

A NEW APPARATUS FOR ACCURATE MEASUREMENTS OF THE DENSITIES OF LIQUEFIED NATURAL GAS (LNG)

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ABSTRACT

For accurate measurements of the densities of liquefied natural gas (LNG) a special densimeter has been developed. This new densimeter will cover the range from $10 \text{ kg}\cdot\text{m}^{-3}$ to $1000 \text{ kg}\cdot\text{m}^{-3}$, thus enabling density measurements in the homogeneous liquid region, along the saturated liquid line (incl. vapor pressures), in the supercritical region as well as in the homogenous gas region. The apparatus is designed for measurements in a temperature range from 90 K to 290 K at pressures up to 12 MPa. The densimeter is based on the Archimedes (buoyancy) principle and is a single-sinker system incorporating a magnetic suspension coupling. The density is obtained directly without the need for calibration fluids. The expanded uncertainty ($k = 2$) for density measurements in the homogeneous liquid (incl. an additional uncertainty resulting from the sample gas analysis) is estimated to be smaller than 0.05 %.

1. INTRODUCTION

Natural gas is an important energy source today and for the future. According to the International Energy Agency [1] the trade with Liquefied Natural Gas (LNG) will increase significantly to ensure a secure energy supply. In this context, the accurate determination of LNG densities is gaining importance for the custody transfer process when determining the transferred energy and also for process simulations, e.g., for modelling of economically and ecologically optimised liquefaction and evaporation processes. Today, even the best available calculation models used for natural gas only offer uncertainties of 0.1 % to 0.5 % in the liquid phase. To reduce these relatively large uncertainties new accurate sets of experimental p - ρ - T - x -data are essential.

For example, in Europe custody transfer calculations for LNG are carried out according to the GIIGNL – LNG Custody Transfer Handbook [2]. Therein the revised Klosek and McKinley method [3] is given for determining densities of LNG. This empirical calculation method can only be applied in a very limited temperature and pressure range and was simply fitted to a small number of experimental data. Within the present project, the uncertainty of these data, mostly measured by Miller and Hiza [4] as well as by Hiza and Haynes [5-7], was estimated to be about 0.3 %. Thus it can be clearly stated that an uncertainty of 0.1 %, given in [3] for calculated densities, is certainly underestimated.

Detailed studies at Ruhr-University Bochum have shown that comparisons between density calculations with the revised Klosek and McKinley method and the GERG-2008 wide-range reference equation of state for natural gases of Kunz and Wagner [8] lead to deviations of up to 0.2 %. Thus, currently no calculation model can be clearly recommended for the billing of LNG. Furthermore, density calculations in process simulations (e.g. with Aspen Plus or Hysys) have been validated. In this context mostly cubic equations of state (e.g. Peng-Robinson oder Redlich Kwong Soave) are used. Comparisons between the cubic equations and the GERG-2008 equation of state have shown deviations of up to 10 %.

To verify the thermophysical models used for the mentioned purposes, accurate experimental data for LNG densities over wide temperature and pressure ranges are needed. The data situation for the relevant fluid regions (saturated liquid densities and homogeneous liquid densities), however, is evidentially poor (compare [8-10]). The small number of data results from the technical difficulties related to the measurement of the densities of multi-component mixtures in the liquid phase (e.g., changes in composition of the fluid mixture). That is why new measurements are definitely necessary.

2. APPLICATION AND TECHNICAL SPECIFICATIONS

An extensive analysis of several different density measurement methods [9] made clear that it is very difficult to measure the density of natural gas at low temperatures in the homogeneous liquid phase as well as in saturated-liquid and saturated-vapor states. Consequently, as already mentioned, only very few experimental values are available in these regions, and the measured data which are available often involve relatively large measurement uncertainties. This is also the reason why the uncertainty of the GERG-2008 equation of state is still quite large in this region of the fluid state. Therefore, the uncertainty given for LNG densities calculated with this equation of state is approx. 0.1% to 0.5%, also at low pressures. (In contrast, the uncertainty given for densities in the homogeneous gas phase calculated with this equation is smaller than 0.1 %.) Although these uncertainties are relatively good for a fluid property model for mixtures, Kunz and Wagner [8] emphasize repeatedly in their publication that reliable measured data in the homogeneous liquid phase over wide temperature and pressure ranges are absolutely necessary. The demand for more accurate thermophysical property models has also become stronger in the field of LNG process simulation (liquefaction, marine transportation, regasification), see Dauber [10] as well as Dauber and Span [11]. To optimize the required thermophysical property models new measured data with small uncertainties are essential.

Against this background a new special densimeter and a new measurement procedure have been developed. This new densimeter will allow the densities of LNG to be measured both in the homogeneous liquid phase and along the saturated-liquid line (including vapor pressures). To illustrate

the planned measurements, Figure 1 shows the p , T -diagram of a natural gas with a typical LNG composition. The p , T diagram contains the phase boundary (blue) and the critical point (yellow) as well as the points to be measured (red). It is obvious that the measurements are made along isotherms and that also measurements for the description of the supercritical region at low temperatures should be possible. Figure 1 also shows four selected isochors. These are plotted to give an idea of the order of magnitude of the liquid densities to be measured and to illustrate that the slopes of the isochors at low temperatures are very steep¹.

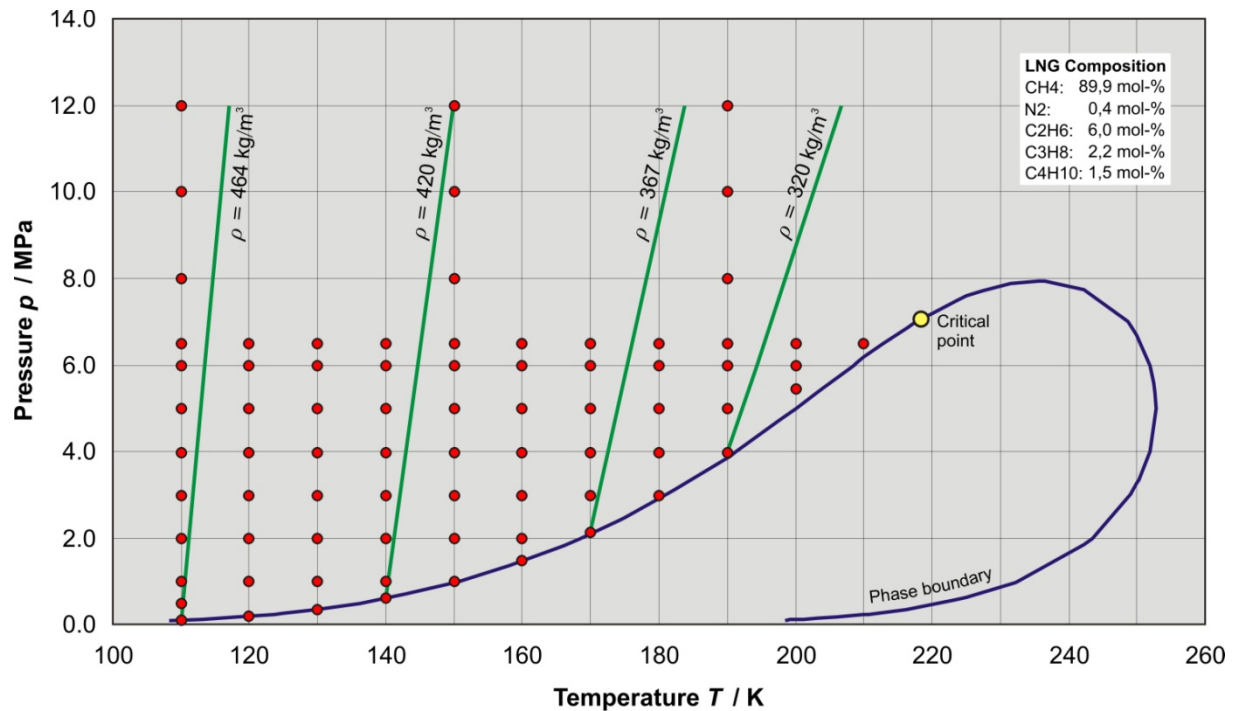


Figure 1: p , T -diagram of a natural gas with typical LNG composition calculated with the GERG-2008 equation of state of Kunz and Wagner [8]. The figure shows the envisaged measurement points and some isochors to illustrate the order of magnitude of the densities to be measured.

The new densimeter is a precision instrument specifically designed for the accurate measurement of LNG densities. This apparatus serves to measure densities in the homogeneous liquid phase and on the saturated-liquid line, thus also allowing vapor pressures to be measured. Due to the applied density measurement technology it will also be possible to measure densities in the homogeneous gas phase with a relatively small uncertainty. Table 1 lists the most important technical specifications of the new densimeter. The information within the table confirm that all requirements for performing accurate density measurements on LNG have been met. The most important results in this context are the expanded measurement uncertainty ($k = 2$) in density of 0.02% (plus an uncertainty of approx. 0.03 % associated with the sample analysis) and the fact that only a single analysis of the sample gas is required.

In a study carried out for E.ON Ruhrgas AG, Germany it was additionally shown that it is extremely difficult to design an experimental set-up which also enables precision density measurements in the vapor liquid equilibrium (VLE) and measurements to determine dewpoint temperatures.

¹ Please note: The Isochors only represent the densities of the homogeneous liquid phase within the measuring cell. They are not valid for the entire measuring system. Within the following it will become obvious that the new densimeter will consist of three sections: measuring cell, vapor-liquid-equilibrium-cell (VLE-cell) and pressure measurement circuit. These three sections are located at different temperatures so that for every single section a different density can be assumed. E.g. the pressure measurement circuit is located at ambient temperature. Hence, the natural gas will be in the homogeneous gas state. Therefore the density will be much smaller than in the measuring cell.

Table 1: Technical specifications of the new LNG-densimeter.

Measured value	Density of LNG <ul style="list-style-type: none"> • in the homogeneous liquid phase • on the saturated-liquid line including vapor pressure • in the homogeneous gas phase (where required)
Temperature range	90 K to 290 K
Pressure range	0.05 MPa to 12 MPa
Density range	10 kg/m ³ to 1,000 kg/m ³
Total measurement uncertainty	$\Delta\rho/\rho = 0.02\%$ ($k = 2$) in the homogeneous liquid phase (plus uncertainty associated with gas analysis, ca. few 0.01%)*
Measurement principle	Single-sinker density measurement method (silicon sinker: $V \approx 26.1 \text{ cm}^3$, $m \approx 60.7 \text{ g}$)
Temperature control	$\pm \leq 0.005 \text{ K}$
Temperature measurement	Uncertainty approx. 0.015 K ($k = 2$)
Pressure measurement	Uncertainty approx. 0.01% ($k = 2$)
Density measurement	Uncertainty approx. 0.01% (for liquids) ($k = 2$)
Gas analysis*	Only one analysis from 50 L gas cylinder required
Thermostating	Liquid Nitrogen (LN ₂)
Insulation	Outer cylinder with Argon at approx. 20 mbar as insulating gas

* Only a single gas analysis is necessary from the required 50 L gas cylinder (or similar sample container). The gases to be measured may be produced gravimetrically to reduce the final measurement uncertainty (e.g. at Physikalisch Technische Bundesanstalt (PTB, Germany), at Bundesanstalt für Materialforschung und -prüfung (BAM, Germany) or at Dutch Metrology Institute (Van Swinden Laboratorium).

3. SOLUTIONS OF THE FUNDAMENTAL PROBLEMS IN LNG DENSITY MEASUREMENT

By studying selected density measurement methods in detail [9], three fundamental problems in LNG density measurement have been identified. Additionally, it should be mentioned that these three problems can occur for any mixture in the homogeneous liquid state or saturated liquid state. Moreover, these problems do not only exist for density measurements but also when measuring other thermo-physical property data (e.g. speed of sound, viscosity etc.). Furthermore, the discovered problems could be relevant for the gas industry when taking samples from LNG transfer lines. The three fundamental problems can be summarized as follows:

1. The fluid may separate into two phases already during the filling procedure of the measuring device. This could lead to a change in composition of the fluid. (Hence, the apparatus needs to be filled in a specific manner to avoid this problem.)
2. It is not possible to measure pressure or differential pressure accurately at low temperatures. (This means pressure must be measured at ambient temperature.)

- As the pressure can only be measured at ambient conditions, a phase transition (vapor-liquid) will occur in the measuring cell or at another point of the densimeter. Consequently, the composition of the liquid phase will change. (This must be avoided in an appropriate way.)

Solving these three main problems was absolutely crucial when the new concept for the LNG-densimeter was developed. The results are summarized in Table 2:

Table 2: Three main problems identified in LNG density measurement and solutions to the problems.

Problems	Solutions
1. Change in composition of the fluid during filling procedure	Filling of the densimeter at ambient temperature T_a to a pressure $p > p_c$ and subsequent isobaric cooling (e.g. at 12 MPa)
2. Accurate pressure and differential pressure measurement is technically not possible at low temperatures	Pressure measurement at T_a and integration of special VLE-cell ⇒ controlled phase transition liquid-gas (VLE) in a special VLE-cell and specific adjustment of the fluid pressure
3. Change in composition of the fluid in the measurement cell resulting from the existing VLE state (A phase transition liquid-gas is unavoidable because the pressure sensor has to be located at ambient conditions)	<ul style="list-style-type: none"> Only homogeneous liquid phase in the measuring cell (due to integration of a VLE-cell; see Item 2) At most 1% to 2% vapor volume in the measuring cell during measurement of saturated-liquid densities ⇒ special design of the upper part of the measuring cell

An important result of the present project is that the mixture composition remains unchanged because the instrument is filled at ambient temperature to a pressure above the critical pressure with subsequent isobaric cooling. The unchanging mixture composition of a natural gas is ensured by not crossing the two-phase region, and no changes in the mixture concentration can occur due to a change of state in the supercritical region. However, because of the pressure measurement at ambient temperature a phase transition to the low-temperature measuring cell is not avoidable. So the only remaining possibility is to create a special auxiliary device to ensure that density measurements are carried out with the correct mixture composition of the homogeneous fluid. As a result a special "VLE-cell" (VLE: Vapor-Liquid-Equilibrium) is integrated into the connection line between the measuring cell and the pressure measurement circuit. This novel VLE-cell serves as a controllable "buffer" for the unavoidable phase transition. By means of the VLE-cell it is ensured that the measuring cell contains only homogeneous liquid with the same composition as the composition of the mixture in the sample cylinder. The connection line between the measuring cell and the VLE-cell is specifically designed to avoid a possible diffusion process between the two cells during the time of a density measurement run. To give a better insight into the developed solutions of the fundamental problems in LNG density measurement, the instrument filling procedure and the functional principle of the VLE-cell are described in more detail in Section 4.

4. FILLING OF THE DENSIMETER AND MEASUREMENT PROCEDURE

In this section the filling of the densimeter and the basic procedure of running the densimeter are described. To illustrate both operations, the p , T -diagram in Figure 2 is used.

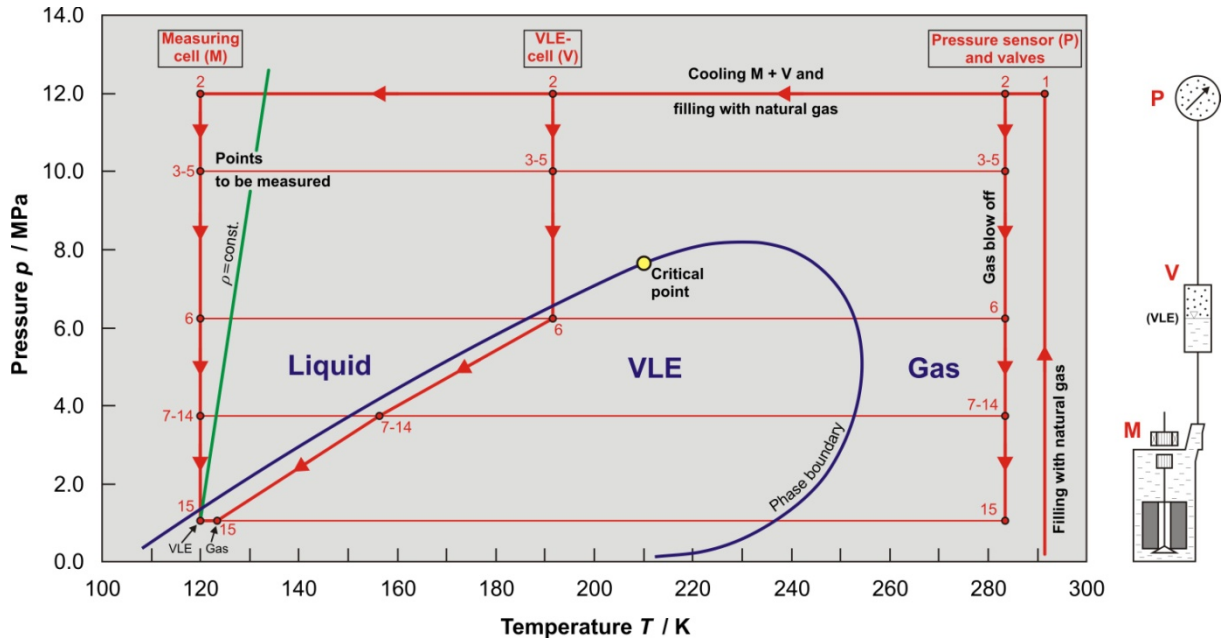


Figure 2: Left: p , T -diagram of a typical natural gas. Right: schematic presentation of the measurement system consisting of the measuring cell (M), VLE-cell (V) and pressure measurement system (P). The p , T -diagram shows the changes of states during the filling of the system and the points to be measured.

To the right of the p , T -diagram, Figure 2 shows the schematic arrangement of the measuring cell (M), the VLE-cell (V) and the pressure measurement circuit (P). Important in this context is the geometry of the measuring cell which is specifically designed to also allow saturated-liquid densities to be measured (explained later). For this purpose the top part of the measuring cell is specially designed as “vapor space”. Likewise important is the VLE-cell which serves as a buffer for the phase transition (vapor-liquid) which cannot be avoided. Into the VLE-cell as well as into the measuring individually designed liquid-level-indicators are integrated to reliably determine the liquid level. The temperatures of the measuring cell and the VLE-cell are controlled independently of each other. The pressure is the same in all areas of the measurement system as they are interconnected (considering a pressure head correction).

Filling of the measuring device

The measuring device is filled at ambient conditions to a pressure above critical pressure (e.g. $p = 12$ MPa for natural gases). In this way the mixture composition determined for the sample cylinder before filling the instrument is maintained when densities are measured in the homogeneous liquid phase. In Figure 2 this process is shown as “Filling with natural gas”; it ends in the supercritical region at point 1. Subsequently, the measuring cell and the VLE-cell are cooled simultaneously in an isobaric manner until the VLE-cell has reached a temperature just below critical temperature (point 2, VLE-cell). From this point the temperature of the VLE-cell is controlled at the first set-point temperature while the measuring cell is cooled to the temperature of the first isotherm to be measured. Once the temperature of the isotherm has been obtained (point 2, measuring cell), the temperature is controlled to maintain a constant value. The filling of the measuring device is then completed, and the first density measurement point can be determined.

Procedure for the measurement of an isotherm

When the first measurement point has been determined (e.g. at $p = 12$ MPa), a sample is discharged from the system until the next desired pressure has been obtained. The temperatures of the measuring cell and the VLE-cell can be controlled at individual set points. This approach allows the measurement of an arbitrary number of points along an isotherm in the supercritical region (cf. Figure 2, points 3 to 5 for measuring cell and VLE-cell). Point 6 in Figure 2 is the last point obtained via discharging sample from the system, and it is the first point where phase equilibrium can be found in the VLE-cell. As the liquid level in the VLE-cell must be adjusted specifically it is very important that the set point temperature of the VLE-cell is calculated in advance with the GERG-2008 equation of state [8]. For this purpose a special dynamic tableau has been programmed in Microsoft Excel. By means of this program a temperature can be calculated at which the volume of the liquid phase forms approx. 70 % in the VLE-cell for a given mixture composition and a desired pressure (below critical pressure). While phase equilibrium now exists in the VLE-cell, the first density measurement point in the homogeneous liquid phase can be determined in the measuring cell.

From point 6 (Figure 2), the pressures in the system are no longer set by discharging a sample but via the temperature of the VLE-cell. The total mass of fluid in the system thereby always remains constant. If the temperature of the VLE-cell is reduced, the pressure in the entire system will also decrease. Based on calculations with the GERG-2008 equation of state it was confirmed for several typical LNG compositions that decreasing the temperature of the VLE-cell leads to substance flowing from the measuring cell into the VLE-cell. This ensures that no changes in concentration occur in the measuring cell as the thin connection capillary between the measuring cell and the VLE-cell is automatically flushed in the direction of the VLE-cell when moving towards a new measurement point. To set a new measurement point, the temperature to be obtained for the VLE-cell must be determined in advance. This temperature is also calculated with the program based on the GERG-2008 equation of state, mentioned in the previous paragraph, with the composition and the pressure as known input values. The result is a temperature just above saturation temperature for a liquid volume in the VLE-cell between 30% and 70%. This approach leads to measurement points 7 to 14 shown in Figure 2. The last measurement point on an isotherm (cf. point 15 in Figure 2), located below and very closely to the saturated-liquid line, is obtained by discharging a small quantity of fluid from the measurement system. This measurement point must then be set precisely in such a way that a state of phase equilibrium exists with a vapor volume in the measuring cell of not more than 1 % to 2 %. In this state the VLE-cell only contains the gas phase from the state of phase equilibrium in the measuring cell at a temperature which is some K higher. The slightly higher temperature of the VLE-cell is indispensable to avoid condensation of individual mixture components in the VLE-cell. This could lead to a change in vapor pressure. Moreover, in measurement point 15 (Figure 2) the special geometry of the measuring cell becomes very important because its upper part is specifically designed to be used as "vapor space". This also ensures that the permanent magnet of the magnetic suspension coupling is always immersed in liquid, and thus precluding detrimental effects on the function of the magnetic suspension coupling. In this way saturated-liquid densities and also vapor pressures can be measured simultaneously. Hence, the saturated-liquid density is measured as the last point on an isotherm.

Different approaches for the densimeter operation

If, for example, the saturated-liquid density as the last measurement point on an isotherm has been measured, the measurements will continue on the next higher isotherm. It could basically be assumed that, starting from the last measurement point on an isotherm (cf. for example point 15 in Figure 2), the next measurement point could be obtained by completely refilling the measuring device. But this is only one possibility. The calculations made by Richter [9] confirm other approaches as feasible options to operate the densimeter. These different approaches are rather complex and are not suitable to be described in the present paper. An additional publication will be required to point out the details first specified in [9]. It should be noted that the different approaches for the densimeter operation are only based on theoretical calculations successfully carried out for three different LNG-qualities. The best way of operating the densimeter must be investigated experimentally! Thereby it is essential that the measurement data are always reproducible with the chosen way of operation. After the setup of the apparatus a test of the different approaches will demonstrate which one is the most suitable.

5. PRINCIPLE OF DENSITY MEASUREMENT

The density measurement with a single-sinker densimeter is based on the Archimedes (buoyancy) principle to provide an absolute determination of the density. This method is applied in combination with a magnetic suspension coupling and a basic load compensation (differential method). This general type of instrument is described by Wagner and Kleinrahm [13]. The functional principle of the single-sinker technique is shown schematically in Figure 3 and is only briefly described here.

A sinker of known Volume $V_S(T,p)$ is weighed in the fluid of interest. The balance reading of the sinker immersed in the fluid $m_{S,fluid}$ is the difference between the mass of the sinker and the buoyancy of the fluid:

$$m_{S,fluid} = m_{S,vac} - \rho_{fluid} \cdot V_S(T,p) ,$$

where $m_{S,vac}$ corresponds to the mass of the sinker, which may be determined by weighing in an evacuated measuring cell. To yield the fluid density the equation can be simply rearranged:

$$\rho = \frac{m_{S,vac} - m_{S,fluid}}{V_S(T,p)}$$

The sinker (silicon monocrystal: $V \approx 26.07 \text{ cm}^3$, $m \approx 60.71 \text{ g}$, $\rho \approx 2.329 \text{ g/cm}^3$) is located in a pressure-tight measuring cell (CuCr1Zr). For density measurement the sinker is connected to a commercial analytical balance via a coupling device. The magnetic suspension coupling transmits the gravity and buoyancy forces on the sinker to the analytical balance, thus isolating the fluid sample (which may be at high pressure and very low temperature) from the balance, which is placed under ambient conditions. The central elements of the coupling are two magnets, one on each side of a nearly nonmagnetic, pressure-separating wall. The top magnet, which is an electromagnet with a ferrite core, is attached to the under-pan weighing hook of the balance. The bottom (permanent) magnet is immersed in the fluid sample; it is held in stable suspension with respect to the top magnet by means of a feedback control circuit making fine adjustments in the electromagnet current.

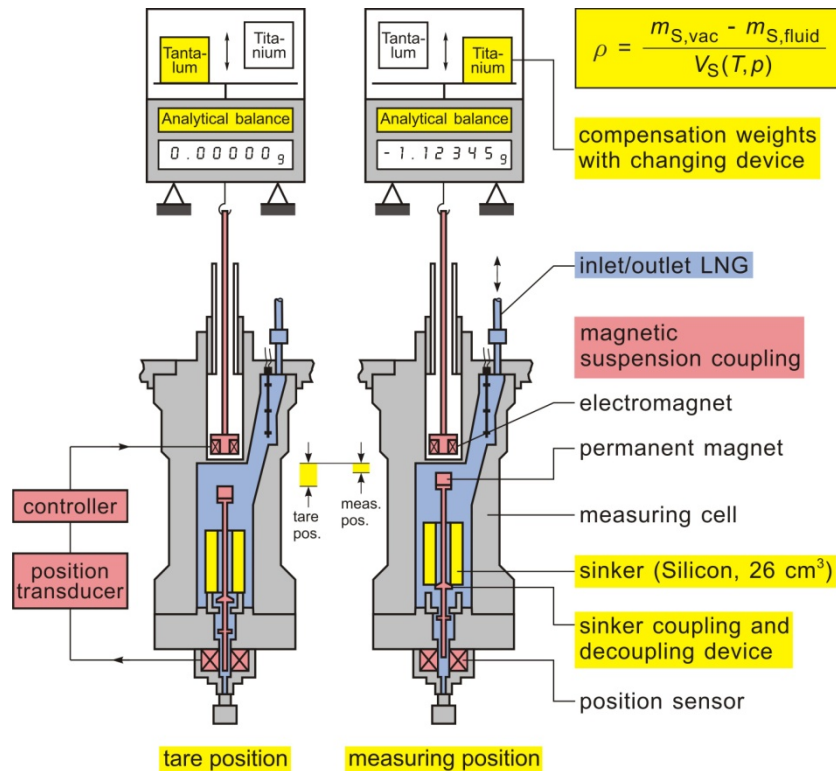


Figure 3: Principle of the single-sinker densimeter technique (with buoyancy-free basic load compensation).

To couple and decouple the sinker to the balance, the permanent magnet can be moved up and down in a vibration-free manner. In the tare position the permanent magnet is in stable suspension at a relatively large distance (approx. 4 mm) to the pressure-separating wall of the coupling housing. In this position of the permanent magnet, the sinker rests on the bottom of the cell, and the balance is tared. To obtain the measuring position, the permanent magnet is smoothly moved upwards (up to a distance of approx. 1 mm to the pressure-separating wall) and lifts the sinker via the sinker coupling and decoupling device. In this position the sinker is suspended to the balance and can be weighed. By moving the sinker several times into the two stable suspension positions the weighing result can be confirmed statistically, and the zero point drift of the balance can be recorded. As the permanent magnet transfers the entire load almost exclusively to the ferrite core of the electromagnet the coil only serves to stabilize the equilibrium. Normally current-free operation prevents heating of the coupling housing and thus detrimental effects on the thermal equilibrium in the measuring cell.

According to Wagner and Kleinrahm [13] the single-sinker method allows for compensation of almost all interfering side effects. But an effect which absolutely needs to be taken into account in highly accurate density measurement is the force transmission error of the magnetic suspension coupling. The force transmission error was therefore thoroughly investigated by McLinden, Kleinrahm and Wagner [14]. The result presented by McLinden et al. is an empirical model for the determination and correction of the force transmission error.

6. DESIGN OF THE LNG-DENSIMETER

Density measurement

The detailed design of the core apparatus of the new densimeter is shown by a sectional drawing in Figure 4. The core apparatus basically consists of the measuring cell, the magnetic suspension coupling (manufactured by Rubotherm, Germany), the intermediate plate, the VLE-cell, the intermediate (radiation) shield, the insulation cylinder and the analytical balance. The measuring cell unit which is connected to the intermediate plate via three stainless steel rods consists of the measuring cell (made of CuCr1Zr) containing the sinker made of a silicon monocrystal ($V \approx 26.07 \text{ cm}^3$, $m \approx 60.71 \text{ g}$, $\rho \approx 2.329 \text{ g/cm}^3$), the bottom portion of the measuring cell (made of Alloy A-286) including the position sensor, the magnetic suspension coupling and the measuring cell plate carrying the ring-thermostat as well as the measuring cell (radiation) shield. The intermediate plate which is connected to the base plate via another three stainless steel rods carries the intermediate (radiation) shield and a ring-thermostat. The VLE-cell is located on the same level as the intermediate plate and is connected to the measuring cell via a thin approx. 0.15 m long stainless steel tube (3 mm inside diameter). Via another tube in the upper part of the VLE-cell, the VLE-cell and the measuring cell are connected to the filling line, the pressure measurement circuit, the vacuum circuit and the waste gas lines. Measurements of LNG densities in the homogeneous gas region are not included within the present project. Nevertheless, the measuring cell is provided with an additional fitting on the bottom portion of the measuring cell which can be connected to the filling line. In this way the measuring cell can be filled and it can also be purged with the relevant gas sample for measurements in the gas phase if required later on. The gas purge is necessary to preclude any measurement errors resulting from sorption effects of single components of the gas mixture to be measured with regard to the inner surfaces of the measuring cell. These effects could significantly distort gas composition and thus also the density measured for the sample gas.

For measuring the densities of mixtures in the homogeneous liquid phase, the liquid-level in the VLE-cell needs to be measured using a special liquid-level indicator [15]. Especially for measuring saturated-liquid densities, a second liquid-level indicator of the same design is installed in the measuring cell. For this purpose the upper part of the measuring cell is specifically designed to create a small vapor volume of not more than 2 % of the measuring cell volume. The liquid-level indicator mentioned is installed in this part of the measuring cell. The calculations made for checking the measurement method resulted in different volumes for the measuring cell and the VLE-cell [9]. The optimum combination identified was a measuring cell volume of 100 cm^3 and a VLE-cell volume of 30 cm^3 .

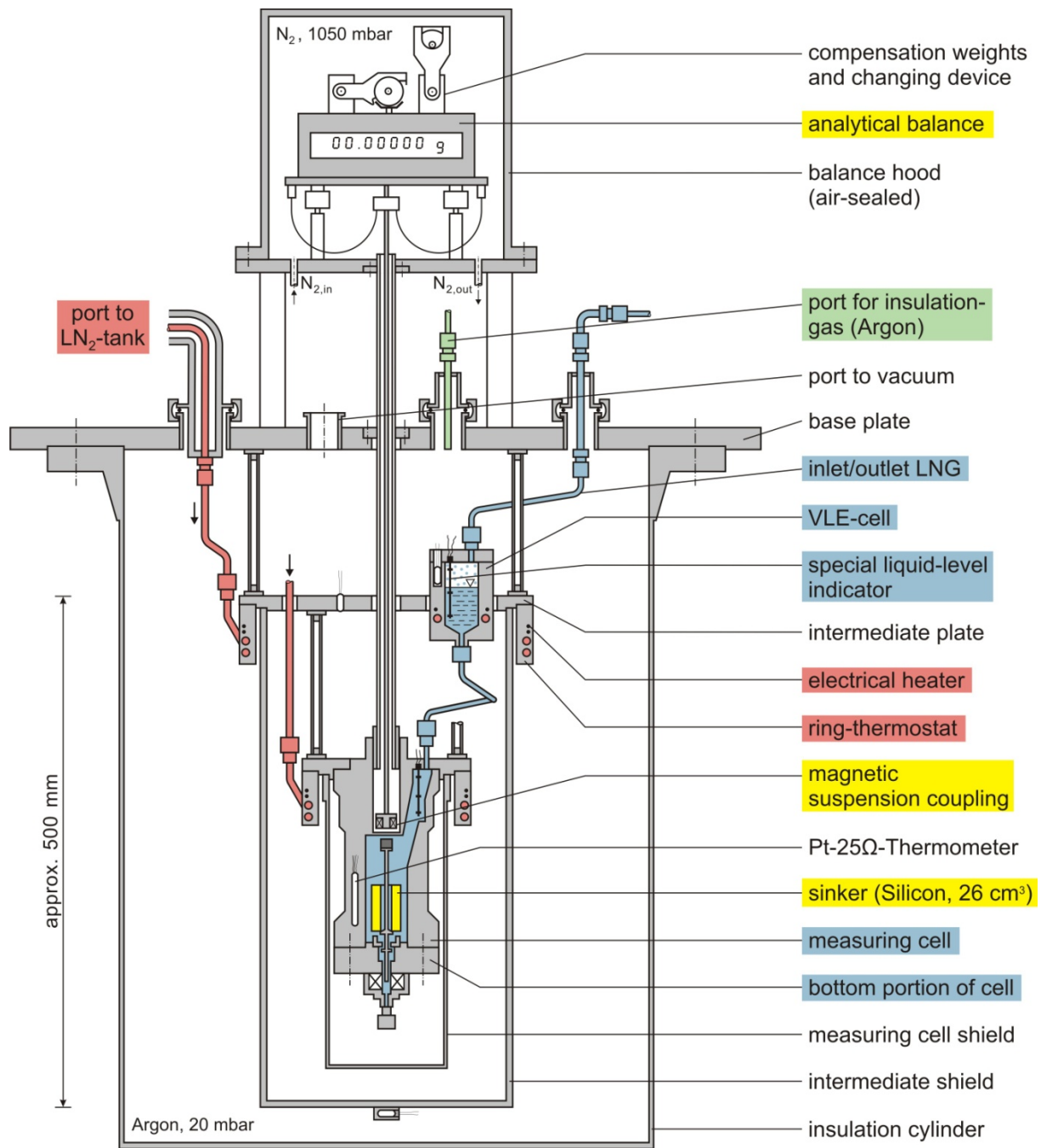


Figure 4: Detailed design of the core apparatus of the new single-sinker densimeter for the accurate measurement of LNG densities.

Details of the density measurement principle have already been given in Section 5. Briefly, for density measurement the sinker can be connected to the analytical balance (model XP of Mettler) by means of an appropriate coupling device. The force is transferred from the measuring cell (pressure chamber) to the balance (ambient atmosphere) via a non-contact magnetic suspension coupling which is controlled electronically. The magnetic suspension coupling can move into two positions: the tare position, which is the lower position, and the measurement position, which is the upper position. To measure the density of the fluid in the measuring cell the sinker is coupled to and decoupled from the balance several times to ensure that the buoyancy force is determined with higher accuracy by calculating an average value.

Pressure measurement

For pressure measurement highly accurate pressure sensors based on the quartz crystal resonator technology of Paroscientific are used which can be connected directly to the measuring cell depending on measurement range. Several devices covering different measurement ranges are necessary to ensure that the envisaged measurement uncertainty for pressure of approx. 0.01% of the measured value is observed over the entire pressure measurement range from 0 MPa to 12 MPa. One way of ensuring that the envisaged measurement uncertainty is achieved is the use of three pressure sensors (measurement uncertainty each 0.01 % of full scale) covering the measurement ranges from 0 MPa to 0.31 MPa, 0 MPa to 6.89 MPa and 0 MPa to 13.8 MPa. The measurement accuracy of the sensors can be traced to a national standard and is certified by a calibration certificate. Moreover, to regularly check the measurement uncertainty associated with the pressure sensors, a dead-weight gauge of DH Budenberg (model 5200, measurement range: 0.14 MPa to 20 MPa, measurement uncertainty: 0.005% of measured value) is used, which is isolated from the pressure measurement circuit via a differential pressure transducer of Rosemount (model 3051, measurement range: - 16 mbar to + 54 mbar). In addition, to accurately determine air pressure, a Digiquartz[®] barometer of Paroscientific (model 1650-1010) is used covering a measurement range from 0.08 MPa to 0.11 MPa. The pressure sensors and the differential pressure transducer are assembled on the panel of the densimeter which is thermostated at a constant temperature of 40 °C. Thus, the sensors are decoupled from disturbing outer influences. Also it is ensured that no droplets of liquefied natural gas can get into the sensors.

Temperature control and measurement

The measuring cell, measuring cell shield, intermediate plate and intermediate shield as well as the base plate and insulation cylinder are arranged in such a way that the heat flows from heat conduction and heat radiation into the measurement device are kept to a minimum. Instead of an elaborate insulation by high vacuum the insulation cylinder is filled with Argon (insulation gas) at a low pressure of about 20 mbar. This allows a simple design without requiring an expensive turbo-molecular pump. The described arrangement of components ensures an almost adiabatic condition of the measuring cell during the measurement process (e.g. at $T = 90$ K the heat flow to the measuring cell is only 4 mW). The temperature gradient along the cell is calculated to be less than 1 mK so that the measurement results are not influenced.

The temperatures of the measuring cell and of the VLE-cell are set with a PC control system. The temperature of the measuring cell is maintained constant within ± 2 mK, and the temperature of the VLE-cell is maintained within ± 5 mK. To obtain the desired temperature of the measuring cell liquid Nitrogen flows through the two ring-thermostats attached to the intermediate plate and to the measuring cell plate. As soon as a value just below set point temperature is obtained the liquid Nitrogen mass flow is controlled by a mass flow controller and a rotameter. The temperature of the intermediate plate is set approx. 3 K lower than the temperature of the measuring cell and is controlled by an electric heater of Thermocoax (model ZUZ) installed in the ring-thermostat. The current for the electrical heater is provided by a modular power supply of Agilent (model N6730/40/70 series) and digitally controlled by a PC. During stationary operation liquid Nitrogen no longer flows through the ring-thermostat which is attached to the measuring cell plate. The measuring cell is exclusively cooled by the intermediate plate and by the intermediate (radiation) shield attached to the intermediate plate. The temperature of the measuring cell is also controlled via an electric heater installed in the ring-thermostat. Temperature control for the VLE-cell is similar, but it is independent of the control circuit for the measuring cell and the intermediate plate. In this case as well a controlled mass flow of liquid Nitrogen is sent through special lines in the wall of the VLE-cell, which also carries an electric heater.

The temperature of the measuring cell is measured by two 25 Ω platinum resistance thermometers (model 162D of Goodrich, USA) which are installed in opposite thermometer wells in the measuring cell wall. A precision resistance bridge (model F18 of ASL, UK) is used to determine the resistance ratios between one of the two thermometers each and a thermostated 25 Ω reference resistor of Tinsley. The temperatures of the intermediate plate and the VLE-cell each are measured with a 100 Ω platinum resistance thermometer (model S1059PA of Minco, USA), the temperature values being determined automatically with a resistance bridge with an internal reference resistor (model MKT 50 of

Anton Paar, Austria). Because of the temperature measurement range from 90 K to 290 K the thermometers are calibrated in accordance with ITS-90 at the triple points of Argon ($T_{tr,Ar} = 83.8058$ K), Mercury ($T_{tr,Hg} = 234.3156$ K) and Water ($T_{tr,H_2O} = 273.1600$ K) plus at the melting point of Gallium ($T_{melt,Ga} = 302.9146$ K). Since only few calibration services have the Argon fixed point, the boiling point of Nitrogen ($T_{b,N_2} \approx 77.35$ K) may be used as a calibration point instead of the triple point of Argon. The total measurement uncertainty for temperature is estimated to be less than 15 mK based on the measurement uncertainty involved in the envisaged temperature measurement chain for the measuring cell and the planned temperature control as well as based on the experimental experience available at the Chair of Thermodynamics at Ruhr-University Bochum.

Overview of total system

Figure 5 shows a schematic of the configuration planned for the new densimeter. At the centre is the frame (Item GmbH) with the core apparatus which is mounted below the base plate. The analytical balance with the compensation weights is installed above the base plate under a draft hood. To the right of the frame with the core apparatus is another frame (Item GmbH). This frame carries the thermostated panel (valve plate) with all valves required for filling the measuring cell circuit and the pressure measurement circuit. To the right of this valve plate another valve plate is placed, carrying the flow control valves for adjusting the Nitrogen cooling flow through the ring thermostats on the measuring cell plate and on the intermediate plate as well as through the VLE-cell. Below the two valve plates the figure shows the dead-weight gauge with the required weights to check the pressure sensors or to determine in the pressure in the measuring cell when necessary. Below the frame a slide vane rotary vacuum pump for evacuating the measuring cell and a membrane vacuum pump for evacuating the insulation cylinder are placed. To the left of the frame with the core apparatus in Figure 5 a 150 L tank for liquid Nitrogen is placed. This tank provides the coolant for thermostating the densimeter. To the left of the tank a 19" instrument-rack is located, carrying the entire measurement electronics.

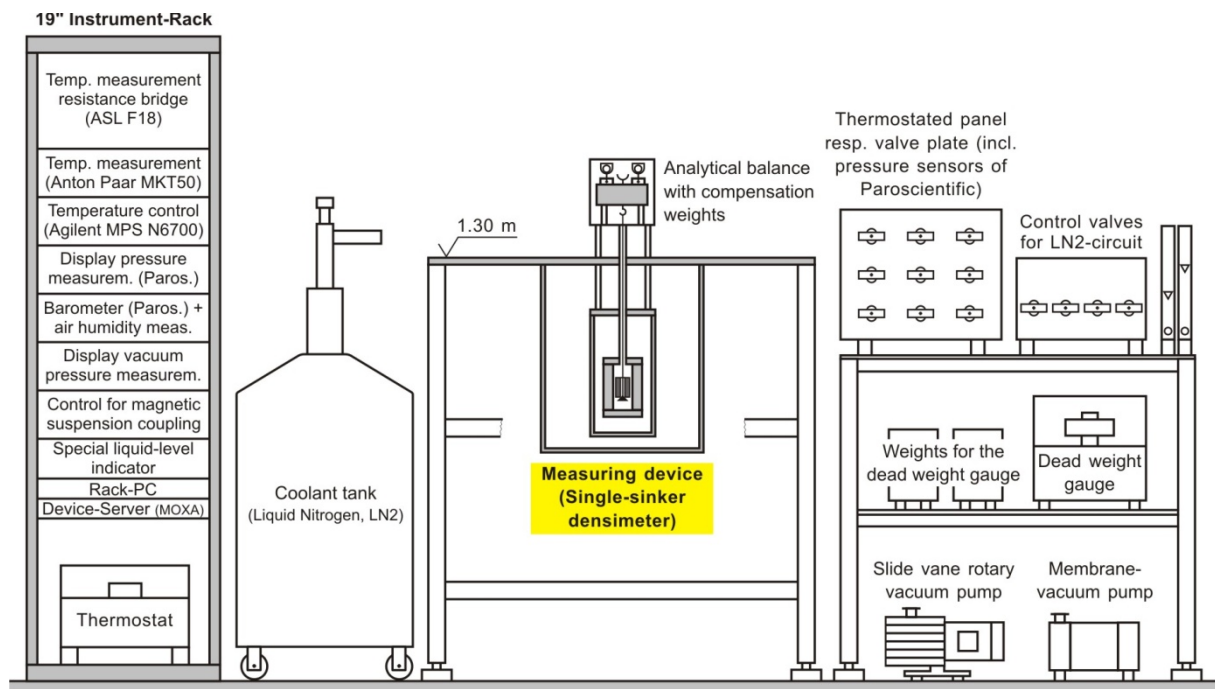


Figure 5: Schematic of the new single-sinker LNG-densimeter.

7. CONCLUSION AND OUTLOOK

The designed densimeter will probably achieve a measurement uncertainty for density of 0.02 % ($k = 2$). This value does not include the uncertainty associated with gas analysis which is to be added. The influence on density corresponds to approx. few 0.01 %. The new measurement method is expected to ensure that mixture composition will not change during the entire measurement process. Thus, the certified uncertainty of a gas analysis can be considered valid for measurements with the new densimeter. The better the gas analysis, the more accurate the measurement results. In the case of binary mixtures the composition could also be determined very accurately via the density at standard conditions [15]. Although the densimeter has been developed specifically for measuring LNG densities, the new measurement method is also suitable for measuring other mixtures. However, modifications could be required depending on the mixture to be measured.

The densimeter will be set up in 2011 and 2012 within the scope of the joint research project "Metrology of LNG" (www.lngmetrology.info) of the European Metrology Research Programme (EMRP) and a research project of the European Gas Research Group (involved GERG-partners: E.ON Ruhrgas AG, Germany; Statoil, Norway; Shell Global Solutions International, The Netherlands; Enagas, Spain). Until the middle of 2013 these projects include the measurement of the densities of four different LNG-qualities in the homogeneous liquid phase and along the saturated-liquid line (including vapor pressures). Data at supercritical pressures will also be measured. All the newly measured data are going to be used to evaluate widely used thermophysical mixture models such as the Revised Klosek and McKinley Method of McCarty [3], and the GERG-2008 Equation of State for Natural Gases of Kunz and Wagner [8]. If necessary the models will be adjusted as far as possible or additional data will be measured to make further improvements on the relevant equations of state.

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