ kg/m^3 and $\leqslant 0,000\ 3$ kg/m^3 for $\rho < 2$ kg/m^3. In order to determine the molar mass from density measurements, a least squares fit to 14 single measurement is performed. The expanded uncertainty of the measured molar mass is quoted as $\leqslant 0,02$ % (relative).

A.3.4.3 Reference calorimetry

A full-error propagation calculation in accordance with GUM was performed by Ofgas for their reference calorimeter. The expanded uncertainty of the calorific value as determined by the procedure given by Ofgas was calculated at 0,034 % (relative) for a 95 % confidence interval.

The sources of uncertainty are the following:

⎯ heat evolved during analysis, contributing 6 % of the total uncertainty;

⎯ mass determination by weighing, contributing 94 % of the total uncertainty.

A.3.4.4 Gas chromatography of natural gas samples

Initially, an uncertainty estimate of the gas chromatographic results was made on the basis of the repeatability that had been measured in part 1 of the inter-comparison. This uncertainty estimate can be found in the error bars in Figures A.7 to A.12.

It is clear that that repeatability in analytical chemistry does not include all possible uncertainty sources. A better uncertainty estimate also includes reproducibility. Reproducibility can be derived only from a number of completely independent measurements, which are difficult to obtain. The inter-laboratory variance, however, is a good estimate of reproducibility. These values are listed in Table A.16. The inter-laboratory variance gives a good estimate of the method uncertainty of natural gas analysis by gas chromatography.

Table A.16 — Comparison of calculated (mean of the inter-comparison participants) physical property values for the natural gas samples with the reference values

Parameter	Sample	Reference	Reference uncertainty	Laboratory	Laboratory uncertainty	Difference %	Statistical z-test
Calorific value	H-NG	52,563	0,018	52,561	0,015	0,003	0,09
	L-NG	44,688	0,015	44,701	0,024	0,027	0,79
Density	H-NG	0,755 1	0,000 2	0,754 9	0,001 0	0,034	1,25
	L-NG	0.775 2	0.000 2	0.774 8	0.001 0	0.048	1.85
Molar mass	H-NG	18,121 7	0,003 6	18,115 1	0,005 5	0,036	1,78
	L-NG	18,611 8	0,003 7	18,603 5	0,006 7	0,045	2,16

A.3.4.5 Method uncertainty of gas chromatography

On the assumption that the best possible calibration technique is used, the calorific value of type H gases can determined by gas chromatography with a method uncertainty of 0,02 % (95 % confidence interval), if the uncertainty of the calorific value of methane (0,1 %) is neglected. The uncertainty of the calorific value determined by gas chromatography increases with increasing inert gas content.

Density and molar mass can be determined with an uncertainty of 0,04 % to 0,05 %. Most of the uncertainty of the molar mass is due to a bias resulting from components below the detection limit. This bias is negative, the molar mass determined is always smaller than the true value.

A.4 Exploitation and dissemination of the results

The VAMGAS project was presented at the Gas Analysis Symposium held in Eindhoven, in November 1999. The final project presentation was held in Brussels, in April 2000. Furthermore, the results of the VAMGAS project were presented at the IGRC, in November 2001, in Amsterdam.

The results of the VAMGAS project are published as this Technical Report.

In order to disseminate the results into the European metrological society, the working group decided to submit a proposal to EUROMET to officially acknowledge the VAMGAS project. Since a EUROMET proposal can only be submitted by a national metrological institute, the proposal was presented to EUROMET in January 1999, by Anton Alink of NMi. EUROMET did well recognize the quality of the results presented. However, EUROMET decided not to accept the project as an official EUROMET project, because no additional metrological institutes could participate in the project.

As a spin-off of the VAMGAS project, a working group was formed within GERG to perform a feasibility study for reference calorimeter. The companies involved in this GERG reference calorimeter study are PTB, Advantica, Ruhrgas and SNAM. The study was concluded in October 2000.

A.5 Conclusions

A.5.1 Project

The project has demonstrated that the confidence currently shown in state-of-the-art methods for the production of reference gas mixtures is justified. For the first time, it was possible, with considerable effort, to verify gas mixtures of the highest quality produced by gravimetric methods using independent methods with an uncertainty equivalent to that of the production process. In the future, calibration gas producers will be able to verify their uncertainty claims for the production of precision gas mixtures using the methods demonstrated in this project. As discussed in A.5.2, customers have called for such verification. This Technical Report contains the results obtained in the project.

The results of the project underline the importance of reference methods of gas density measurement and calorific value determination for gas analysis. However, it is necessary to note that there has been a drastic fall in the number of reference measurement facilities in operation. During work on the project, the reference calorimeter operated by Ofgem was the only reference calorimeter in service in the world. In this context, the practical use of the procedure described for customers is naturally severely restricted. National metrological laboratories are called upon to become active with respect to this or other reference methods with a view to restoring the variety of processes that was once available.

The superior calorific values listed in ISO 6976 are only based on two investigations. The uncertainties of 0,1 % stated are no longer acceptable. It is also necessary to review and correct these values in order to ensure fair and equitable treatment for consumers. This is a future task for metrological institutes in cooperation with the gas industry. A project of this type has already been initiated under the auspices of GERG.

The possibility demonstrated in this project of highly precise determination of the molar mass of a gas is of special scientific importance in the field of metrology. In this way, it is possible to establish a metrological link between gas measurements and the SI unit, the mole.

The round-robin tests carried out as part of the product have shown that uncertainty levels in routine natural gas analyses in Europe are very low. These results of the round-robin tests have given organizations involved in gas analysis considerable confidence in the comparability of their results. In general, the participants expressed satisfaction with the results. In the future, it will be necessary to conduct further high-quality round-robin tests covering gas mixtures occurring naturally in addition to synthetic mixture.

A.5.2 Requirements of calibration gas users

The VAMGAS project has shown that highly precise calibration gases on the level of primary reference materials can be produced by gravimetric methods. The very low uncertainty obtained is feasible if extreme care is taken and highly precise balances and highly pure gases are used in an optimized production process for gases sufficiently far from the two-phase range.

It is necessary that users take due care in handling these valuable gases with a view to ensuring that this very low uncertainty is maintained over the duration of use of the gas mixtures.

The rules to be followed were documented.

The uncertainties stated in manufacturers' certificates are often higher than the mathematical uncertainty of the weighing process. These uncertainty values often include a component representing the uncertainty of analytical verification of the gas mixtures produced. In this way, the manufacturers attempt to take account of all the error sources that cannot be assessed in quantitative terms, e.g. minor deviations in the manufacturing process. In addition, these uncertainties are intended to cover possible adverse affects of shipment (e.g. by air freight). After all, manufacturers' certificates guarantee compliance with the uncertainty values stated.

At the final project presentation, the round-robin test participants, who are all users of calibration gases, stated that they would prefer manufacturers to be less generous in their handling of uncertainty values in manufacturers' certificates. In addition, users are interested in a further extension in the shelf lives (stability periods) of costly calibration gases. In this context, calibration gas producers are called upon to engage in more intensive dialogue with their customers.

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