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Exploring the Relationship between Speed of Sound, Density, and Isentropic Exponent

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ABSTRACT

Mass density is a key property in gas metering applications. When establishing uncertainty in calculated mass density, standards developed for lean natural gases are often used, even for gases not covered by these standards, such as rich natural gases. Consequently, significant errors in calculated mass density may exist without being properly reflected in the uncertainty budget. These errors are often associated with uncertainties in the molar mass of the gas. By utilizing measured speed of sound from ultrasonic flow meters and its relation to the mass density and the isentropic exponent, the uncertainty contribution from molar mass can be significantly reduced, resulting in a more accurate determination of mass density. This relationship is also shown useful in multiple other gas metering applications.

1 INTRODUCTION

In fiscal rich gas metering stations in the North Sea, allocation is often performed on a mass basis per component, while ultrasonic flow meters are commonly used to measure the volumetric flow rate of the gas. The total uncertainty in the mass flow used for allocation will therefore be a direct function of the uncertainty in mass density. While the mass density of a gas can be measured directly, a more frequently used approach is to calculate it based on pressure, temperature and composition using equations published in the AGA report number 8 [1, 2]. Limitations in these equations can, for certain applications, produce uncertainties in calculated properties exceeding requirements stipulated by standards and/or governmental regulations [3]. Besides the accuracy of the models, a potential even greater contributor to uncertainty is the input variables to the models. While pressure and temperature are normally measured with high accuracy, measuring gas composition by means of gas chromatography (GC) can be challenging in certain applications. For rich natural gases, the uncertainty in mass density will often be dominated by the heavier components, mainly affecting uncertainty in molar mass. The speed of sound in a gas is directly influenced by the molar mass, suggesting that for rich natural gases, the uncertainty in molar mass, and thereby mass density, can be effectively reduced by combining the measured speed of sound from ultrasonic flow meters with the calculated isentropic exponent.

In the novel measurement applications of CO_2 and H_2, this method may also be deployed with satisfactory accuracy, since the composition range in these applications is limited. For CO_2 applications care needs to be taken since the speed of sound becomes frequency dependent.

2 FUNDAMENTALS

The DETAIL equation of state is published in the AGA report no 8. Part 1 [1], and is commonly used in fiscal flow computers for calculating gas properties, while the GERG-2008 equation, published in the AGA8 report no. 8 part 2 [2] is an improved equation and considered the more accurate of the two. In both equations, hereby referred to as the AGA8 equations, thermodynamic properties of the gas are derived from the Helmholtz Free energy, typically using pressure, temperature, and composition as input. These properties include but are not limited to compressibility factor, molar density, speed of sound and isentropic exponent.

However, in fiscal flow measurement, the mass density is usually the property of interest, and is used for converting between mass and volume, or as direct input to metering equations. The mass density can be calculated by the real gas equation, utilizing the compressibility factor, Z, and the molar mass, M, obtained from the AGA8 equation in use, which is a popular method in fiscal flow computers.

$$\rho = M\frac{P}{ZRT} \tag{1}$$

The total molar mass of the gas is calculated as a weighted average based on the individual component's molar mass and mole fraction.

$$M = \sum_{i=1}^{N} x_i M_i \tag{2}$$

The speed of sound of the gas, w [m/s], is also an output from the AGA8 equations and is expressed in terms of the partial derivative of pressure (P) with respect to molar density (d), at constant entropy (s) and composition (x). Note that the speed of sound is a direct function of the molar mass (M).

$$w = \sqrt{\frac{\left(\frac{\partial P}{\partial d}\right)_{s,x}}{M}} \tag{3}$$

The relationship between the dimensionless isentropic exponent, kappa (κ), and the speed of sound, is given by the following equation, also from AGA report no 8 part 2. Although it may appear so from the equation, the isentropic exponent is not a direct function of the molar mass, as it is already encompassed in the speed of sound calculation.

$$\kappa = \frac{w^2 M}{ZRT} \tag{4}$$

By combining the real gas equation (1) with the equation for isentropic exponent (4), the mass density can be calculated based on pressure, isentropic exponent and speed of sound.

$$\rho = \frac{\kappa P}{w^2} \tag{5}$$

Equation 5 is just another way of expressing the mass density from properties obtained by the AGA8 equations and will produce identical results as the real gas equation (1) when utilized for these equations of state.

3 COMPOSITIONAL UNCERTAINTIES INFLUENCE ON GAS PROPERTIES

Exceeding limitations given by the AGA8 equations may increase the uncertainty in calculated gas properties, and potentially produce significant systematic errors [3, 4]. A potential even greater contributor to uncertainty in calculated properties, is uncertainties in the input variables to the equation, namely pressure, temperature, and gas composition. While pressure and temperature can be measured with relatively high accuracy, the measurement of gas composition by a gas chromatograph (GC) is associated with much more complexity, especially when dealing with richer natural gases. Several international standards are available describing methods used to measure gas composition by GC analysis. ASTM D1945 [5] and ISO 6974-3 [6] are two standards that are frequently referred to by uncertainty budgets from laboratories and fiscal metering stations utilizing compositional analysis. Common for both standards is that they are primarily developed for lean gases, and therefore do not address the issue of uncertainty in heavier hydrocarbon components. In ASTM D1945, it is stated that the precision of the method is determined for pipeline quality natural gas (38 MJ/m^3), which is normally referred to export quality gases with limited amounts of heavier components.
These two standards also provide values of repeatability and reproducibility, that are often utilized in uncertainty budgets. However, in ASTM D1945, the confidence level of these parameters is not stated. Neither is it clarified whether these numbers are given as relative numbers or in mole-%. Consequently, various interpretations of these estimates are found in different uncertainty budgets. Similar ambiguities exist in ISO 6974-3 but are slightly easier to interpret by the support from equations, examples, and data attached.

Measuring heavier components increases the complexity of both the gas chromatograph design and the composition of the calibration gas. It may be difficult to produce and handle a calibration gas covering all the components present in a rich gas, and simpler calibration gases are often used. A compositional analysis of a rich natural gas can consist of more than 100 components, where most of these components are typically absent in the calibration gas. For these components, various methods are utilized to establish the response factor. According to ISO 6975-1, main components up to C3 shall be analysed using multiple calibration points, while for C4 and C5, single-point calibration may be used, but not required. For nC6 and upwards, referred to as trace components, calibration is not required, and response factors based on relation to one of the main components (relative response factors) in the gas can be used.

It is therefore reasonable to assume that the relative uncertainty in the mole percentage of heavier components is significantly higher than for the lighter components. Failing to address the issue of increased uncertainty for the heavier components will lead to underestimation of uncertainty in calculated properties, such as mass density. This will for instance occur in metering stations measuring composition up to C6+ and where uncertainty estimates based on reproducibilities from ASTM D1945 are utilized for the C6+ components.

In addition to the uncertainty in the mole percentage of the C6+ components, there also exist a significant uncertainty in the C6+ molar mass, due to the issue of component grouping and assignment [3]. This effect is generally not considered in uncertainty budgets due to the limitation of 21 fixed components in the AGA8 equations. This can for example be observed in the NFOGM Fiscal Gas Metering Station Uncertainty application [7], where component molar mass is not an available input. This will also cause underestimation of uncertainty in mass density.

Given these points, compositional uncertainties could potentially constitute the main contributor to the total uncertainty for certain metering applications, while the uncertainty budgets may not reflect this.

4 UNCERTAINTY ANALYSIS FOR CALCULATED GAS PROPERTIES

To investigate how uncertainties in pressure, temperature and composition influences the uncertainties in calculated properties, an uncertainty analysis was conducted for 471 gas compositions retrieved from K-lab Technology test centre's sample database. The database covers compositions ranging from export-quality lean gas to rich gases exceeding 1 mol% of C6+. The objective of the uncertainty analysis was to evaluate the uncertainty in calculated properties as a function of the input variables, and therefore does not consider the accuracy of the equation of state itself.

4.1 Method

In the uncertainty analysis GERG-2008 was used to calculate gas properties. For each gas composition the combined standard uncertainty was calculated using the standard uncertainty (s_i) of each input variable together with the sensitivity coefficient (c_i), as described by equation 11a in the Guide to the Expression of Uncertainty in Measurement (GUM) [8]. The sensitivity coefficients were established numerically, by calculating the change in each output property due to a small step in each input variable. In addition, Monte Carlo simulation was used to validate the uncertainty calculations, providing close to identical results.

To ensure single-phase gas in all cases and to avoid the supercritical region, the analysis was performed at a pressure of 50 bara and a temperature of 90 °C for all the gases. Fixed values of 0.05 bara and 0.09 °C was used as uncertainty input for pressure and temperature (k=1). The input uncertainties used for gas composition was based on a comparison test of 107 pairs of gas samples sent to two different accredited laboratories. The compositional uncertainty estimate is further described in APPENDIX A, where the compositional uncertainties are expressed as a function of the mole percentage, returning the estimated standard uncertainty. A summary of the input data used in the uncertainty analysis is presented in Table 1.

Since the AGA8 equations are limited to the normal alkanes in the C6+ fraction, it is not possible to consider the uncertainty in molar mass of the C6+ components, which will consequently underestimate uncertainty in calculated properties.

Table 1 – Input uncertainties used in the uncertainty analysis

Input	Value	Standard uncertainty (k=1)	Unit
Pressure	50	0.05	bara
Temperature	90	0.09	°C
Composition	Given for each gas	See Table 2, APPENDIX A	mol%

The output from the uncertainty analysis is the estimated uncertainties for all properties calculated by the GERG-2008 equation for each of the 471 gases, due to uncertainties in input variables.

4.2 Results: Mass density, molar mass and compressibility factor

The relative uncertainties (95 % confidence) in mass density, molar mass and compressibility factor are plotted for each gas against the molar mass in Fig. 1. For the lean gases constituting the lowest molar mass, uncertainties are relatively low for all the properties. However, the uncertainties in molar mass and mass density increases significantly when moving towards richer gases with a higher molar mass. This is because the rich gases contain small amounts of components where the individual component's molar mass is much greater than the average molar mass of the gas. As these components are also associated with a higher relative uncertainty in measured mole fraction, they will have a large impact on the uncertainty in the total molar mass and thereby mass density.

NORSOK I-106:2014 [9] specifies that when calculating density using gas composition, the uncertainty in molar mass (U_M) should be less than 0.20% of the molar mass (M). The same number is found in the Norwegian metering regulations [10] as an uncertainty requirement for both the molar mass of gas samples as well as for molar mass from online chromatographs during verification and calibration. Based on the results presented in Fig. 1, the uncertainty requirements for molar mass seems reasonable for lean gases, but could be difficult, if not impossible, to achieve in certain rich gas applications.

The compressibility factor (Z) on the other hand, appears to be much less affected by uncertainties in the heavier components. When considering the calculation of the Z factor by the AGA8 equations, it is derived from molar based properties, and are therefore not directly influenced by the molar mass.
In summary, the analysis shows that uncertainty in mass density for rich gases is mainly dominated by the uncertainty in molar mass, originating from compositional uncertainties of the heavier components.

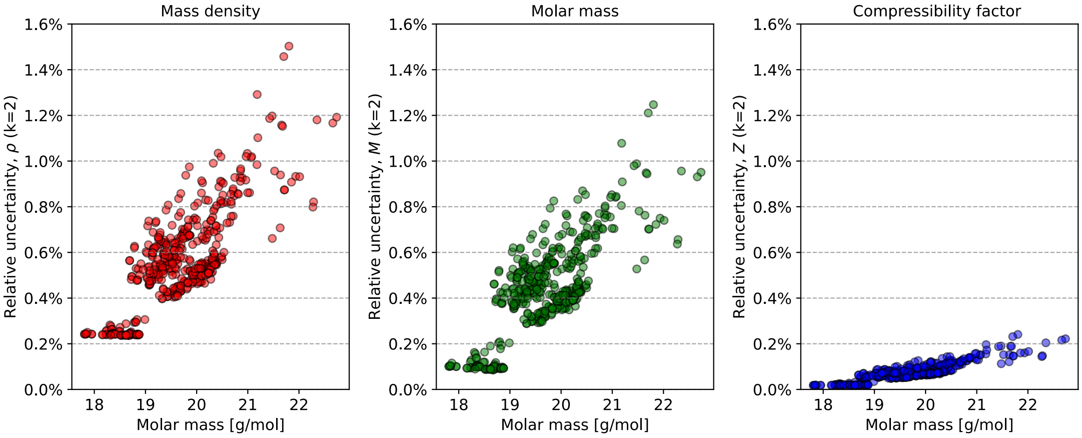

Fig. 1 – Relative expanded uncertainty (95 % confidence level) in mass density, molar mass and compressibility factor for different gas compositions

To illustrate the influence of the heavier components for different gases, the contributions from the different input variables to the uncertainty in mass density were evaluated for a lean gas and a rich gas. The uncertainty contribution for each input variable is given by the following expression:

$$\frac{(c_i u_i)^2}{\sum_{i=1}^{N}(c_i u_i)^2} \tag{6}$$

Where c_i and u_i represent, respectively, the sensitivity coefficient and standard uncertainty for each input variable as defined by GUM [8]. A characteristic of this method is that the sum of the uncertainty contributions equals 100%.

The contributions from each input variable to the total uncertainty in mass density is presented in Fig. 2 for the lean gas and shows that the uncertainty in pressure dominates the total uncertainty in mass density. For the rich gas, presented in Fig. 3, the uncertainty in mass density is dominated by uncertainty in mole fraction of the heavier molecules (C6+), which has a large impact on the uncertainty in molar mass and thereby also the mass density. The components (N2-nC10) represent composition input on a molar basis.

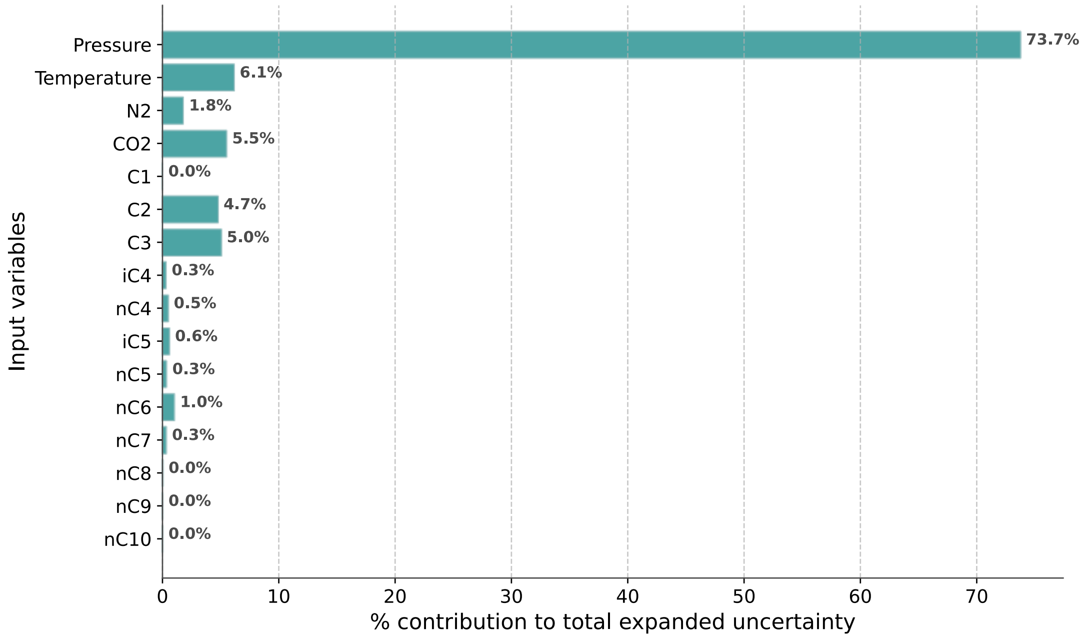

Fig. 2 – Percentage contribution of each input variable to the Relative Expanded Uncertainty in mass density for a lean gas

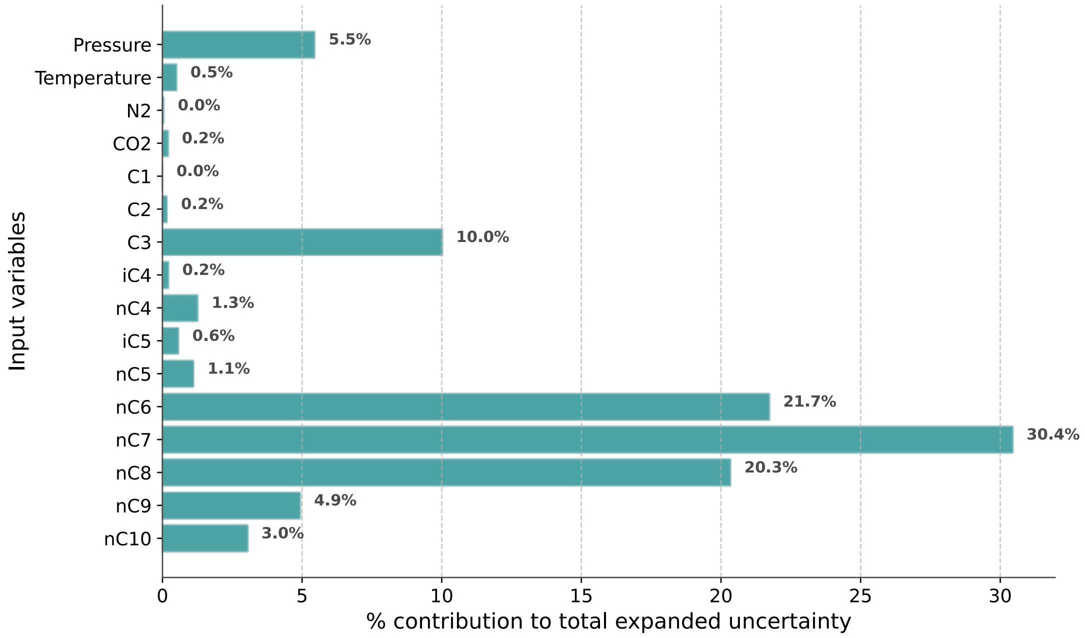

Fig. 3 - Percentage contribution of each input variable to the Relative Expanded Uncertainty in mass density for a rich gas

4.3 Results: Speed of sound and isentropic exponent

Equation 5 demonstrates that the mass density could alternatively be calculated from pressure, speed of sound and the isentropic exponent, rather than from the compressibility factor and molar mass. The uncertainties in speed of sound and isentropic exponent are also outputs from the same uncertainty analysis shown in Fig. 1. Fig. 4 shows the relative uncertainties (95 % confidence) in mass density, speed of sound and isentropic exponent from the analysis. The uncertainty in mass density is the same as displayed in Fig. 1, but has been included for comparison. Similar as for the compressibility factor, Z, the uncertainty in isentropic exponent (κ) seems to be much less sensitive to uncertainties in the heavy components. The uncertainty in speed of sound on the other hand, is much more affected. Equation 3 shows that the speed of sound is a direct function of the molar mass, which appears to explain the strong correlation between uncertainty in speed of sound and uncertainty in molar mass.

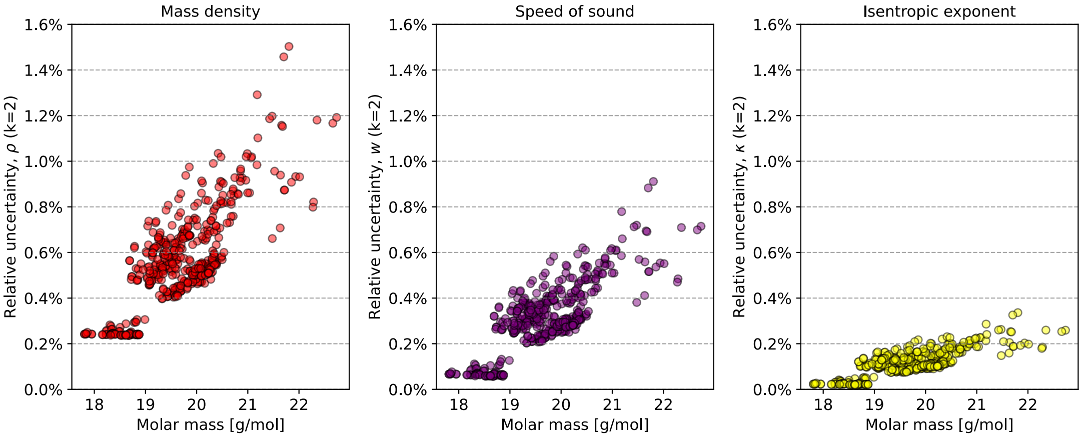

Fig. 4 - Relative expanded uncertainty (95 % confidence level) in mass density, speed of sound and isentropic exponent for different gas compositions

It is important to notice that properties calculated by the AGA8 equations are strongly correlated (e.g. the isentropic exponent is strongly correlated with speed of sound etc.). Therefore, if one utilizes output properties from DETAIL or GERG-2008 as inputs to equations such as equation (1) or equation (5), one should be careful when the uncertainty analysis is performed. Erroneous uncertainty estimates will be produced if one fail to incorporate these correlations. The simplest and most robust solution to this problem is to incorporate the complete model in the uncertainty analysis, starting with pressure, temperature and composition as inputs to an equation of state.

5 DENSITY FROM MEASURED SPEED OF SOUND AND ISENTROPIC EXPONENT

The uncertainty analysis demonstrates that for rich gases containing small amounts of molecules of higher molar mass, the uncertainty in total molar mass, and thereby also the uncertainty in mass density and speed of sound, may become significant. It is also shown that the compositional uncertainties appear to have a much smaller effect on the calculated isentropic exponent.

When measuring volumetric flow rate by the means of ultrasonic flow meters, the fluid speed of sound is also measured with a high accuracy. These meters often comprise multiple sound paths providing several individual measurements of the speed of sound across the entire pipe cross sectional area, without the need for a slipstream or sampling, which is normally required by most online gas chromatographs and density meters.

The results from the uncertainty analysis imply that for applications where the speed of sound can be measured with a higher accuracy than the calculated speed of sound from the AGA8 equations, the overall uncertainty in mass density may be reduced. This is because the calculated speed of sound encompasses uncertainty in molar mass, while the isentropic exponent appears to be less influenced by this. Equation 7 show the mass density (ρ_w), calculated from measured speed of sound (w_{meas}), pressure (P) and the isentropic exponent (κ) from the AGA8 equations (GERG-2008 in this paper). This method is hereby referred to as the **SOS-kappa method.**

$$\rho_w = \frac{\kappa P}{w_{meas}^2} \qquad (7)$$

In addition to potentially reducing uncertainty in mass density, the SOS-kappa method can also provide a simpler and cheaper option compared to installing a complex gas chromatograph analysing components up to C10+. The isentropic exponent still needs to be established from one of the AGA8 equations, but it may be sufficient to utilize a C6+ GC for this purpose. The implementation of the method only requires a single equation where all the input variables are normally available in the flow computer.

Establishing mass density based on measured speed of sound from ultrasonic flow meters is not something new and has previously been successfully demonstrated by various equations and algorithms [11-13]. However, to the authors knowledge, the direct use of the isentropic exponent together with measured speed of sound have not been used in flow measurement applications. The findings in the uncertainty analysis suggests that the uncertainty contribution from molar mass is reduced by using measured speed of sound. Similar as for the SOS-kappa method, existing algorithms based on measured speed of sound are also expected to reduce the uncertainty contribution from molar mass [11-13]. Only the SOS-kappa method has been evaluated in this paper.

6 VALIDATION AGAINST FIELD DATA FROM K-LAB

The performance in calculated mass density from the SOS-kappa method (equation 7) was tested on 8 different rich gas compositions at the K-lab VGII multiphase test loop at Kårstø. The samples were taken at various pressures between 37-127 bara and temperatures between 50-80 °C.

6.1 Method

For each of the 8 gas compositions, two gas samples were sent to two different accredited laboratories, where the compositions were analysed up to C10+. For gas nr. 7 and 8, only a single analysis was available, because one of the laboratories encountered some challenges with their equipment and were unable to analyse these samples.

The gas speed of sound was measured by an 8-inch Krohne ALTOSONIC V12 Ultrasonic flow meter (USM) comprising 6 reflecting sound paths. 5 of the sound paths are used to establish the average measured speed of sound, while the 6th path is only used for diagnostics. The calculations utilized the average speed of sound measurement from the meter.

The reference gas density was based on the measured density from two Micro Motion gas density meters (GDM) in series, corrected to the pressure and temperature at the ultrasonic flow meter location and averaged. The relative uncertainty of the reference gas density at the ultrasonic flow meter conditions is estimated in the range from ±0.3% to ±0.4% (95% confidence), where the pressure measurements used for the conversion accounts for most of the uncertainty.

For each compositional analysis the mass density was calculated from pressure and temperature at the USM conditions using AGA8 GERG-2008 equation of state. In addition, the measured speed of sound and pressure, together with the isentropic exponent from GERG-2008, was used to calculate the mass density from equation 7 (SOS-kappa method).

Below is a summary of the densities of interest:

- ρ_{ref} - Measured density of two GDM's in series, corrected for P, T to the USM conditions and averaged
- ρ_{GERG} - Density calculated at P, T and x, using GERG-2008
- ρ_w - Density from the SOS-kappa method, using measured speed of sound, together with isentropic exponent (κ) from GERG-2008 based on P, T and x

The density estimates were then compared against the reference density (ρ_{ref}), by evaluating the percentage relative deviation. The relative deviation between the GERG calculated density (ρ_{GERG}) and the reference density was calculated by equation 8:

$$\delta\rho_{GERG} = 100 \cdot \frac{\rho_{GERG} - \rho_{ref}}{\rho_{ref}} \tag{8}$$

Similarly, equation 9 was used to calculate the relative deviation between the density from measured speed of sound (ρ_w) and the reference density:

$$\delta\rho_w = 100 \cdot \frac{\rho_w - \rho_{ref}}{\rho_{ref}} \tag{9}$$

A schematic illustration of the methodology for validating the rich gas density estimates (ρ_{GERG} and ρ_w) against the reference density (ρ_{ref}) is presented in Fig. 5.

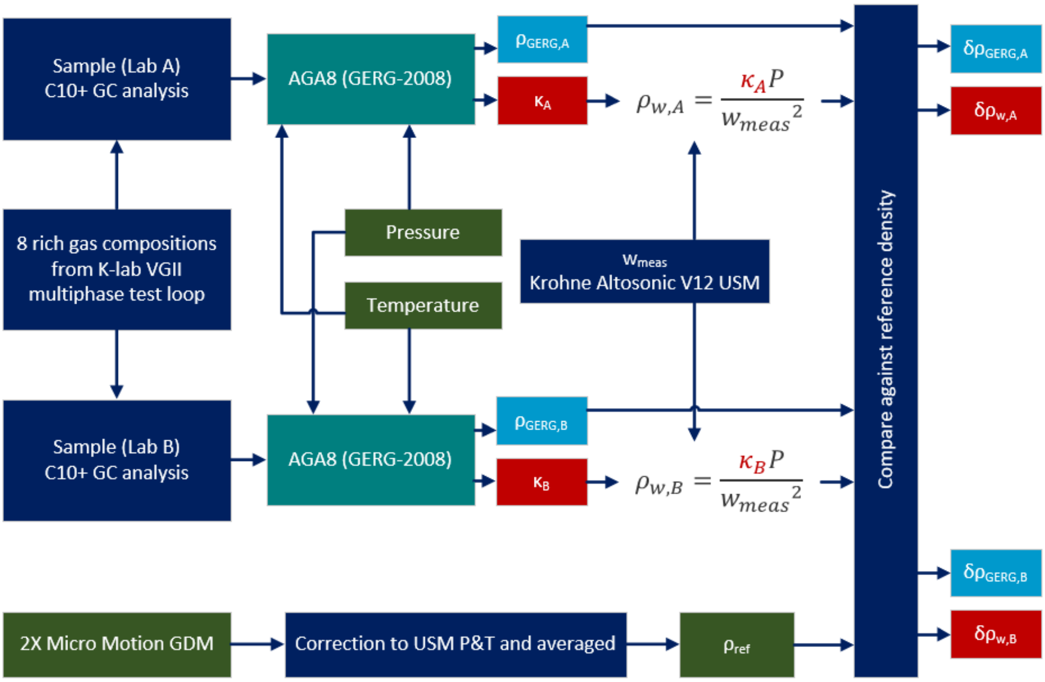

Fig. 5 – Methodology for comparing GERG-calculated mass density (ρ_{GERG}) and mass density from the SOS-kappa method (ρ_w) against reference density (ρ_{ref})

6.2 Results

Fig. 6 presents a bar plot of the relative deviation (%) from the reference density, both for the density obtained using GERG-2008, and for the density from the SOS-kappa method. The results demonstrate that the calculated mass density is significantly improved by using measured speed of sound. The only exception (Gas 6, Lab B) is inconclusive, as the deviation is less than the uncertainty of the reference density.

The results also demonstrate that the GERG-2008 calculated mass density for a single gas, based on compositional analysis conducted by two different laboratories, can produce significant differences in mass densities, with the largest difference of approximately 10% (for gas 2). It should be noted that several of these sample analyses would normally not pass the QA process conducted for all gas samples taken at the K-lab test facility. However, they were included in this dataset, both to demonstrate how rich gases pose challenges with regards to the accuracy of compositional analysis, and to investigate whether the SOS-kappa method can help reducing the uncertainty in mass density for such applications, which it does.
All the gases have a relatively high C6+ content, ranging between 0.6-1.9 mol%, except for gas 2, lab A, reporting a C6+ content of 2.9 mol%, while lab B reports 1.6 mol% for the same gas. Since gas 1-6 has a higher C6+ content compared to gas 7-8, larger uncertainties in ρ_{GERG} are expected for these gases, which is supported by the results.

Even though the SOS-kappa method significantly improves the density estimate (ρ_w), some deviations remain. The uncertainty of the method is limited by the uncertainty in the measured speed of sound and pressure, as well as the calculated isentropic exponent.

The measured speed of sound used to establish ρ_w has not been compensated for the effect of changes in path lengths due to pressure and temperature (e.g. meter body expansion) because the necessary factors required for this correction was not available from the vendor. Consequently, a bias in the measured speed of sound may exist, that could potentially explain part of the deviations in $\delta\rho_w$. For the results presented in Fig. 6, it is believed that compensating for the pressure and temperature effect on path length would probably improve the density estimate (ρ_w) even further, as the operating pressure and temperature of all datapoints are significantly higher than the pressure and temperature used for calibrating the path lengths at the factory.

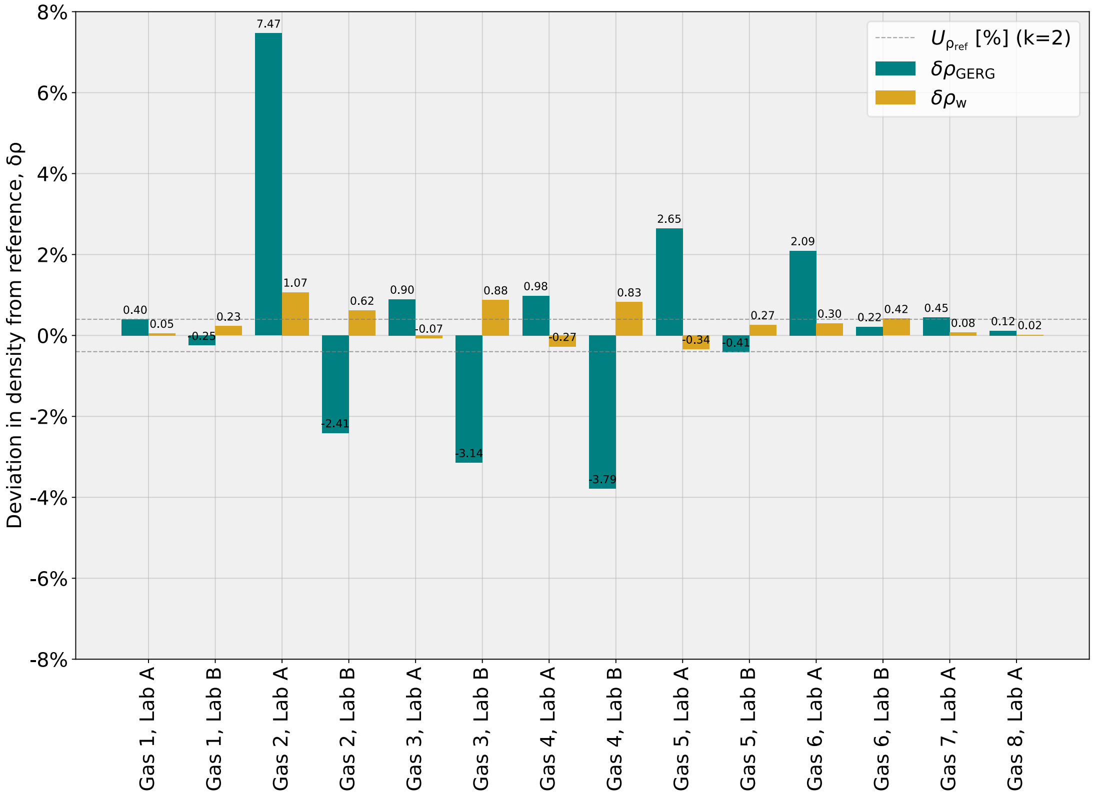

Fig. 6 – Comparison between GERG-2008 calculated mass density (ρ_{GERG}) and mass density from the SOS-kappa method (ρ_w)

The results in Fig. 6 support the claim that if an error in calculated density originates from an error in the molar mass, a corresponding error in the calculated speed of sound will exist. This can be shown analytically, as the relative sensitivity coefficient of speed of sound with respect to molar mass is -0.5 (from equation 3), while the relative sensitivity coefficient of mass density with respect to molar mass is 1 (from equation 1). This means that a 1% error in molar mass will yield a 1% error in calculated mass density and a -0.5% error in calculated speed of sound.

This effect is further demonstrated in Fig. 7, where the relative deviation between calculated (GERG-2008) and measured speed of sound is plotted against the relative deviation between calculated (GERG-2008) and measured mass density, for the same gases used in Fig. 6. These variables are correlated, with a slope of approximately -0.5, indicating that the deviations originate from uncertainty in molar mass.

This relationship may be helpful in applications where both speed of sound, density and composition are measured, to evaluate whether deviations in calculated properties originate from compositional uncertainties, uncertainties in measured pressure and temperature, or uncertainties in measured speed of sound or density.

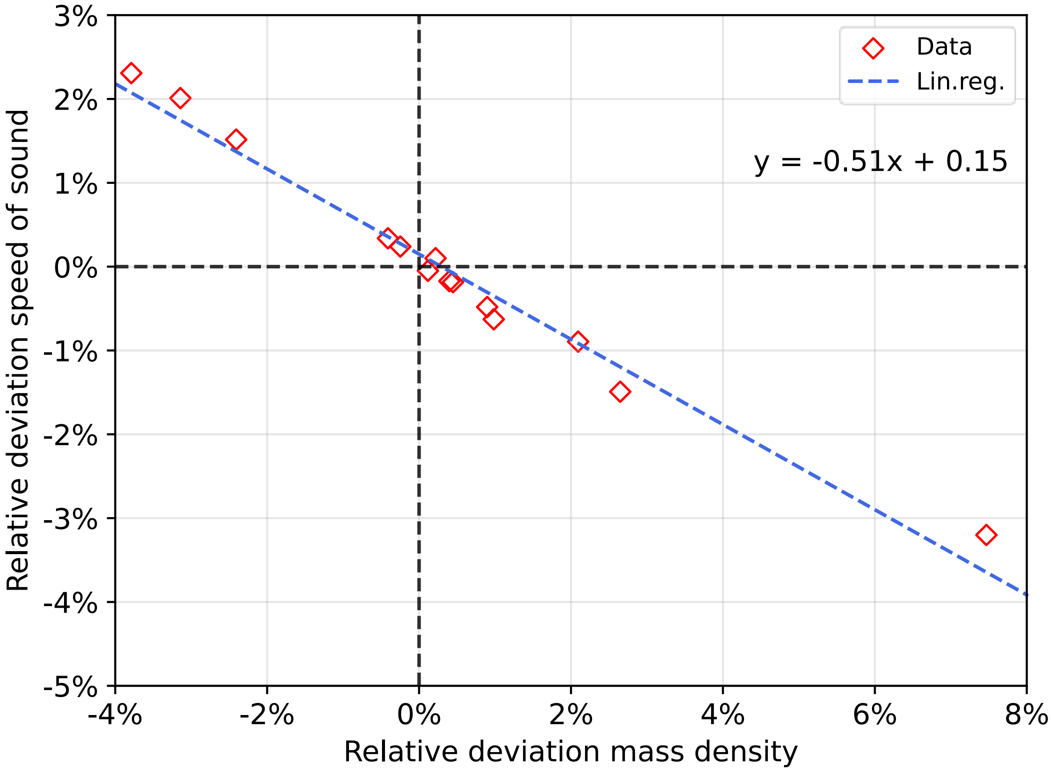

Fig. 7 – Deviation between calculated and measured speed of sound versus deviation between calculated and measured density

7 OTHER GAS MEASUREMENT APPLICATIONS

As demonstrated, the SOS-kappa method is especially suited for applications where the isentropic exponent is insensitive to compositional changes while the density is. Two novel applications in flow metering are the measurement of CO_2 and H_2

7.1 Hydrogen measurement

The molar mass of hydrogen gas is 2.016 g/mol, while the molar mass of most potential contaminants are usually at least 10 times higher. For example, the difference in mass density between 100% H_2 and 99% H_2 + 1% N_2 is approximately 13% for most relevant pressures and temperatures, while the corresponding difference in isentropic exponent lies within 0-0.1% for the same conditions. The difference in mass density is due to the large molar mass difference between N_2 and H_2. If the speed of sound can be measured with sufficient accuracy, the mass density could be estimated with a relatively low uncertainty, without the need for information about the exact N_2 concentration, using the SOS-kappa method.

In addition, the isentropic exponent is much less impacted by changes in pressure compared to the mass density (APPENDIX B). So, in certain applications a constant value for the isentropic exponent may be utilized with acceptable uncertainties.

To illustrate this effect, tests were conducted at the DNV hydrogen flow facility using a 4-inch ultrasonic flow meter under 15 and 35 bar hydrogen (99.9%) and with natural gas for the baseline test. The measured speed of sound was used to calculate the density with the actual input of the isentropic exponent (using pressure, temperature, composition, and the GERG-2008), see Fig. 8, and with a ‘fixed’ isentropic exponent for 99% hydrogen at a fixed temperature of 16 °C, see Fig. 9. As shown in the figures, the calculated density is accurate within 0.2% for both hydrogen and natural gas. Additionally, using a fixed isentropic exponent does not significantly increase the method’s uncertainty. This confirms the effectiveness of using speed of sound measurements to determine density in hydrogen applications.

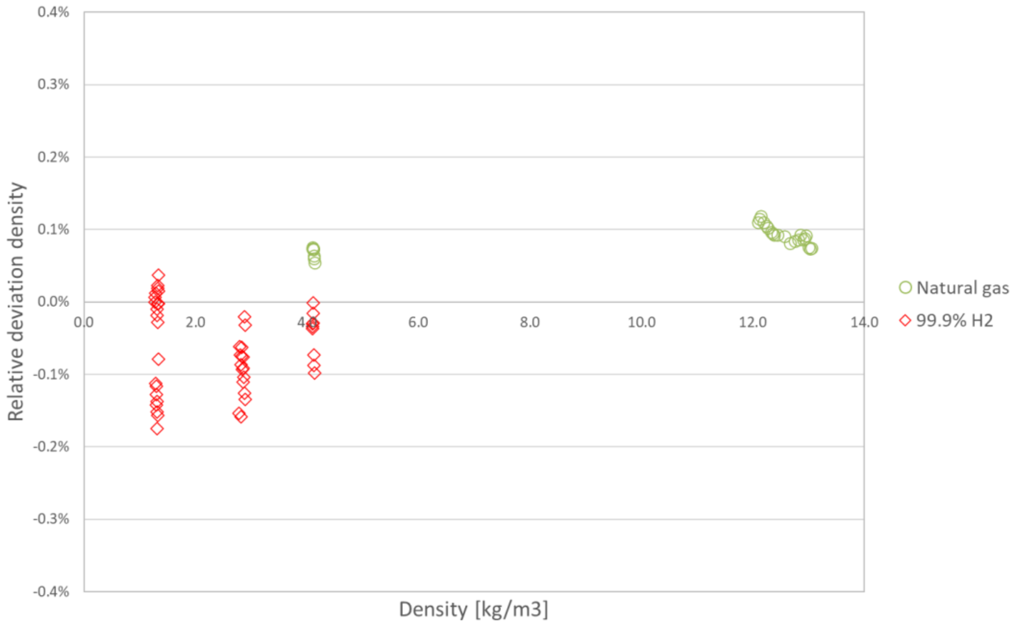

Fig. 8 - Relative density deviation of ρ_w with calculated isentropic exponent for hydrogen and natural gas

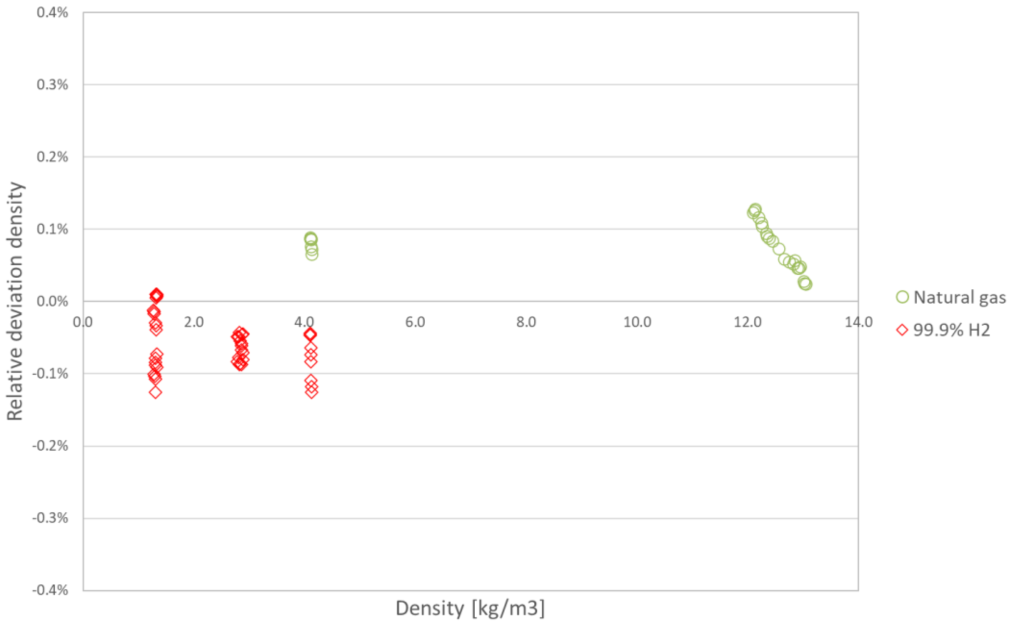

Fig. 9 - Relative density deviation of ρ_w with fixed isentropic exponent for hydrogen and natural gas

7.2 CO_2 measurement

Another application in which the method may be suitable is CO_2-rich streams. Also, in these applications the composition range is limited and the difference between the molar masses of the CO_2 and the contaminants (CH_4, N_2, H_2) may be large depending on the exact composition. Also, CO_2-rich streams require reporting in term of mass and therefore the method may be deployed by ultrasonic flow meters to convert volume to mass.

To evaluate the method's suitability, data from one of the ultrasonic flow meters in the DNV JIP CO2MET Gas project were analyzed. In the JIP, multiple test datasets were created to replicate the applications of onshore pipeline transport and the vapor return in low-pressure shipping. This test included nitrogen as a baseline test and three different CO_2-rich compositions (between 99% and 95% CO_2) under 8, 17 and 33 bara in a temperature range of 0 – 35 °C. Similarly as for hydrogen, the measured speed of sound was used to calculate density, employing the actual input of the isentropic exponent (considering pressure, temperature, composition, and GERG-2008), as shown in Fig. 10, and with a 'fixed' isentropic exponent for a mixture of 98% CO_2 and 2% N_2, as depicted in Fig. 12. The fixed isentropic exponent remains pressure-dependent and is fitted separately for medium (18 °C) and low (0 °C) temperatures with a simple, easily implementable linear fit.

Fig. 10 shows that the baseline nitrogen dataset has an offset of approximately 0.1%. Correcting for this bias in density leads to an estimation of density for the CO_2 datasets of approximately 0.2%. At lower pressures, a systematic negative bias appears due to attenuation effects. It is known that molecular relaxation at ultrasonic frequencies (and especially at lower pressures) causes attenuation and increases the speed of sound [14], leading to density underestimation since the thermodynamic relation assumes the low-frequency limit of the speed of sound. This effect, demonstrated in Fig. 10 for an 80 kHz ultrasonic flow meter, will vary with other frequencies. Successful method deployment thus depends on transducer frequency and pressure. Theoretical methods exist to correct for molecular relaxation (see references in [14]), converting high-frequency speed of sound to the necessary low-frequency value. Deploying this model leads to the improved results in Fig. 11.

Fig. 12 shows the effect of an estimated and fixed isentropic exponent. In the high pressure range the differences in composition (and subsequently the isentropic exponent) become dominant and cause an additional offset of approximately 0.4%. This may be expected since the composition range is relatively large. It is noted that for comparison also the nitrogen data in Fig. 12 uses a fixed isentropic exponent.

In conclusion, the proposed density calculation method based on the speed of sound may be suitable for CO2-rich streams. The density's uncertainty depends on the application's compositional variance (variation in estimated isentropic exponent) and the pressure relative to the signal frequency (molecular relaxation).

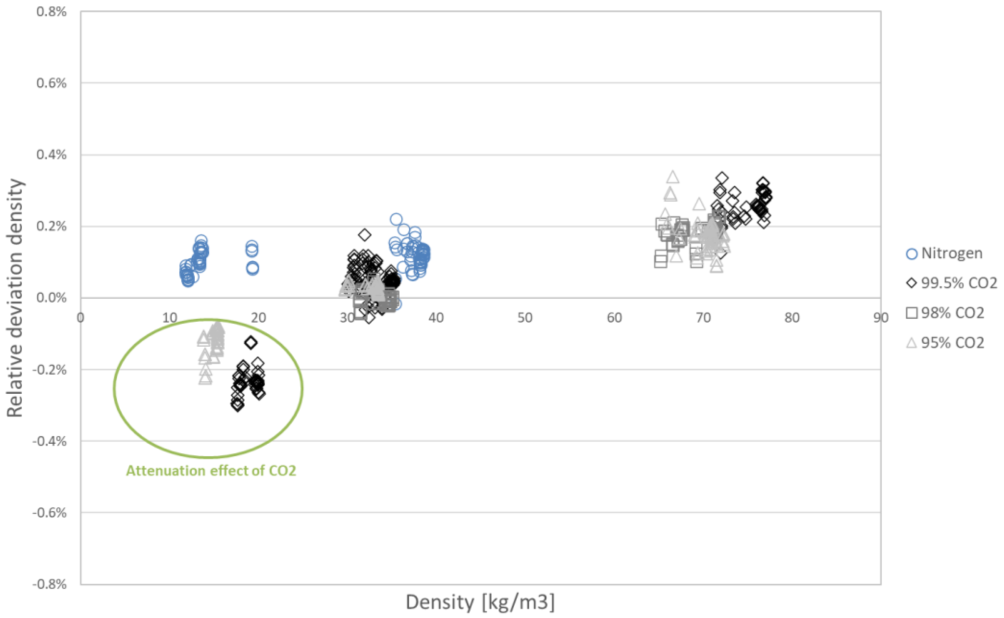

Fig. 10 - Relative density deviation of ρ_w with calculated isentropic exponent for CO_2-rich mixtures and nitrogen

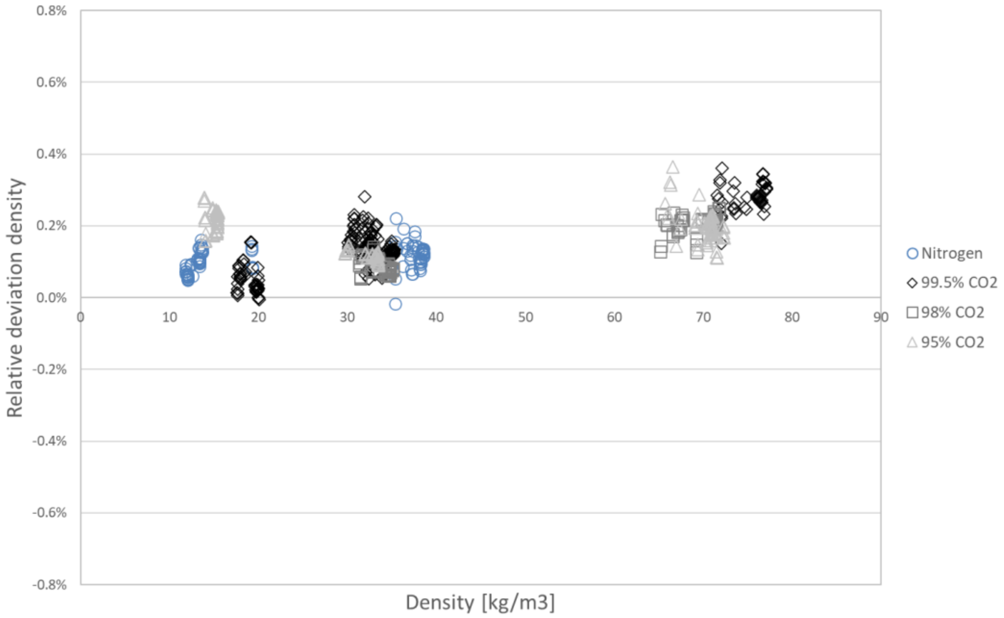

Fig. 11 - Relative density deviation of ρ_w with calculated isentropic exponent for CO2-rich mixtures and nitrogen (speed of sound corrected for molecular relaxation)

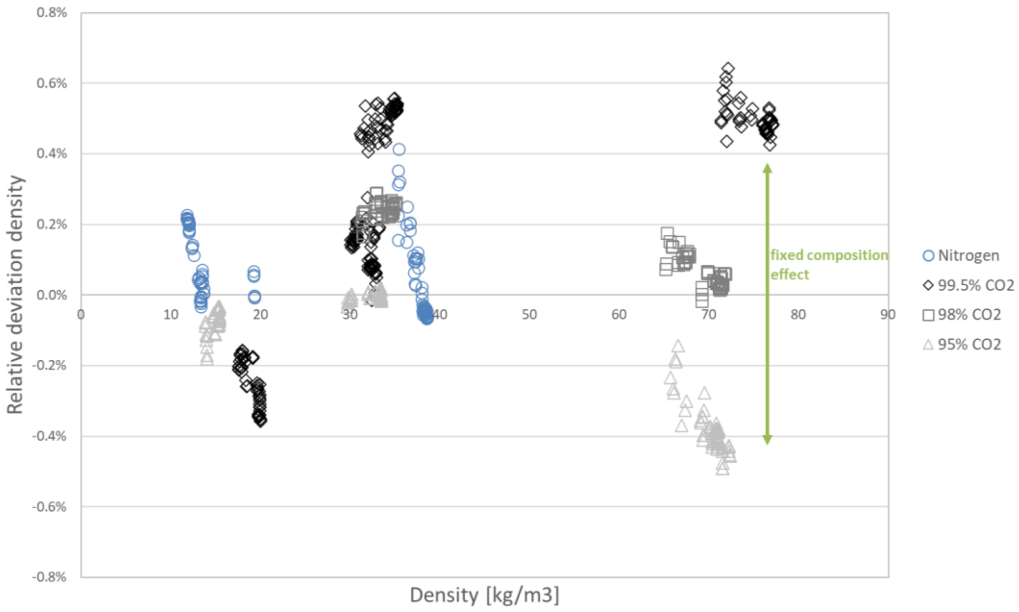

Fig. 12 - Relative density deviation of ρ_w with fixed isentropic exponent for CO_2-rich mixtures and nitrogen

7.3 Calculate speed of sound from measured density

The relationship between isentropic exponent, speed of sound, and mass density could also be used the other way around, by calculating speed of sound based on measured gas density (ρ_{meas}), in metering stations where such measurements are available.

$$w = \sqrt{\frac{\kappa P}{\rho_{meas}}} \tag{10}$$

Several applications exists where this method can be useful:

- For gas density meters based on elements vibrating at the resonance frequency, the measured density is influenced by the difference in speed of sound between the calibration gas and the process gas. Nitrogen (or sometimes Argon) are typically used to calibrate these types of meters, which means that the influence of speed of sound should be compensated for when utilized for hydrocarbon or other types of gases [15]. In fiscal flow computers, simplified models are often used (e.g. the User Gas Equation Method [16]), due to the lack of information about the speed of sound of the process gas. Calculating speed of sound using measured density and isentropic exponent would improve the speed of sound correction for gas density meters. A similar method known as the *“Pressure/density method”* is given in the Micro Motion 7812 manual [16], except that it uses the ratio of specific heats instead of the isentropic exponent, which is valid for ideal gases. Utilizing the isentropic exponent should in theory improve the correction for real gases.

- The influence of speed of sound is also relevant for coriolis flowmeters and influences both mass flowrate and density. Similar as for gas density meters, equation 10 can be used to establish the speed of sound and used for compensation in coriolis meters. This compensation method derived by Hemp and Kutin [17] depends on the tube frequency and the tube size.

- The speed of sound calculated based on measured density can also be used as an additional quality parameter by comparison against measured speed of sound from ultrasonic flow meters.

8 DISCUSSION

- To successfully utilize the SOS-kappa method, accuracy in the speed of sound measurement is key. This is because the relative sensitivity coefficient of mass density with respect to speed of sound in equation 7 equals -2. This means that a 1 % change in speed of sound will correspond to a change of -2 % in mass density. Several factors may influence the measured speed of sound, such as accurate calibration of the path lengths of the ultrasonic flow meter. In addition, compensating for effects that may influence the path length, such as how body/transducers changes as function of pressure and temperature, may also be required to achieve good enough accuracy. Vendors of ultrasonic flow meters should also provide information about the uncertainty in the measured speed of sound, and the performance could potentially be evaluated as part of the flow calibration.

- For lean gas applications, the method of calculating mass density from measured speed of sound and isentropic exponent will not necessarily reduce uncertainty in mass density, as the uncertainty in measured speed of sound may be larger than the calculated speed of sound. It is therefore important to perform an uncertainty evaluation for each case before considering implementing this method. And the findings in this paper highlights the importance of using realistic uncertainty inputs for the heavier components in such evaluation.
  It should also be noted that in lean gas applications, volumetric flowrates at standard conditions are often used, which will eliminate the uncertainty contribution from molar mass [3], given that the flow rate is measured on a volume basis and converted to standard conditions.

- The uncertainty analysis (Fig. 4) show that the calculated isentropic exponent is less impacted by uncertainties in input variables to the AGA8 equations, compared to other calculated properties. However, the model uncertainty of different equations of state should be investigated further. The GERG-2004 database, utilized to evaluate the performance of the AGA8 equations, does not contain data where both speed of sound and density is measured for the same datapoints. Measuring speed of sound and density simultaneously for known gas compositions would be helpful to understand the performance in calculated isentropic exponent from different models.

- Expressing equation 3 in terms of molar mass and replacing the speed of sound with measured speed of sound would likely provide a more accurate determination of the molar mass, based on the findings in the uncertainty analysis. The same could be achieved by calculating molar mass based on measured mass density by rewriting the real gas equation (1). Both methods could be useful for validating the molar mass based on composition from a gas chromatograph.

9 CONCLUSIONS

- Compositional uncertainties for rich natural gases can cause significant uncertainties in calculated mass density, potentially exceeding limits given by standards and/or governmental regulations. Failing to address the increased uncertainty for heavier components (both mole fraction and molar mass) in a rich gas will underestimate uncertainty in mass density, which may constitute the main contributor to the total uncertainty of the metering system.

- The uncertainty analysis demonstrates that properties with a direct dependency on molar mass, such as mass density and speed of sound, are more sensitive to compositional uncertainties compared to properties derived on a molar basis, such as isentropic exponent (κ) and compressibility factor, (Z).

- The SOS-kappa method, which utilizes measured speed of sound and pressure in combination with isentropic exponent from GERG-2008, shows promise for several gas flow measurement applications:
    - **Rich natural gas:** The method effectively reduces uncertainty in mass density caused by compositional uncertainties, as demonstrated by data from the K-lab VGII multiphase test loop for rich gases.
    - **H_2:** Data from the DNV hydrogen flow facility confirm the method's feasibility for hydrogen applications. The large difference in molar mass between hydrogen and potential contaminants makes the method effective for such applications.
    - **CO_2:** Data from the DNV JIP CO2MET Gas project demonstrate that the method may also be suitable for CO_2-rich streams, given that attenuation effects of CO_2 is considered.

- In addition to potentially reducing uncertainty in mass density, the SOS-kappa method may also simplify the design of metering stations, as it reduces the dependency on compositional measurements. In rich gas metering stations, the calculated isentropic exponent from a C6+ GC analysis can yield sufficient accuracy for calculating density. The same applies to H_2 and CO_2 applications, where it may be sufficient to assume a fixed composition of the measured gas.

- Calculating speed of sound from measured mass density, pressure and calculated isentropic exponent can be useful in several applications, such as speed of sound correction in gas density meters and coriolis flow meters, or as an additional quality parameter by comparison against measured speed of sound.

10 NOTATION

c_i	Sensitivity coefficient of input *i*
d	Molar density [mol/m^3]
M	Molar mass [kg/mol]
P	Pressure [Pa]
R	Gas constant [8.134 462 J/(mol·K)]
s	Molar entropy [J/(mol·K)]
s_i	Standard uncertainty of input *i*
T	Temperature [K]
w	Speed of sound [m/s]
w_{meas}	Measured speed of sound [m/s]
x_i	Mole fraction of component *i* [-]
x	Molar composition
Z	Compressibility factor [-]
κ	Isentropic exponent [-]
ρ	Mass density [kg/m^3]
ρ_w	Mass density from w_{meas} [kg/m^3]
ρ_{GERG}	Mass density from GERG [kg/m^3]
$\delta\rho$	Deviation in mass density [%]
σ	Standard deviation

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APPENDIX A COMPOSITIONAL UNCERTAINTY ESTIMATE

The estimated compositional uncertainties used in the uncertainty analysis (Table 2) are based on a comparison test on samples taken at the K-lab multiphase test facility at Kårstø. For every new gas composition encountered at K-lab, two gas samples are taken and sent to two different accredited laboratories for analysis. The sample results are stored in a database covering gas composition from lean gas to relatively rich gases.

It is important to note that these sample data were not collected with the primary intent to investigate uncertainty effects. But in absence of any better compositional uncertainty estimates that addresses uncertainties in the C6+ components, an estimate was established based on available data in the database.

For each pair of gas samples in the dataset, the absolute difference in mole percent, together with the average mole percent of each component, was calculated, and a power regression was established as a function of the mole percent per component.

From statistics, it can be shown that the mean absolute difference (MD) between random pairs drawn from the same normal distribution is directly related to the actual standard deviation (σ) of that distribution, by the following equation.

$$MD = \frac{2}{\sqrt{\pi}}\sigma \approx 1.1284 \cdot \sigma \qquad (11)$$

This relationship was utilized to adjust the power regressions to obtain a function providing an estimate of the standard uncertainty for each component as a function of mole percentage.

In the analysis, the C6+ components were lumped together and treated as a single component, and the same power regression was used for all C6+ components. This was done to exclude uncertainties originating from effects such as different component assignment methods used by different laboratories [3], that would result in much higher uncertainty estimates.

Table 2 – Compositional uncertainty estimates based on comparison test

Input	**Standard uncertainty (k=1)**	**Unit**
N2	$0.034 \cdot x_i^{1.005}$	mol%
CO2	$0.013 \cdot x_i^{0.514}$	mol%
C1	0	mol%
C2	$0.041 \cdot x_i^{-0.118}$	mol%
C3	$0.025 \cdot x_i^{0.970}$	mol%
iC4	$0.018 \cdot x_i^{0.635}$	mol%
nC4	$0.027 \cdot x_i^{0.793}$	mol%
iC5	$0.016 \cdot x_i^{0.383}$	mol%
nC5	$0.023 \cdot x_i^{0.470}$	mol%
nC6	$0.103 \cdot x_i^{0.683}$	mol%
nC7	$0.103 \cdot x_i^{0.683}$	mol%
nC8	$0.103 \cdot x_i^{0.683}$	mol%
nC9	$0.103 \cdot x_i^{0.683}$	mol%
nC10	$0.103 \cdot x_i^{0.683}$	mol%

The resulting power regression for the C6+ components are comparable to reproducibility values given in ASTM D5134 [18], covering analysis of heavier components up to nC9 using flame ionization detector (FID). This standard is developed for liquid hydrocarbon mixtures but are very similar to the methods used for analysing rich gases. It should be noted that the reproducibility estimates in ASTM D5134 are given in weight percentage, and the reproducibility in mole percentage will therefore depend upon the other components present in the fluid analysed. For butane and pentane, ASTM D5134 produces larger values for reproducibility compared to the standard uncertainties from the power regressions presented in Table 2.

The standard uncertainty in C1 mol% is set to zero because the uncertainty in C1 is typically dominated by the uncertainty in other components. As such, the uncertainty is transferred to the C1 mol% when normalized in the calculations.

The uncertainty estimates in total molar mass for different gases showed in Fig. 1 is based on the compositional uncertainty estimates from the power regressions presented in Table 2. To evaluate if these estimates are reasonable, the difference in total molar mass from 62 pairs of parallel samples were evaluated. The absolute relative deviation in total molar mass between each pair of analysis was calculated and plotted as a function of molar mass in Fig. 13.

The comparison shows deviation in molar mass up to 3.6 %, where most of the data exceeds the limitation of 0.2 % given by NORSOK I-106 and the Norwegian metering regulations. In comparison to the estimated uncertainties in molar mass showed in Fig. 1, with maximum uncertainties of ± 1.5 %, the uncertainty estimates seem reasonable, or perhaps slightly on the low side.

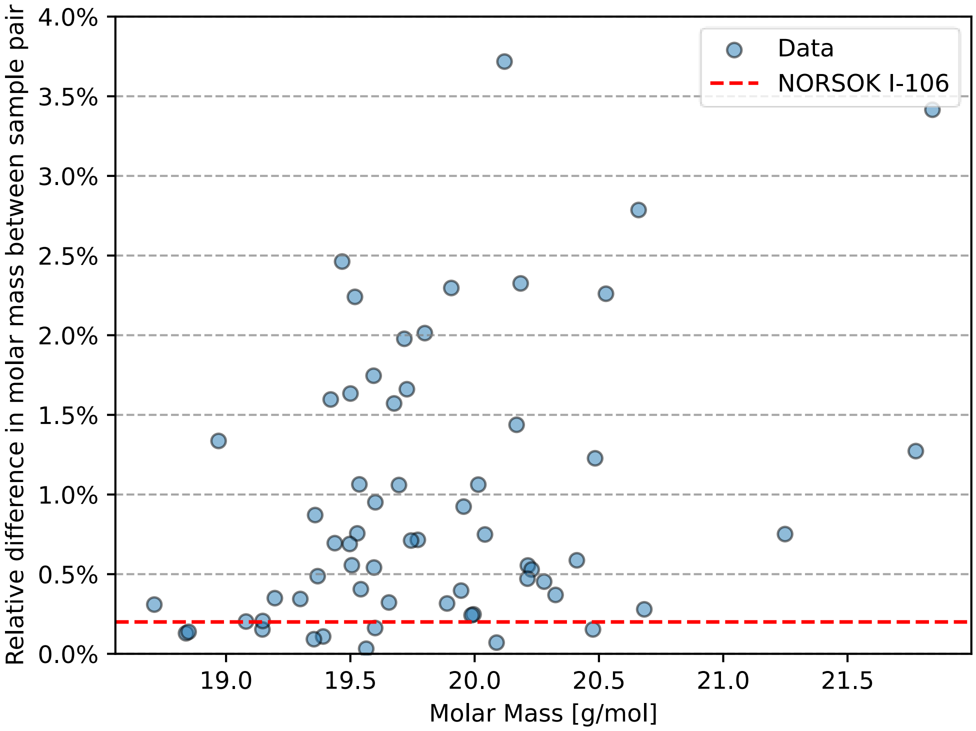

Fig. 13 – Absolute value of the relative difference (%) in molar mass between two parallel samples of the same gas, analysed by two different laboratories

It is possible that the observed molar mass differences may originate from uncertainties in sampling rather than the analysis. However, K-lab has tested this effect on several occasions and has consistently found that the deviations in these tests are mainly due to differences between laboratories rather than sampling errors. Fig. 14 presents the results from a test where the effect of sampling was evaluated. Two rich gas samples were sent to two different laboratories. The molar masses obtained by the two laboratories differed by 3.7%. Sample 1 was then re-analysed by laboratory A, before it was sent to laboratory B for analysis. Laboratory B obtained similar results when analysing sample 1 as they did for sample 2, suggesting that the deviations are not due to sampling, but differences between the two laboratories.

It should be noted that rich gases often exceed the mole percent limitations of the methods utilized by different laboratories. As a result, larger uncertainties should be expected when analysing these types of gases.

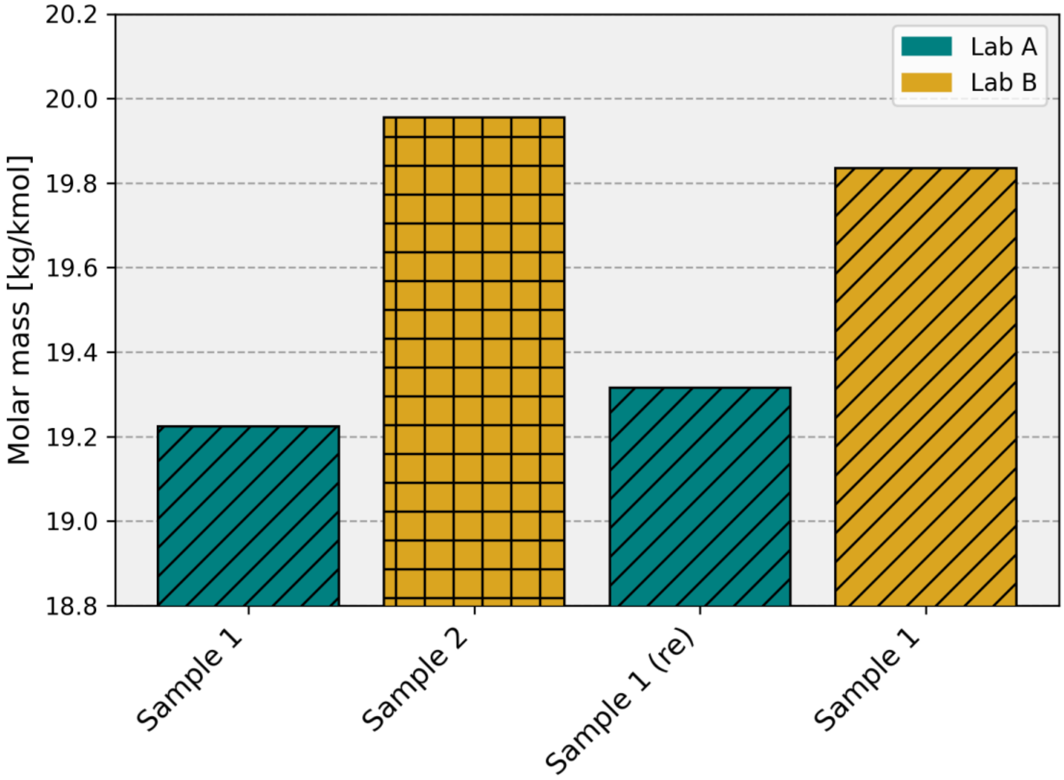

Fig. 14 – Evaluating effect of sampling uncertainty by comparing molar mass between two samples of the same rich gas sent to two different laboratories. Sample 1 was analysed twice by lab A before sent to lab B for analysis

APPENDIX B INFLUENCE OF P&T ON THE ISENTROPIC EXPONENT

The influence of changes in pressure and temperature on the isentropic exponent has been investigated for a lean natural gas and for pure H_2 gas. Density, speed of sound and isentropic exponent was calculated at different pressures and temperatures using the GERG-2008 equation. The properties are compared to the properties at a given reference point, in this case 50 bara and 50 °C, as illustrated for mass density in equation 12. This is to demonstrate the relative changes in the different properties as a function of pressure and temperature.

$$\rho_{rel} = \frac{\rho(P,T)}{\rho(50\ bara, 50\ °C)} \tag{12}$$

The results are plotted in Fig. 15 (lean gas) and Fig. 16 (H_2), and show how density, isentropic exponent and speed of sound is affected by changes in pressure and temperature. For example, for hydrogen gas, the density at 100 bara will be approximately double the density at 50 bara, while the isentropic exponent is almost unaffected. The results demonstrate that isentropic exponent for H_2 appears to be much less influenced by changes in pressure and temperature than the density. The same applies for the lean natural gas at pressures below 50 bara.

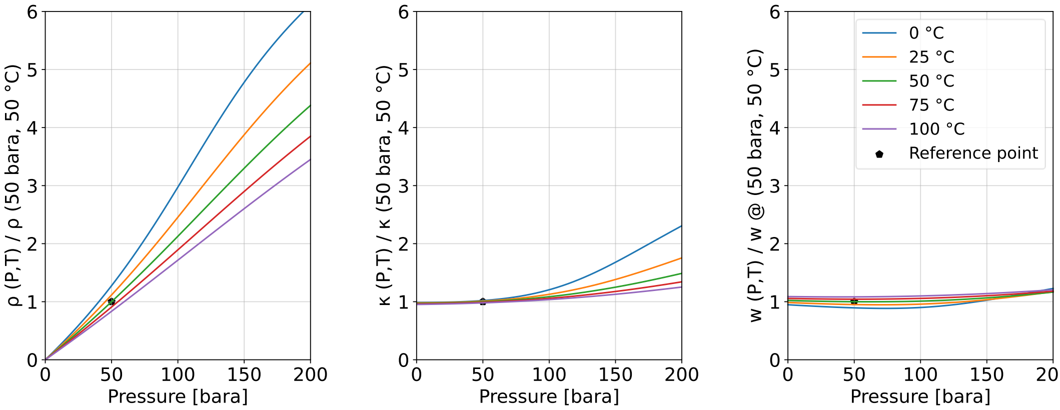

Fig. 15 – Influence of pressure and temperature on relative changes in density, isentropic exponent and speed of sound for a lean natural gas (Cricondentherm = -27 C°)

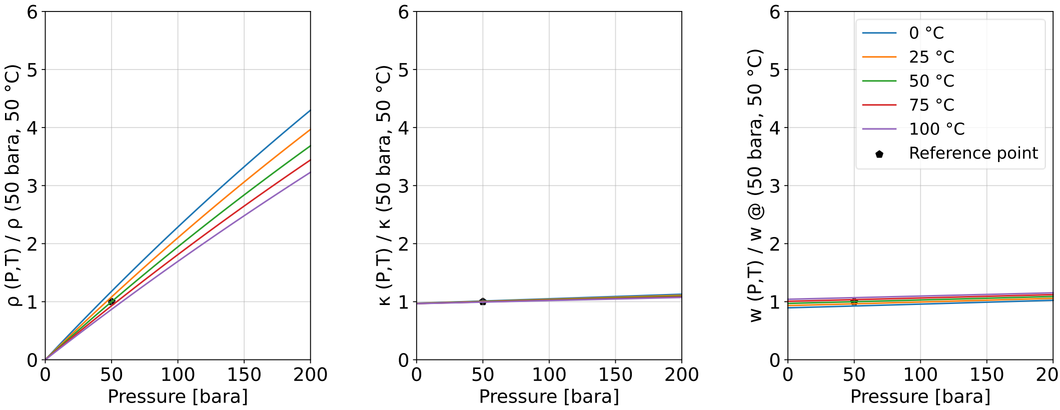

Fig. 16 - Influence of pressure and temperature on relative changes in density, isentropic exponent and speed of sound for 100% H_2