SLOVENSKI STANDARD

SIST-TP CEN ISO/TR 24094:2008

01-januar-2008

Analiza naravnega plina - Validacija metod za plinske referenį ne materiale (ISO/TR 24094:2006)

Analysis of natural gas - Validation methods for gaseous reference materials (ISO/TR 24094:2006)

Erdgasanalyse - Validierungsverfahren für gasförmige Referenzmaterialien (ISO/TR 24094:2006)

Analyse du gaz naturel - Méthodes de validation pour matériaux de référence gazeux (ISO/TR 24094:2006)

Ta slovenski standard je istoveten z: **CEN ISO/TR 24094:2007**

ICS:

75.060	Zemeljski plin	Natural gas

SIST-TP CEN ISO/TR 24094:2008 **en**

TECHNICAL REPORT

RAPPORT TECHNIQUE

TECHNISCHER BERICHT

CEN ISO/TR 24094

November 2007

ICS 75.060

English Version

Analysis of natural gas - Validation methods for gaseous reference materials (ISO/TR 24094:2006)

Analyse du gaz naturel - Méthodes de validation pour matériaux de référence gazeux (ISO/TR 24094:2006)

Erdgasanalyse - Validierungsverfahren für gasförmige Referenzmaterialien (ISO/TR 24094:2006)

This Technical Report was approved by CEN on 2 November 2007. It has been drawn up by the Technical Committee CEN/SS N21.

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Management Centre: rue de Stassart, 36 B-1050 Brussels

Ref. No. CEN ISO/TR 24094:2007: E

Foreword

The text of ISO/TR 24094:2006 has been prepared by Technical Committee ISO/TC 193 "Natural gas" of the International Organization for Standardization (ISO) and has been taken over as CEN ISO/TR 24094:2007 by Technical Committee CEN/SS N21 "Gaseous fuels and combustible gas", the secretariat of which is held by CMC.

Endorsement notice

The text of ISO/TR 24094:2006 has been approved by CEN as CEN ISO/TR 24094:2007 without any modifications.

TECHNICAL REPORT

ISO/TR 24094

First edition
2006-05-15

Analysis of natural gas — Validation methods for gaseous reference materials

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

Reference number
ISO/TR 24094:2006(E)

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

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.

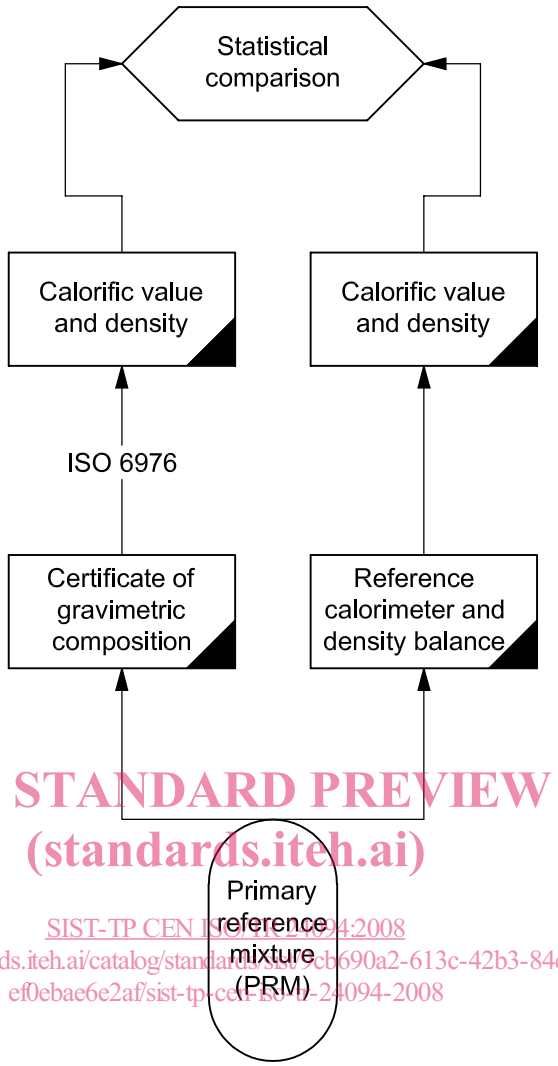

Figure 1 — Schematic concept of part 1 of the VAMGAS project

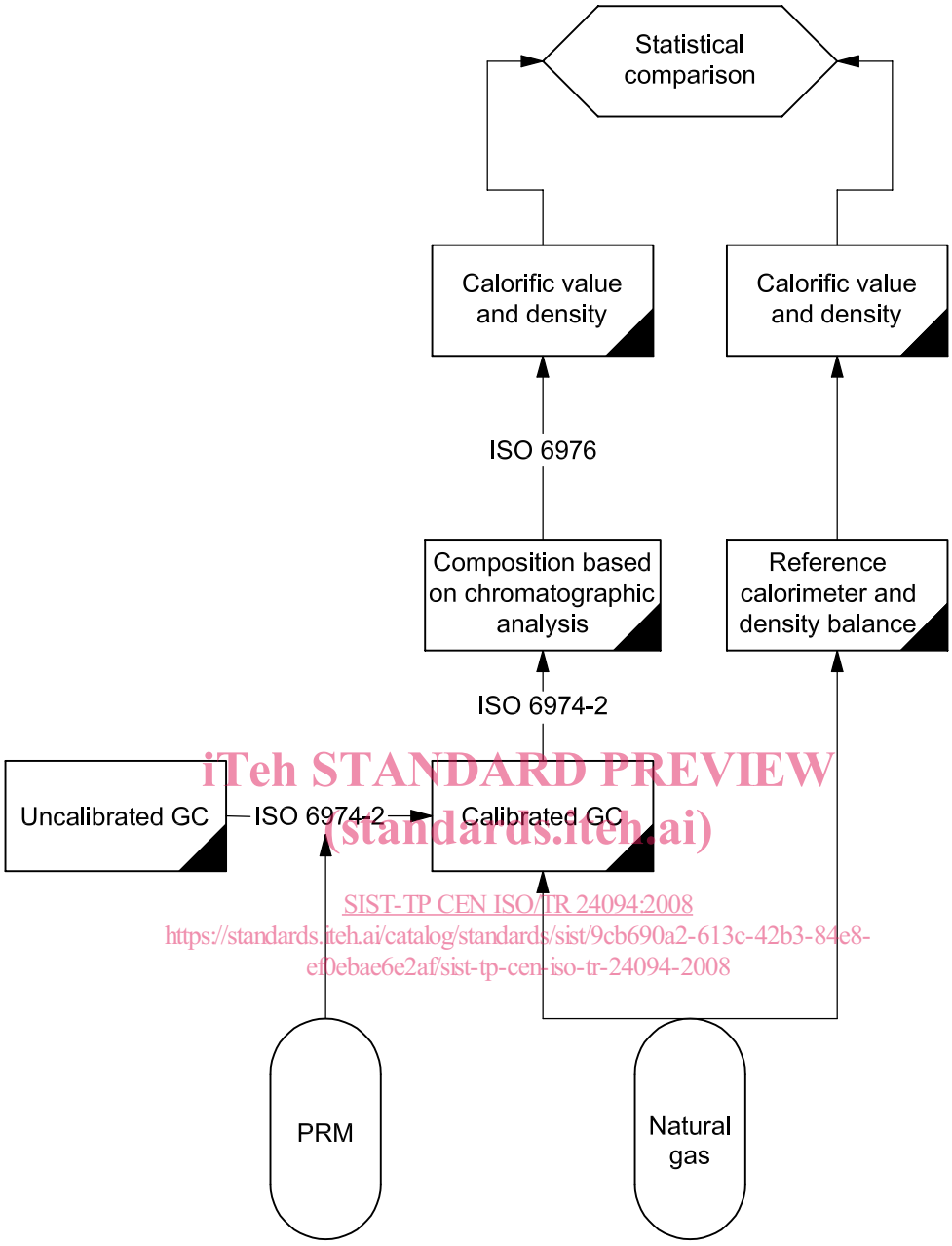

Figure 2 — Schematic concept of part 2 of the VAMGAS project

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