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Uncertainty in Gas Density Originating from Equation of State

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ABSTRACT

Today's industry standards for calculating natural gas properties are constrained by a limited range of compositions and components, which may introduce additional uncertainties or biases when utilized in rich gas applications. This paper attempts to highlight the challenges arising when pushing the boundaries of some of the most used equations in fiscal metering and other systems involved in metering and allocation. In addition, the performance in calculated gas density is evaluated against high accurate measured density data from the GERG-2004 database, covering the intermediate quality range defined by AGA8.

1 INTRODUCTION

When measuring gas flow rate, density is normally required as an input, either for conversion, or as a direct input in the metering equations. In fiscal applications, gas is often measured on a volume basis, but sold on mass or energy basis. An error in estimated gas density will therefore produce a proportional error in the quantity used for sales. Gas density is normally established either by direct measurement or calculation based on composition, pressure, and temperature. For dry export quality sales gas, these methods are well established, and gas density can be estimated with uncertainties well within requirements.

However, when dealing with rich hydrocarbon gases, a series of challenges arises, adding to the uncertainty when establishing gas properties, such as density. The term rich gas is not clearly defined but is usually referred to as natural gas containing heavier components than a dry sales gas, characterized by a higher molar mass and increased dew point temperature.

When sampling rich gas, either for direct density measurement or compositional analysis, higher temperature is required to maintain a representative sample. Analysing heavier components also increases the complexity of the chromatograph design, setup, and calibration gas, resulting in an overall increased uncertainty in the measured composition.

In addition to the uncertainty in the measured composition, the equation of state in use is crucial for the uncertainty in the calculated density. This paper focuses on the limitations and uncertainties for some of the most used equations of state and the challenges arising when utilized for heavier gases.

Fiscal metering systems use equations given by international standards. However, in other metering and allocation systems, alternative equations may often be encountered. Especially in systems where liquid is also present, for example in PVT models used as input by multiphase meters. Therefore, two of the most common cubic equations of state have also been included in this study.

The AGA8 reports are considered the industry standard for calculating gas density from composition. The equations provided in the report contains a list of 21 allowed components, with a specified composition range for each component. In rich gas applications, molar compositions outside the limits of the AGA8 reports may often be encountered, especially for the heavier components. Rich gases usually also

contain components that are not part of the 21 AGA8 components, such as aromatics, naphtenes and alkane isomers, which introduces the issue of component assignment by various methods.
This paper evaluates the performance in calculated gas density by several commonly used equations of state, by comparison against experimental data from the GERG-2004 database [1].
In addition, limitations in the range of validity and the allowed components for the AGA8 equations are investigated through two field case examples, demonstrating systematic errors arising in rich gas applications. In such applications, other methods for establishing gas density should be considered.

2 THEORETICAL FOUNDATION

When gas flowrate is measured on a volume basis, density is required to calculate mass flow, q_m [kg/h], by the following equation:

$$q_m = q_v \rho \tag{1}$$

where q_v [m^3/h] is the volume flowrate and ρ [kg/m^3] is the mass density. In gas metering applications, volumetric flowrate at standard conditions (1.01325 bara & 15 °C), $q_{v_{std}}$ [Sm^3/h], is often used, and is calculated by dividing mass flow by mass density at standard conditions, ρ_{std} [kg/Sm^3].

$$q_{v_{std}} = \frac{q_m}{\rho_{std}} \tag{2}$$

The gas molar density, d [mol/m^3], is the number of moles, n [mol], divided by the gas volume, V [m^3]. At a given pressure and temperature, the molar density relates to the compressibility factor, Z, as shown by equation 3, derived from the real gas equation:

$$d = \frac{n}{V} = \frac{P}{ZRT} \tag{3}$$

where P [Pa] is the pressure, T [K] is the temperature, Z [-] is compressibility factor and R [8.314 462 J/(mol·K)] is the universal gas constant. The mass density can then be found by multiplying molar density by the molar mass M [kg/mol], resulting in equation 4.

$$\rho = M\frac{P}{ZRT} \tag{4}$$

The molar mass can be calculated directly from composition by equation 5:

$$M = \sum_{i=1}^{N} x_i M_i \tag{5}$$

where N is the number of components, x_i [-] is the component mole fraction and M_i [kg/mol] is the molar mass of that component.
Converting actual volume flowrate to volume flowrate at standard conditions can be done by combining equations 1,2 and 4, resulting in equation 6. Assuming molar mass does not change between actual and standard conditions, which is true for single phase gas, the molar mass term disappears in this equation.

$$q_{v_{std}} = q_{v_{act}} \frac{P_{act} Z_{std} T_{std}}{P_{std} Z_{act} T_{act}} = q_{v_{act}} \frac{d_{act}}{d_{std}} \qquad (6)$$

The change in volume flowrate at actual- and standard conditions can thus be considered as the ratio between molar density at the two conditions.

3 EQUATIONS OF STATE

To establish molar density, d, and compressibility factor, Z, a suitable equation of state (EOS) can be used. A series of different equations exists for various applications, with varying performance in calculated properties.

3.1 Cubic Equations of State

Soave-Redlich-Kwong (SRK) [2] was published in 1972 as a modified version of the original Redlich-Kwong equation. SRK was considered good for vapor-liquid equilibrium calculations, but tended to underestimate liquid densities [3]. In 1976 the Peng-Robinson (PR) equation was published [4], improving the calculation of liquid densities. Both SRK and PR are considered cubic equations of state, as they can be written in a cubic form with respect to compressibility.
In 1978 an improved version of the Peng-Robinson equation was presented. The Peng-Robinson 78 (PR 78) equation only affects components with acentric factor, $\omega > 0.49$, which is most common for heavier components. The difference in gas density is therefore normally neglectable between PR and PR 78.
SRK was normally not used for calculating liquid densities until in 1982, when Peneloux et al. [5] suggested an improvement, by introducing a volume translation parameter. The volume translation parameter only affects phase densities, without affecting the phase equilibrium. The Peneloux volume translation parameter can also be used in the Peng-Robinson equation claiming improved density estimates for both gas and liquids [6].

3.2 Equations from AGA Report Number 8

Gas densities obtained from cubic equations of state, like SRK and PR, are considered inaccurate for fiscal gas metering applications. International standards recommend the equations described in AGA report No. 8 for calculating thermodynamic properties in such applications [7], hereby referred to as AGA8.
AGA8 Part 1, second edition [8] comprises the DETAIL and GROSS equations of state. It was published in 1992, where the DETAIL characterization equation, often referred to as AGA8-DC92, has been considered the industry standard for calculation of gas properties for the last couple of decades. The GROSS equation is a simplified model that should only be considered if simplicity is needed and is

therefore excluded in this study. The DETAIL equation is considered more complex, but also the most accurate of the two.

In April 2017 AGA published a revised Third edition of AGA8 Part 1 [9], together with the new AGA8 Part 2 [10], which contains the GERG-2008 equation of state [11]. The GERG-2008 equation is shown to provide a lower uncertainty for a much wider range of pressures, temperatures and compositions compared to the DETAIL equation.

AGA8 Part 1 therefore recommends the use of GERG-2008 instead of DETAIL. It also encourages upgrading to GERG-2008 for existing installations, stating as follows: *"While adoption of the equations in Part 2 is encouraged, the decisions to upgrade existing installations to use AGA Report No. 8, Part 2, are left to the discretion of the parties involved."* Despite these recommendations, the DETAIL equation is still selected for new installations.

Due to the GERG-2008 implementation in the AGA8 reports in 2017, certain historical references are no longer unambiguous, potentially leading to confusion. For example, it's quite common to see documents referring to the DETAIL equation as AGA8, without specifying the actual equation. This can be especially confusing when the reference does not contain the report revision and year published.

Table 1 attempts to provide a simple overview of the AGA8 publications with their corresponding equations.

Table 1 – Overview of the AGA8 Publications with Their Corresponding Equations of State

Year published	AGA8 part 1	AGA8 part 2
1985	1st edition: Equation not named	
1992 (reprint 1994 and 2003)	2nd edition: DETAIL & GROSS	
2017	3rd edition: DETAIL & GROSS	1st edition: GERG-2008

4 LIMITATIONS IN THE AGA8 EQUATIONS

The performance in calculated gas density obtained by the AGA8 equations are considered superior to the performance of the cubic equations. However, unlike the cubic equations, the AGA8 equations are fairly limited in the components allowed, as well as the supported range of compositions.

AGA8 Part 2 distinguish between *pipeline quality natural gas* and *intermediate quality natural gas*, presented in Table 2. The valid limits are not clearly given for each equation. However, the report states that the DETAIL equation is applicable to pipeline quality natural gas, while the GERG-2008 equation is also applicable to intermediate quality natural gas. In rich gas applications, gas compositions exceeding the limits of both pipeline quality and intermediate quality natural gas are common. It has previously been shown that exceeding these limitations can produce significant differences between calculated properties from DETAIL and GERG-2008 [12].

Table 2 – AGA8 Component Mole Percent Ranges for Pipeline- and Intermediate Quality Range

	Pipeline quality range		Intermediate quality range	
Component	Min mole %	Max mole %	Min mole %	Max mole %
C1	70	100	30	100
N2	0	20	0	55
CO2	0	20	0	30
C2	0	10	0	25
C3	0	3.5	0	14
iC4+nC4	0	1.5	0	6
iC5+nC5	0	0.5	0	0.5
nC6	0	0.1	0	0.2
nC7	0	0.05	0	0.1
nC8+nC9+nC10	0	0.05	0	0.05
H2	0	10	0	40
O2	0	0.02	0	2
CO2	0	3	0	13
H2O	0	0.015	0	0.02
H2S	0	0.02	0	27
He	0	0.5	0	0.5
Ar	0	0.02	0	0.05

Another major limitation in the AGA8 equations, is the fixed list of 21 allowed components, where the heavier components (C6+) are only represented by the normal alkanes. Components that are not present in this list, for example neo-pentane or cyclohexane, must therefore be re-assigned to one of the allowed components.

A GC analysis for rich gas can consist of more than 100 components, where the majority constitutes the C6+ fraction, that are typically distributed into pseudo-components from C6 to C10+. In fiscal gas metering stations, C6+ analysis is quite common, where the C6+ fraction is measured and treated as a single component. Some flow computers have implemented the option to set a fixed distribution of the C6+ fraction into the heavier AGA8 alkanes, which may reduce uncertainty in calculated properties. The fixed split is usually based on laboratory sample analysis and must be treated with caution, as is shown later in this paper. However, in all these scenarios, the analysed components must be assigned to the list of 21 AGA8 components before performing calculations.
The 2017 release of the AGA8 reports introduced two different recommendations for component assignment, depending on the properties of interest:

1. Assignment of components for calculating single-phase thermodynamic properties
2. Assignment of components for calculating dew point

The most plausible reason for this is because a component's normal boiling point can differ significantly from that of components of similar molar mass. This is especially true for cyclic molecules and/or molecules with double bonds, such as naphtenes and aromatics. The assignment for calculating single-phase thermodynamic properties (1) aim to minimize uncertainty in calculated gas density and is presented as a table in the AGA8 reports. A similar table is given by ISO 12213-2:2006.

The method for assigning components for dew point calculations (2) is described mathematically and is based upon the normal boiling point of the component.

To the authors knowledge, assigning components into pseudo-components according to normal boiling point also seems to be the most used method in laboratory gas compositional analysis. The method appears to have originated from experimental data related to vapor-liquid equilibrium calculations [13]. The direct use of sample analysis, utilizing this method, would therefore contradict the AGA8 recommendation for calculation of single-phase thermodynamic properties. For example, when using this method in a laboratory analysis, Toluene would be assigned to C8, due to its high normal boiling point. But according to the AGA8 recommendation for single-phase property calculation, it should be assigned to n-Hexane (nC6).

Slight variations in component assignment can be observed in various applications, but most of the methods seems to be based on either normal boiling point, molar mass, or carbon number. In addition, personal evaluations of single component assignment seem to occur.

5 COMPARING DIFFERENT EQUATIONS OF STATE AGAINST THE GERG-2004 DATABASE

The GERG-2004 database contains more than 100,000 data points of high accuracy measured thermodynamic properties used in the development of the GERG-2004 equation of state, the predecessor to the GERG-2008 equation.

More than 70,000 of the data points are measured densities for given compositions, divided between binary mixtures and multi-component mixtures. 30,252 of the binary mixtures were used for parameter fitting in the development of the GERG-2004 equation. The stated relative uncertainty is ± 0.05-0.1% for the most accurate density measurements, according to the manual.

Table 3 – Number of Density Datapoints in the GERG-2004 Database

	Number of density datapoints
Binary mixtures	49 749
Multi-component mixtures	21 769
Total	71 518

The data points from the binary mixtures have been excluded from the results in this study for several reasons. The binary mixtures contain a large number of data points for mixtures that are not relevant for reviewing natural gases. It would also be an unfair comparison to evaluate multiple equations on a dataset that has been used for parameter fitting in the development of one of the equations.

Also, a significant proportion of the binary mixture data are quite old, with the earliest reference being from 1916. Some of these data comprise uncertainties too large for reviewing the performance of today's equations.

5.1 Method

Composition, pressure, and temperature in the database have been used to calculate density for the following equations:

- Soave-Redlich-Kwong (SRK)
- Soave-Redlich-Kwong Peneloux (SRK Peneloux)
- Peng Robinson 78 (PR 78)
- Peng Robinson 78 Peneloux (PR 78 Peneloux)
- AGA8 part 1: DETAIL
- AGA8 part 2: GERG-2008

The original Peng Robinson equation was also evaluated, but as the results were identical to Peng Robinson 78, it is not included in the presented results. The identical results are expected, since the improvement in Peng Robinson 78 only affects components with acentric factor $\omega > 0.49$, which do not occur in the GERG database.

Calsep's PVTsim Nova 6.1 Open Structure programming interface was used for calculating the cubic equations, SRK and Peng Robinson, both with and without Peneloux correction. PVTsim default component parameters were used in the calculations. For the AGA8 equations, DETAIL and GERG-2008, the RUST implementation in the NIST AGA8 Github repository was used [14]. The calculated densities from GERG-2008 was also verified against the PVTsim GERG-2008 implementation, with neglectable differences. All calculations were initiated using Python scripts.

The calculated densities were then compared against the measured reference data from the GERG database, utilizing the density deviation (*Δρ/ρ*) obtained by the following equation:

$$\Delta\rho/\rho\ [\%] = 100\frac{\rho_{calc} - \rho_{meas}}{\rho_{meas}} \tag{7}$$

ρ_{calc} is the calculated gas density from the given equation of state, while ρ_{meas} is the measured reference gas density from the GERG database.

To evaluate the overall performance of the equations, the *mean absolute percentage deviation (MAPD)* was calculated for each EOS:

$$MAPD\ [\%] = 100\sum_{i=1}^{n}\frac{|\Delta\rho_i/\rho_i|}{n} \tag{8}$$

where n is the number of datapoints in the dataset. In addition, the 95% coverage interval has been computed, providing a range that contains the central 95% of density deviations for each equation.

For certain points in the GERG database, some of the cubic equations predicts liquid dropout. As this study evaluates performance in calculated gas density for different equations, the dataset has been filtered to remove any data points where liquid may be present. As the NIST AGA8 equations do not support vapor-liquid equilibrium calculations, the cubic equations have been used to filter out data points that may contain liquid. If any of the cubic equations predicted liquid dropout, the given data point was removed. PVTsim do not distinguish between single-phase gas and supercritical, and the difference has therefore not been considered in this study.

The following bullet points represents a summary of the filters applied to the dataset prior to analysis:

- Only single-phase gas points included
- Pressure below 300 bara included
- Temperature between 0 - 100 °C included
- Binary mixtures excluded
- Excluded datapoints from earlier than 1980

After applying these filters, the remaining data set contains 15 409 datapoints from 204 different gases.

When reviewing the gas compositions given in the GERG-2004 database, it appears that the maximum mole % for multicomponent mixtures have been used to establish the maximum mole % for the *intermediate quality natural gas*, given in Table 2.

For all gas compositions presented in this paper, the component mole percent exceeding the natural gas quality ranges are colour coded according to Table 4, based on the limits given by Table 2. For some components in Table 2, the quality ranges are lumped together, for example iC4+nC4. In that case, both components are coloured if the sum exceeds the given limit.

Table 4 – Colour Coding for Composition Mole Percent Outside Limits for AGA8 Pipeline/Intermediate Quality Range

Natural gas quality	Colour coding
Outside pipeline quality range	🟨
Outside intermediate quality range	🟥

5.2 Results

The relative deviation between calculated density and measured density from the database are presented as histograms for each EOS in Fig. 1, and as a scatter plot in Fig. 2. In addition, the mean absolute percentage error has been calculated and presented in Table 5, together with the 95% coverage interval. For the cubic equations, density deviations of up to 6% can be observed, while the change in density deviation by switching from SRK to Peng Robinson is even greater, with differences exceeding 9%. SRK seem to underpredict gas density, while Peng Robinson tend to overpredict, at least without the Peneloux correction.

When considering the Peneloux volume correction, it seems to provide a small improvement in predicted gas density for the SRK equation. However, for Peng Robinson 78, the results are completely different when the Peneloux correction is applied. This is surprising, as the Peneloux correction is supposed to improve density predictions for both gas and liquid.

When these cubic equations are used in metering applications, for example as input to multiphase flow meters, one should be aware of the varying performance for different gases and operating conditions, including the effect of the Peneloux correction.

Table 5 – Mean Absolute Percentage Deviation and 95% Coverage Interval for Density Deviations from Various Equations of State Compared to Measured Density in the GERG-2004 Database

EOS	Mean absolute percentage deviation [%]	95% coverage interval [%]
SRK	1.86	(-5.09, 0.00)
SRK Peneloux	1.34	(-3.84, 0.05)
PR 78	2.04	(0.22, 3.61)
PR 78 Peneloux	1.27	(-3.55, 1.25)
DETAIL	0.07	(-0.17, 0.48)
GERG-2008	0.05	(-0.22, 0.11)

The density deviations obtained by DETAIL and GERG-2008 lies within the uncertainty stated by the AGA8 reports, yielding a performance superior to any of the cubic equations evaluated. It could be argued that this comparison is somewhat unfair since the database only contains components within the AGA8 component list. This is partly true, but the database covers such a wide range of compositions, pressures, and temperatures, that it is probably representative for the majority of fiscal metering applications found in the oil and gas industry today. The exception is rich gas applications exceeding the composition ranges for intermediate natural gas. The results also support the claim that GERG-2008 performs slightly better than DETAIL overall.

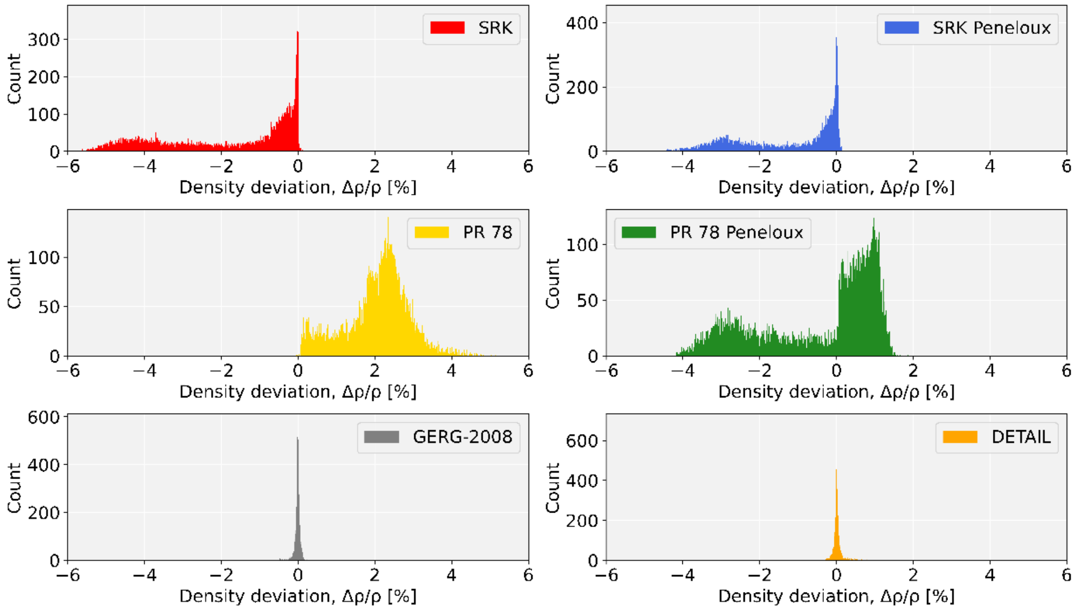


Fig. 1 – Histogram of Density Deviations (Δρ/ρ) Between EOS Calculation and Measured density in GERG-2004 Database for Multicomponent Mixtures

It is also important to note that the density deviation distribution do not necessarily provide a representative picture of the equations uncertainty for a given field application. For a given field composition and operating conditions, a certain density deviation could be regarded as a systematic bias that may persist over the lifetime of the field, rather than an uncertainty. According to GUM [15] every effort should be made to identify and quantify systematic biases, and they should be corrected for if significant in size.

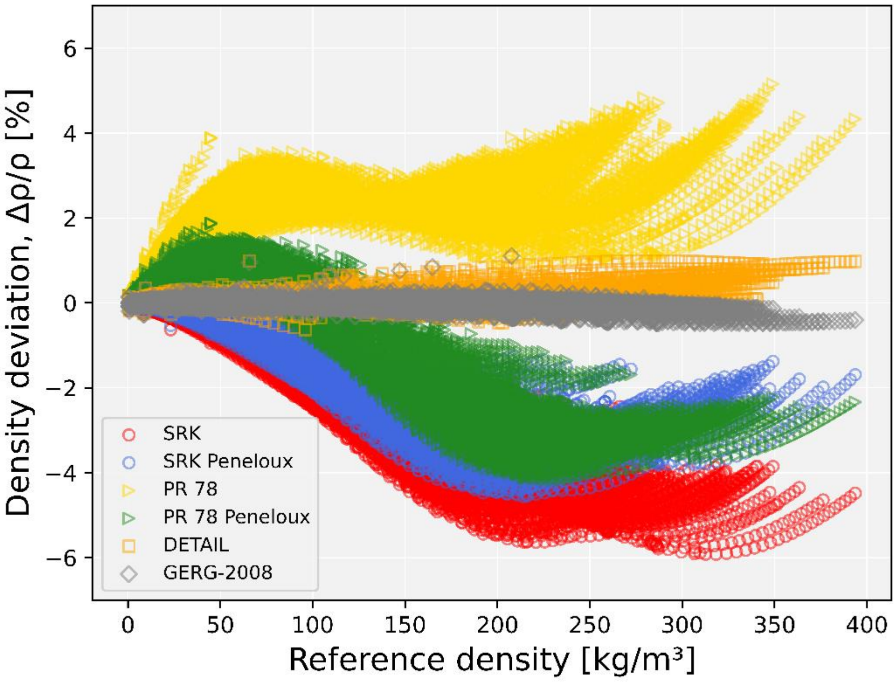


Fig. 2 – Density Deviation Between EOS Calculated Density and Measured Density From the GERG-2004 Database vs Reference Density for Different EOS

The density deviation between the various equations become quite significant for gas compositions exceeding the limits of pipeline quality range. Gas ID 1024 in the GERG-2004 database provides a good example of this, with a relatively large content of ethane, propane, and butane. Such gases seem to be problematic for both the cubic equations, as well as for DETAIL. GERG-2008 should therefore be considered in these cases. The gas composition for gas ID 1024 is presented in Table 6, while the density deviation for this gas is shown in Fig. 3 for the various equations of state.

Table 6 – Composition for Gas ID: 1024

Component	Mole %
N2	5.0006
CO2	5.9924
C1	59.0013
C2	9.9969
C3	14.0265*
nC4	5.9822

*The maximum propane content given for intermediate quality is 14 mole %

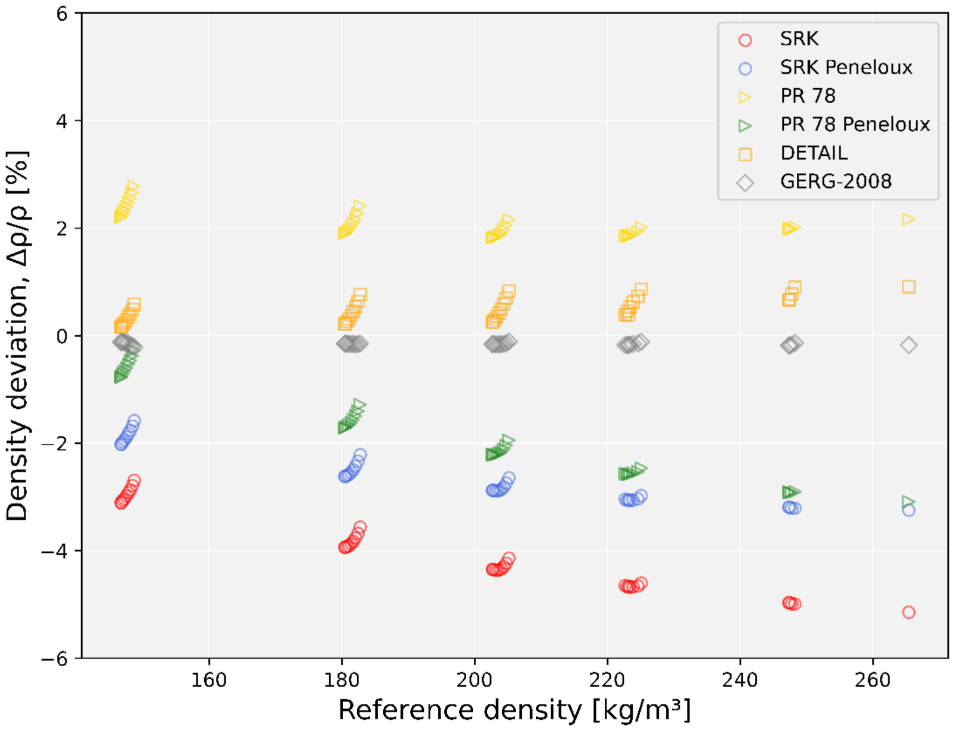


Fig. 3 – Example of Density Deviation Between EOS Calculated Density and Measured Density From the GERG-2004 Database for Gas ID 1024 in the GERG-2004 Database

To further investigate the difference in performance between GERG-2008 and DETAIL, 18 natural gases from the database with propane content exceeding 8 mole % (up to 14 mole %) were evaluated (gas ID in GERG-2004 database: 2111, 356, 359, 1024, 1025, 1026, 1027, 1028, 1029, 1030, 1031, 1041, 1042, 1043, 1044, 1045, 1046, 1047). The results are presented in Fig. 4, and show that GERG-2008 outperforms DETAIL for most of these cases, with some exceptions. This can be observed in Fig. 5 where the same comparison between DETAIL and GERG-2008 density deviation is presented as an x-y plot. The points where DETAIL is performing slightly better, seems to be most frequent at pressures exceeding 150 bar, with the most extreme case corresponding to a density deviation of -0.4% for GERG-2008 and 0.25% for DETAIL.

When considering these gases, GERG-2008 tends to slightly underestimate gas density, whereas DETAIL tends to overestimate for the same data points, resulting in an even larger density difference between the two equations. It has previously been shown that the difference between DETAIL and GERG-2008 become even larger when moving outside the intermediate quality range [12]. However, since the database does not cover compositions outside the intermediate quality range, it is not possible to conclude on the real performance of the AGA8 equations for such gases, based on these data. But the tendency from the DETAIL equation is that the performance deteriorates when moving outside the pipeline quality natural gas and could also potentially be the case when the mole fraction moves outside the intermediate quality range as well.

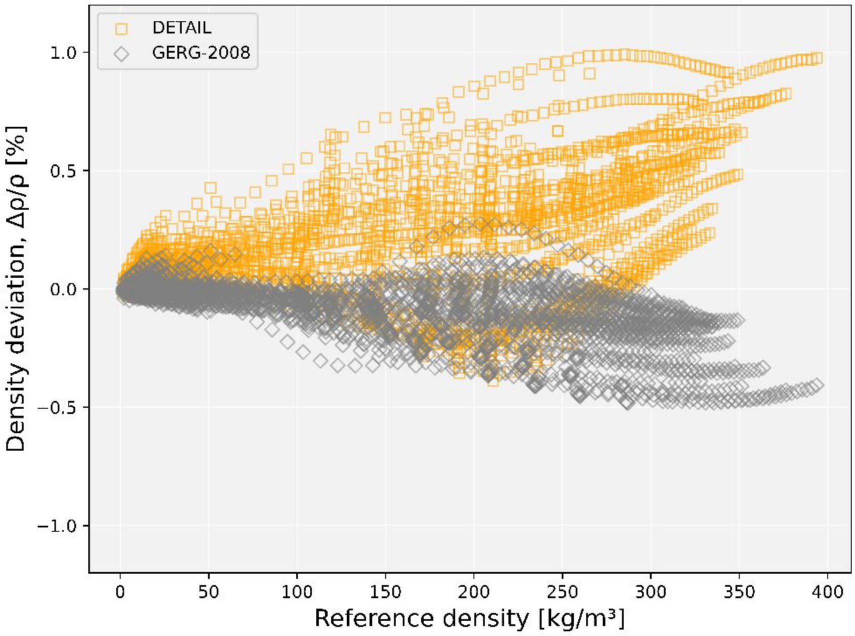


Fig. 4 – Density Deviation Between EOS Calculated Density and Measured Density From the GERG-2004 Database for Gases with High Content of C2, C3 and C4, using DETAIL and GERG-2008

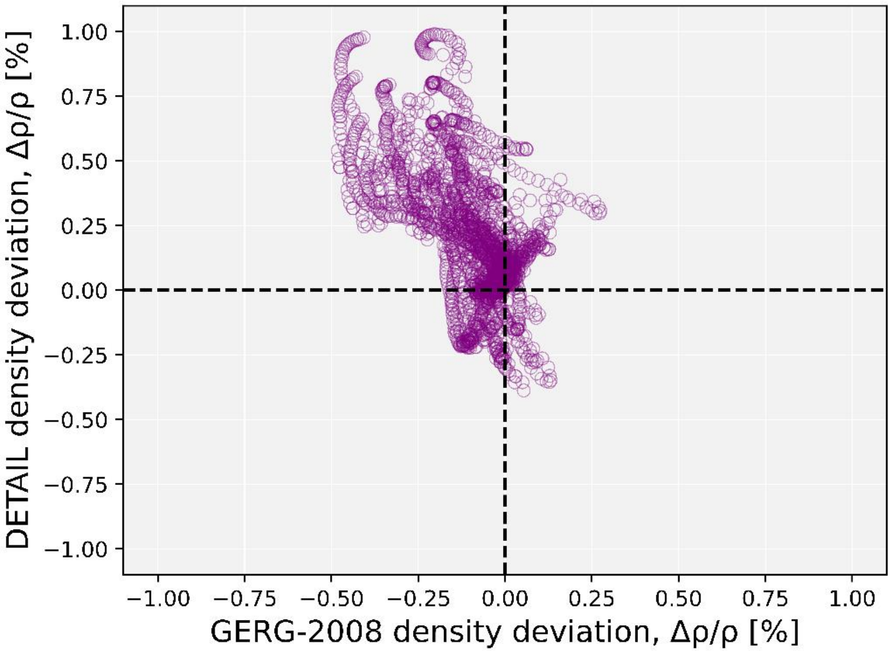


Fig. 5 - Density Deviation Between EOS Calculated Density and Measured Density From the GERG-2004 Database for Gases with High Content of C2, C3 and C4. Comparison Between GERG-2008 and DETAIL.

6 FIELD CASE A: FISCAL METERING STATION WITH HIGH PROPANE CONTENT

In field case A, a fiscal gas metering station in the North Sea was chosen as an example to illustrate the issue of high propane content in the gas phase. The gas composition is measured by online gas chromatographs with composition up to C6+, where the C6+ fraction is assigned to nC6 in the calculations. Due to small amounts of C6+, the effect on gas density due to nC6 assignment will be small. In this metering station, the DETAIL equation is used for calculating gas properties, even though the composition is way outside the maximum limits for pipeline quality natural gas, both for ethane, propane, and butane. Most of the components lies within the limits for intermediate quality natural gas, except for propane, which slightly exceeds the limit for periods of time. According to AGA8, GERG-2008 would therefore yield a more accurate calculated density for this metering station. However, it should be noted that the metering station was designed prior to the release of the 2017 AGA8 reports.

6.1 Method

2.5 years of production data was analysed, and 3 cases were selected, covering the variations in gas composition and operating conditions during this period. The compositions for the 3 cases are given in Table 7. The difference in gas density between GERG-2008 and DETAIL was calculated for each case, both for the actual operating conditions as well as a series of pressures and temperatures, to evaluate how changes in conditions would affect the density difference. The NIST AGA8 codes [14], for both DETAIL and GERG-2008, were used for calculating densities, while PVTsim Nova 6 GERG-2008 was used to verify no liquid dropout. To avoid liquid dropout, the minimum temperature was kept above 31 °C while calculating series for different pressures and temperatures.

- Case 1 - Large difference in calculated density
- Case 2 - Medium difference in calculated density
- Case 3 - Small difference in calculated density

Table 7 – Gas Compositions, Pressure and Temperature For Different Cases Given by Field Case A

	Case 1	Case 2	Case 3
Component	Mole %	Mole %	Mole %
N2	2.03	2.06	2.07
CO2	0.33	0.35	0.34
C1	62.21	63.03	63.40
C2	16.32	16.13	15.97
C3	14.89*	14.03*	13.69
iC4	1.62	1.60	1.59
nC4	2.20	2.29	2.35
iC5	0.21	0.25	0.28
nC5	0.16	0.20	0.23
nC6	0.03	0.06	0.07
Operating conditions			
Pressure [bara]	120.6	120.5	125.9
Temperature [C]	33.9	36.4	46.3

*Case 1 and 2 is just outside the upper C3 limit of 14 mole % for intermediate quality natural gas, but way outside the limit of 3.5 mole % for pipeline quality natural gas

6.2 Results

The density difference between GERG-2008 and DETAIL are presented in Fig. 6. The coloured lines in the plot represent the density difference for a given temperature, with changing pressure. The operational point is also included in the plot for each case. The average difference in density was -0.4% for the 2.5 years of production, meaning that GERG-2008 estimates a lower density than DETAIL.
Chapter 5.2 demonstrates that GERG-2008 in general has a lower density deviation than DETAIL for gases with high propane content. Based on that, the uncertainty in gas density would likely be reduced by replacing DETAIL with GERG-2008 for this metering station.
The gas composition changes slightly between the three cases, with an increase in density deviation as propane and ethane content increases. This can be observed as a shift in the curves between the cases. The largest density deviations are observed close to the dew point line, that occurs as temperature approaches 31 °C, and pressures in the range of 80-100 bar.
If operating conditions and/or fluid compositions changes during the lifetime of the field, it may cause even greater density difference between the equations. During abnormal operating conditions, density differences of up to 1% was observed.
Even though replacement of the equation in use may be constrained by contractual aspects and/or cost, the comparison between the AGA8 equations could easily be implemented to monitor changes in difference between the equations over time.

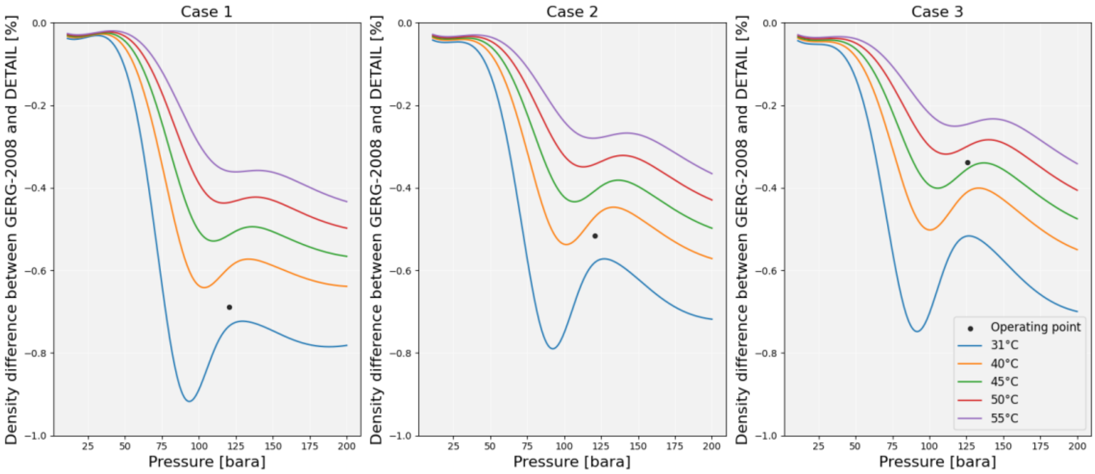


Fig. 6 – Density difference between GERG-2008 and DETAIL for the 3 cases

7 FIELD CASE B: K-LAB RICH GAS WITH HIGH C6+

Equinor K-lab is a full-scale multiphase test facility, located at Kårstø gas processing plant on the western coast of Norway. In multiphase testing with hydrocarbons at real conditions, the gas phase can become quite enriched with heavier components, and molar compositions exceeding the intermediate quality range is quite common. A gas sample from a test in the VGII multiphase flow loop at K-lab has been selected as a rich gas example. This sample demonstrates the challenges arising from compositions exceeding the AGA8 quality ranges and where naphtenes and aromatics dominates the C6+ fraction, creating difficulties with respect to component assignment.

In the VGII flow loop at K-lab, hydrocarbon gas and liquid are separated in a scrubber. The gas goes through a suction filter before it enters a two-impeller centrifugal compressor, where the sampling quill is located at the compressor discharge. The sample was sent to an accredited lab for a C10+ PNA analysis, where 92 components are measured.

7.1 Method

In this study, three methods have been chosen to evaluate the effect of component assignment to the AGA8 component list. Method 1 constitutes the assignment of C6+ to nC6, as this is a commonly used method in fiscal metering. Method 2 assumes that a full gas analysis is available and that the components are assigned based on boiling point, representing the procedure often used in laboratory sample analysis.

Method 3, also requiring a full gas analysis, is the recommended approach for calculating single-phase properties from the AGA8 2017 reports, which seems less commonly used than method 1 and 2. The three methods are presented in Table 8.

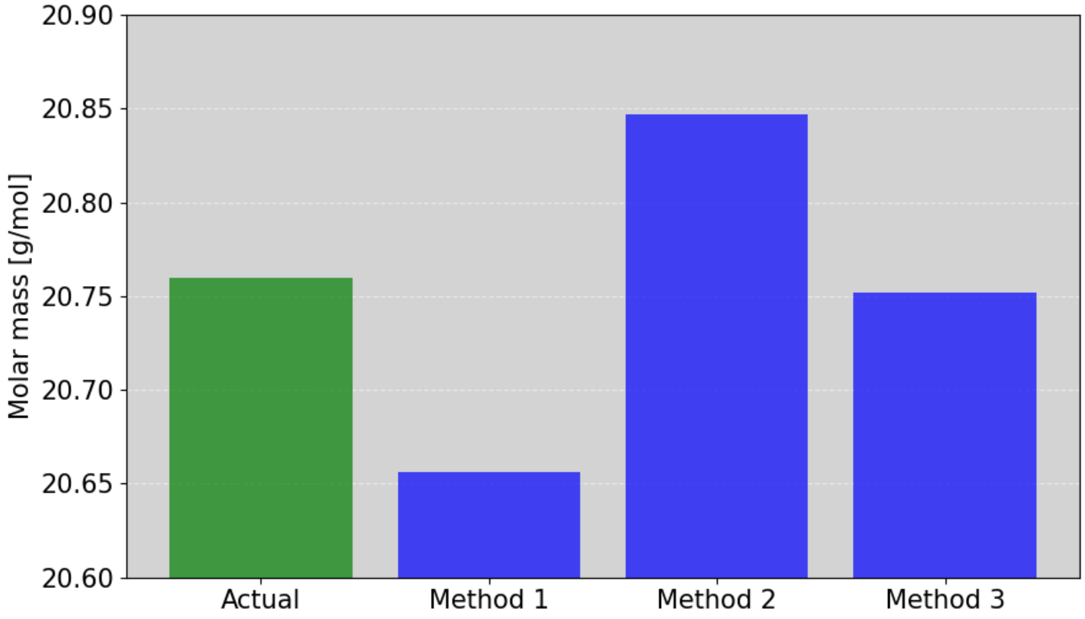
Table 8 – Methods for Assigning Components from GC Analysis to AGA8 Component List

	Description
Method 1	Assigning C6+ to nC6
Method 2	Assignment based on component normal boiling point
Method 3	AGA8 assignment for calculation of single-phase thermodynamic properties

The 92 components were assigned to the AGA8 component list according to the three methods. The single-phase properties were calculated using GERG-2008.
The total molar mass from each method were compared against the actual molar mass from the full gas analysis.
With regards to compressibility factor (Z) and density, the true values are unknown. However, according to AGA8, method 3 should provide the best estimate for calculated density and compressibility, Z. Therefore, the calculated density and compressibility from method 1 and 2 have been compared to the corresponding properties from method 3.

7.2 Results

According to the Norwegian measurement regulations [16], the molar mass from a gas analysis shall be determined with an uncertainty of less than 0.2%. In Fig. 7 the molar mass from each assignment method is compared against the actual molar mass from the K-lab rich gas sample analysis, demonstrating differences well above this requirement.
As expected, Method 1 underestimates the molar mass, as the entire C6+ fraction is assigned to nC6, which is much lighter. Method 2, on the other hand, overestimates the molar mass by almost the same amount. The reason for this is because the heavy fraction of the gas is dominated by naphtenes and aromatics. These molecules have a relatively low molar mass compared to the n-alkane assigned to by boiling point, resulting in a higher total molar mass after assignment. The total difference in molar mass between method 1 and 2 is 0.92%. Not surprisingly, the AGA8 recommended approach (method 3), yields the best result, with a deviation in molar mass of -0.04%.



	Actual	Method 1	Method 2	Method 3
Molar mass	20.760	20.656	20.847	20.752
Deviation [%]		-0.50	0.42	-0.04

Fig. 7 – Comparing molar mass from various assignment methods to actual molar mass from the full compositional analysis. Note that difference in molar mass between method 1 and 2 is 0.92%

In Table 9, the gas composition of the K-lab rich gas is presented, together with the calculated properties at the sample point operating conditions of 118.5 bara and 78.9 °C. The results indicate that method 1 yields the lowest density, whereas method 2 produces the highest density, similar as in the molar mass comparison. In addition, the impact of component assignment on the Z-factor is less than the impact on the molar mass.

Since the effect on molar mass and Z-factor goes in opposite directions, the effect on gas density is amplified, resulting in a 1.3% density difference between method 1 and 2, which are two widely used methods.

When compared to method 3, which can be assumed to be the most accurate method, method 1 underestimates the density by -0.6%, while method 2 overestimates the density by 0.6%.

However, it should be noted that the given composition exceeds the composition limits for both pipeline quality and intermediate quality natural gas, so it’s not possible to know the real uncertainty of the Z-factor estimate.

Currently, no good alternatives to the AGA8 equations exists for such gases, and the GERG database do not contain any relevant gases that can be used for comparison. The K-lab example gas contains 1.2 mole % C6+, while the maximum C6+ content for gases in the GERG-2004 database is 0.2 mole %, limited to n-alkanes.

For a metering station where C6+ is assigned to nC6 and flowrate is measured on a volume basis, the mass flow rate will be underestimated. By distributing the C6+ fraction between the heavier AGA8 components, a better density estimate could be achieved. However, if this is performed by a laboratory analysis like in method 2, the mass flow rate could then be equally overestimated. It is therefore important to be aware of this when distributing the C6+ fraction.

It should also be noted that if a volume flowrate is converted from actual meter conditions to standard conditions, the molar mass term will disappear, reducing the error in standard volume flowrate to the error in Z-factor, as shown by equation 6. When combining uncertainties from sampling and compositional analysis with the uncertainties and systematic biases originating from the equations of state, the total uncertainty for rich gas applications can easily exceed requirements stipulated by government metering regulations. To cope with these challenges, K-lab have implemented measured gas density as a reference, in combination with calculated density and additional verification against measured speed of sound from ultrasonic flowmeters.

Table 9 – Field Case Example: K-lab Rich Gas

Component	**Method 1**	**Method 2**	**Method 3**
	Mole %	Mole %	Mole %
N2	1.36	1.36	1.36
CO2	1.71	1.71	1.71
C1	83.22	83.22	83.22
C2	5.86	5.86	5.86
C3	4.45	4.45	4.45
iC4	0.39	0.39	0.39
nC4	0.87	0.87	0.87
iC5	0.42	0.42	0.42
nC5	0.61	0.49	0.61
nC6	1.12	0.43	0.65
nC7		0.43	0.30
nC8		0.26	0.10
nC9		0.07	0.03
nC10		0.04	0.04
Calculated properties using GERG-2008			
Molar mass [kg/kmol]	20.66	20.85	20.75
Density [kg/m^3]	97.66	98.90	98.28
Z-factor [-]	0.8567	0.8537	0.8552
Difference in properties compared to method 3 [%]			
Molar mass	-0.46	0.46	
Density	-0.63	0.64	
Z-factor	0.17	-0.17	

To utilize method 3, a complete gas analysis is required, without lumping of components into pseudo-components. In rich gas analysis, the full composition is often unavailable in the analysis report, while the total molar mass is usually given. The same will apply in applications where the gas phase originates from a flash calculation, such as PVT input models to multiphase meters, where molar mass of the gas phase is an output from the flash.

The error in molar mass introduced by converting such compositions to the AGA8 format could be eliminated by calculated density using actual molar mass, instead of using the AGA8 molar mass.

Table 10 presents the calculated gas densities by using the actual molar mass from the analysis in combination with the Z-factor from GERG-2008 for each method.

It can be observed that the difference in calculated density equals the difference in Z-factor from Table 9, but with opposite sign. These data indicate that density should always be calculated based on the best available estimate of molar mass in combination with the Z-factor obtained from an equation of state, as this will eliminate the errors in molar mass due to assignment of trace components to the AGA8 component list.

Still, many fiscal flow computers utilize the molar mass from AGA8 instead of the actual molar mass from the GC analysis.

Note that the true value of Z-factor is unknown for such gases, and efforts should be made to investigate the effect of component assignment on Z-factor.

Table 10 – Calculated Density by Using Actual Molar Mass

	Method 1	**Method 2**	**Method 3**	**Unit**
Density	98.15	98.49	98.32	kg/m^3
Dev from method 3	-0.17	0.17		%

8 CONCLUSIONS

- Based on evaluation of calculated density against measured densities from the GERG-2004 database, it is shown that the performance in calculated gas densities by the AGA8 equations (DETAIL and GERG-2008) are superior to the performance of the cubic equations (SRK and PR 78) in the AGA8 pipeline- and intermediate quality range. Metering applications using cubic equations, such as multiphase meter PVT models, should evaluate adopting GERG-2008 for calculating gas properties.
- For most cases, GERG-2008 appears to provide a better estimate of the gas density than DETAIL, especially for gases outside the pipeline- quality range. The AGA8 part 1 recommendation to upgrade from DETAIL to GERG-2008 is thus supported by the findings in this paper. If switching equation, for some reason, is not feasible, the difference in calculated density between DETAIL and GERG-2008 should be evaluated for the given application. It is also important to be aware that the difference may change over time, with changing pressure, temperature and/or composition.
- Component assignment can have a significant impact on calculated gas density using AGA8, especially for gases where the heavy fraction is dominated by naphtenes and aromatics. In such applications, a full compositional analysis is critical, and component assignment should be performed according to the AGA8 recommendation for calculating single-phase properties.
- If laboratory GC-analysis is used in metering applications, it is important to be aware that assignment according to normal boiling point is commonly used and will cause errors if used directly as input to the AGA8 equations for calculating single-phase properties.
- For rich gas applications, the combined uncertainty from compositional analysis, component assignment and from using equations outside their applicable ranges, may easily exceed requirements stipulated by government regulations. In such applications, additional methods of estimating gas density should be considered, such as direct measurement.
- It appears that component assignment methodology has a bigger impact on molar mass than on Z-factor. Hence, a more accurate density estimate can be achieved by using the best available molar mass, rather than the molar mass calculated by AGA8.

9 FURTHER WORK

- For natural gases with components that are not present in the AGA8 component list and/or mole fractions exceeding the intermediate quality range, the performance of the AGA8 equations is unknown. Efforts should be made to verify the equations uncertainty for such gases.
- Compositional uncertainties on rich gas analysis can be difficult to establish and can have a great effect on calculated molar mass and density. The uncertainty in rich gas density originating from compositional uncertainties should therefore be further investigated.
- Calculation of gas calorific value is described by ISO 6976:2016. Density and molar mass are used as input in the calculations, and their contribution to the uncertainty in calorific value should therefore be studied in more detail. The effect of component assignment should also be considered.

10 NOTATION

ρ	Mass density
d	Molar density
M	Molar mass
M_i	Molar mass of component *i*
n	Number of moles
P	Pressure
q_v	Volume flowrate
q_m	Mass flowrate
R	Universal gas constant
T	Temperature
V	Volume
Z	Compressibility factor
x_i	Mole fraction of component *i*

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12 REFERENCES

1. Bochum, R.-U., *Description of the GERG-2004 Database of Thermodynamic Properties of Mixtures Used for the Development and Evaluation of the GERG-2004 Wide-Range Reference Equation of State for Natural Gases*. 2005
2. Soave, G., *Equilibrium constants from a modified Redlich-Kwong equation of state.* Chemical engineering science, 1972
3. Pedersen, K.S., P.L. Christensen, and J.A. Shaikh, *Phase Behavior of Petroleum Reservoir Fluids (2nd Edition)*. 2015, Taylor & Francis
4. Peng, D.-Y. and D.B. Robinson, *A new two-constant equation of state.* Industrial & Engineering Chemistry Fundamentals, 1976
5. Péneloux, A., E. Rauzy, and R. Fréze, *A consistent correction for Redlich-Kwong-Soave volumes.* Fluid phase equilibria, 1982
6. Jhaveri, B.S. and G.K. Youngren, *Three-Parameter Modification of the Peng-Robinson Equation of State To Improve Volumetric Predictions.* SPE Reservoir Engineering, 1988
7. ISO, *ISO 12213-2: Natural gas - Calculation of compression factor - Part 2: Calculation using molar-composition analysis*. 2009
8. AGA, *AGA Report No. 8 Part 1 Second Edition*, in *Compressibility Factors of Natural Gas and Other Related Hydrocarbon Gases*. 1992
9. AGA, *AGA Report No. 8 Part 1 Third Edition*, in *Thermodynamic Properties of Natural Gas and Related Gases - DETAIL and GROSS Equations of State*. 2017
10. AGA, *AGA Report No. 8 Part 2 First Edition*, in *Thermodynamic Properties of Natural Gas and Related Gases - Gerg-2008 Equation of State*. 2017
11. Kunz, O. and W. Wagner, *The GERG-2008 wide-range equation of state for natural gases and other mixtures: an expansion of GERG-2004.* Journal of chemical & engineering data, 2012
12. Glen, N., et al. *Errors Due to Use of the AGA8 Equation of State Outside of Its Range of Validity*. in *North Sea Flow Measurement Workshop*. 2016.
13. Katz, D. and A. Firoozabadi, *Predicting phase behavior of condensate/crude-oil systems using methane interaction coefficients.* Journal of Petroleum Technology, 1978
14. Ovesen, R.V. *NIST AGA8 Rust implementation*. [Github repository] 2022; URL: https://github.com/royvegard/aga8/releases/tag/v0.1.2. Commit: cd7b48b
15. Metrology, J.C.f.G.i., *Evaluation of measurement data—Guide to the expression of uncertainty in measurement.* JCGM, 2008
16. *Forskrift om fiskal måling i petroleumsvirksomheten (måleforskriften)*. 2023; URL: https://lovdata.no/LTI/forskrift/2023-04-21-532. Kapittel 4, § 10