

# Development of a new densimeter for the combined investigation of dew-point densities and sorption phenomena of fluid mixtures

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**Abstract.** For the determination of dew-point densities and pressures of fluid mixtures, a new densimeter has been developed. The new apparatus is based on the well-established two-sinker density measurement principle with the additional capability of quantifying sorption effects. In the vicinity of the dew line, such effects cause a change in composition of the gas mixture under study, which can significantly distort accurate density measurements. The new experimental technique enables the accurate measurement of dew-point densities and pressures and the quantification of sorption effects at the same time.

**Keywords:** saturated vapor density; dew point; sorption phenomena; two-sinker densimeter

## 1. Introduction

The investigation of the phase behavior of fluid mixtures is a major focus of thermophysical property research. For the improvement of mixture models that describe the phase boundary between liquid and vapor, accurate experimental data are necessary. Considering that the dew line, which separates the homogeneous vapor region from the heterogeneous two-phase region, is very difficult to determine accurately, a significant need for further research arises.

During the measurement of mixture properties, Richter and Kleinrahm [1] showed that the effect of sorption phenomena can be significant. Especially close to the phase boundary, sorption effects can cause a change in mixture composition and, therefore, a change in density. Generally, in the field of thermodynamic property measurements, only a few researchers have considered and reported such distorting effects, *e.g.*, in acoustic measurements [2,3]. To go beyond the state-of-the-art, a better understanding of sorption phenomena is required, and a new experimental technique for the measurement of dew-point densities of fluid mixtures, which overcomes the difficulties in existing techniques, is needed.

The most accurate method for the measurement of fluid densities is the two-sinker density measurement principle, which was developed in the early 1980s by Kleinrahm and Wagner [4,5]. This method is based on the Archimedes' buoyancy principle, which is used in a differential method, thus,

providing an absolute determination of density. Through the use of two sinkers with equal mass, equal surface area, and equal surface characteristics, but different volumes, a two-sinker densimeter cancels the effects of adsorption to first order (in so far as they affect the density), but it does not compensate for changes in mixture composition due to sorption effects within the measuring system.

The measuring system presented in this technical design note is based on the two-sinker measurement principle and extends it to also quantify the effects of adsorption. The result is a novel four-sinker densimeter, which allows the combined measurement of dew-point densities with high accuracy and the investigation of sorption effects close to the dew line.

## **2. Preparatory work**

Richter and Kleinrahm [1] showed that adsorption and desorption can significantly influence the accuracy of density measurements. In that study, the density of a 15-component natural gas mixture was measured along isotherms at least 25 K above the maximum dew-point temperature. The measurements were carried out with a two-sinker magnetic suspension densimeter, and even with a relatively large distance to the dew line, sorption effects caused significant errors in density of up to 0.1 %. It was recommended to avoid porous materials inside the measuring cell (including elastomeric seals) and mechanically polished surfaces (in preference to electrolytically polished surfaces) to reduce sorption effects.

McLinden and Richter [6] investigated a novel method for the detection of dew-point densities and pressures using the NIST two-sinker densimeter [7]. The density of three (methane + propane) mixtures was measured along isotherms with pressure increasing from the homogeneous gas phase into the two-phase region. By using an alternative solution of the working equations, the adsorbed mass on the sinker surfaces was determined. It was demonstrated that the “adsorbed mass” analysis of isothermal experiments provides a comparatively accurate determination of the dew-point temperature, pressure, and density, but there was uncertainty in the composition of the vapor phase.

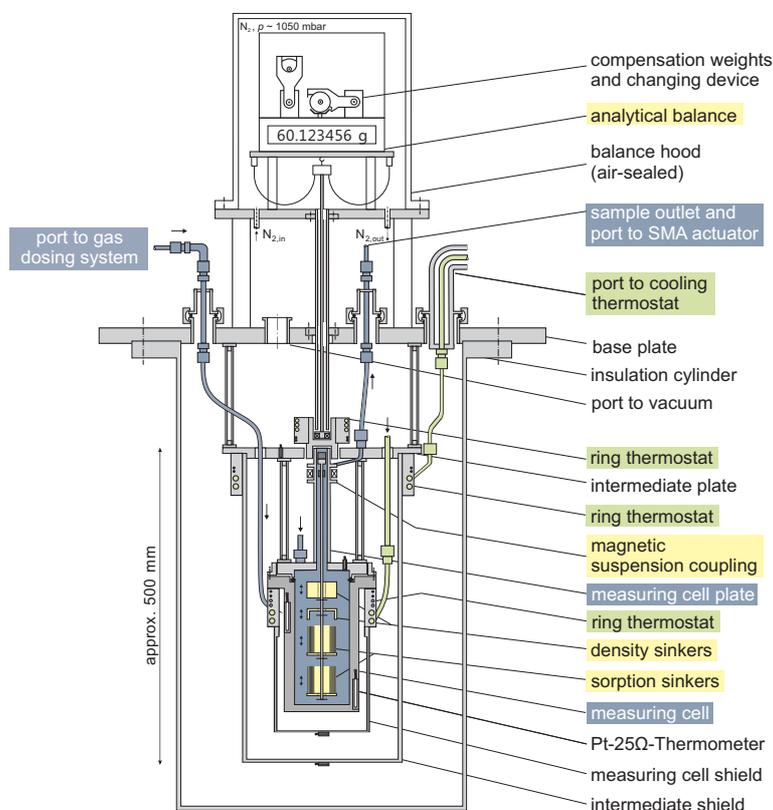
Further work by Richter and McLinden [8] investigated the quantification of sorption phenomena on nonporous media near the dew point of binary mixtures. They used the same two-sinker densimeter as in the previous study [6] but with a modification of the sinkers. Instead of using the “normal” sinkers with nearly the same mass, same surface area and significantly different volume, they used sinkers with nearly the same mass and volume but different surface areas (ratio  $\approx 2.24$ ). This modification allowed an increased sensitivity to sorption effects. However, this came at the expense of increasing the uncertainty in density. Measurements were carried out along isotherms, starting with a low pressure and increasing into the two-phase region. The results with (methane + propane) and (argon + carbon dioxide) mixtures showed three different regions, namely (1) the homogeneous gas region with minor sorption effects, (2) a transition region, indicated by a sharp increase in the amount of adsorbed mass and (3) the region of bulk condensation. The transition region corresponds to capillary

condensation followed by wetting in microscale pits and scratches, and the authors hypothesized that the dew point lay within this second region.

### 3. Apparatus description

The preparatory work reveals that the investigation of dew-point densities requires a new experimental technique. As a result, a novel four-sinker densimeter has been developed and designed. The novelty of this apparatus is the application of the traditional two-sinker technique for the accurate measurement of fluid density together with two additional “sorption sinkers.” This will allow a combined investigation of densities and sorption phenomena in the homogeneous gas phase and close to the dew point.

The densimeter is designed for the accurate investigation of dew-point densities and the  $(p, \rho, T, x)$  behavior of mixtures in the homogeneous gas region over a wide range of temperature and pressure (193.15 K to 423.15 K; 0.1 MPa to 20 MPa). The apparatus basically consists of a gold-plated copper measuring cell (which contains the four sinkers), a magnetic suspension coupling, an analytical balance on the top, a measuring cell plate (*i.e.*, top closure of the measuring cell combined with the bottom housing of the magnetic suspension coupling), two temperature controlled shields and an outer insulation cylinder. A schematic diagram of the new apparatus is illustrated in Figure 1.



**Figure 1** Schematic diagram of the novel four-sinker densimeter.

### 3.1. Density measurement principle

A detailed description of the density measurement principle is given by Kleinrahm and Wagner [4,5], and only a brief description is given here. Two density sinkers are required for density measurements. The first sinker is made of single-crystal silicon (mass  $m_1 \approx 60$  g; surface  $A_1 \approx 57$  cm<sup>2</sup>; volume  $V_1 \approx 25.7$  cm<sup>3</sup>, gold plated surface), and the second sinker is made of stainless steel ( $m_2 \approx 60$  g;  $A_2 \approx 57$  cm<sup>2</sup>;  $V_2 \approx 7.6$  cm<sup>3</sup>, gold plated surface). Both sinkers have nearly the same mass, the same surface area and the same surface finish but a significant difference in volume (ratio  $\approx 3.4$ ). Each sinker is weighed separately (via the magnetic suspension coupling described in section 3.3) with an analytical balance (Sartorius MSA66S-000-DH\*, weighing range 0 – 65 g, resolution 1  $\mu$ g) while they are suspended in the fluid of unknown density. In addition to the sinkers, two calibration masses ( $m_{\text{tare}} \approx 22$  g,  $m_{\text{cal}} \approx 82$  g), made of titanium and tantalum, respectively, are weighed directly on the balance pan. The buoyancy force on the sinkers is equal to the weight of the submerged fluid. Thereby, the density can be determined by the basic equation:

$$\rho_{\text{fluid}} = \frac{(m_1 - m_2) - (W_1 - W_2)}{V_1 - V_2} \quad (1)$$

where  $m$  and  $V$  are the sinker mass and volume,  $W$  is the balance reading and the subscripts refer to the two sinkers. But equation (1) must be extended to account for sorption effects and the so-called “force transmission error”. The analysis of the force transmission error was developed by McLinden, Kleinrahm and Wagner [9]; basically, they wrote out the forces acting on the balance for each of the weighings and solved the resulting system of equations for the unknowns of interest. Weighing data for two “density sinkers” together with the two calibration masses are sufficient to solve for the fluid density  $\rho_{\text{fluid}}$ , a parameter  $\Phi$  considering the small force transmission error of the magnetic suspension coupling, a parameter  $\beta$  related to the masses that are identical for all weighings, and a balance calibration factor  $\alpha$ . In [6], the equations were solved in a different way to yield the difference in adsorbed mass  $\Delta m_{\text{sorp}}$  on sinker 2 relative to that on sinker 1, but  $\Phi$  could no longer be determined, and the uncertainty in  $\rho_{\text{fluid}}$  was larger. Thus, additional weighing data are required to provide both, accurate fluid densities and quantification of sorption effects. This is done here with two additional sinkers, which we term “sorption sinkers.”

### 3.2. Sorption measurement principle

The two sorption sinkers (sinker 3 and 4) are made of stainless steel and are identical in construction but have a different surface finish ( $m_3 \approx m_4 \approx 60$  g;  $A_3 \approx A_4 \approx 440$  cm<sup>2</sup>;  $V_3 \approx V_4 \approx 7.6$  cm<sup>3</sup>). These sinkers are made up of six concentric rings of foil welded to a bottom support disk. The surface of

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\* Certain trade names and products are identified only to adequately document the experimental equipment and procedure. This does not constitute a recommendation or endorsement of these products by the National Institute of Standards and Technology, nor does it imply that the products are necessarily the best available for the purpose.

sinker 3 is gold plated like sinkers 1 and 2, while sinker 4 has a rough surface. Furthermore, the surface area of the two sorption sinkers is much greater than that of sinkers 1 and 2 (ratio  $\approx 7.7$ ).

As in the original data analysis [6-9], the forces on the balance for the weighings of each sinker and calibration mass can be written as:

$$W_1 = \alpha \cdot \left[ \phi \cdot \left\{ (m_1 + m_{\text{sorp},1}) - \rho_{\text{fluid}} \cdot \left( V_1 + \frac{m_{\text{sorp},1}}{\rho_{\text{condensate}}} \right) \right\} + \beta \right] \quad (2)$$

$$W_2 = \alpha \cdot \left[ \phi \cdot \left\{ (m_2 + m_{\text{sorp},2}) - \rho_{\text{fluid}} \cdot \left( V_2 + \frac{m_{\text{sorp},2}}{\rho_{\text{condensate}}} \right) \right\} + \beta \right] \quad (3)$$

$$W_3 = \alpha \cdot \left[ \phi \cdot \left\{ (m_3 + m_{\text{sorp},3}) - \rho_{\text{fluid}} \cdot \left( V_3 + \frac{m_{\text{sorp},3}}{\rho_{\text{condensate}}} \right) \right\} + \beta \right] \quad (4)$$

$$W_4 = \alpha \cdot \left[ \phi \cdot \left\{ (m_4 + m_{\text{sorp},4}) - \rho_{\text{fluid}} \cdot \left( V_4 + \frac{m_{\text{sorp},4}}{\rho_{\text{condensate}}} \right) \right\} + \beta \right] \quad (5)$$

$$W_{\text{cal}} = \alpha \cdot [(m_{\text{cal}} - \rho_{\text{air}} \cdot V_{\text{cal}}) + \beta] \quad (6)$$

$$W_{\text{tare}} = \alpha \cdot [(m_{\text{tare}} - \rho_{\text{air}} \cdot V_{\text{tare}}) + \beta] \quad (7)$$

where  $m_{\text{sorp},i}$  is the adsorbed mass on sinker  $i$  and  $\rho_{\text{condensate}}$  is the density of the adsorbed mass. The parameter  $\beta$  accounts for the masses associated with the electromagnet and permanent magnet (subscripts e-mag and p-mag, respectively) of the magnetic suspension coupling and is given by:

$$\beta = \Phi \cdot \left\{ (m_{\text{p-mag}} + m_{\text{sorp,p-mag}}) - \rho_{\text{fluid}} \cdot \left( V_{\text{p-mag}} + \frac{m_{\text{sorp,p-mag}}}{\rho_{\text{condensate}}} \right) \right\} + (m_{\text{e-mag}} - \rho_{\text{air}} \cdot V_{\text{e-mag}}) + W_{\text{zero}} \quad (8)$$

As an extension of the original analysis, the equations also include the adsorbed mass and the change in volume due to the adsorbed material on each sinker and the permanent magnet. By assuming that the amount of adsorbed mass mostly depends on the surface area, the adsorbed mass can be simplified to:

$$m_{\text{sorp},i} = \gamma_i \cdot A_i, \quad (9)$$

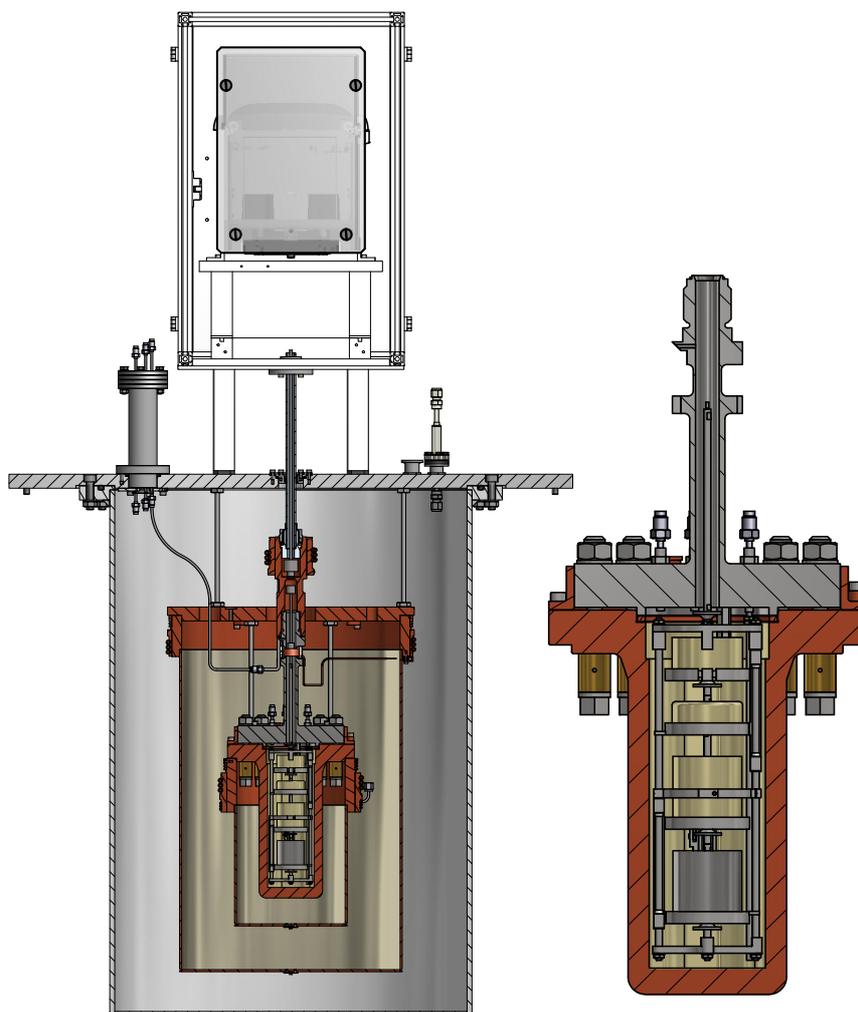
where  $\gamma_i$  is a proportionality factor and depends on the surface finish (smooth versus rough surface). Since sinkers 1, 2 and 3 are all gold-plated, the surface characteristics are similar so that the surface finish factor  $\gamma_{1,2,3}$  is equal for these three sinkers. Sinker 4, however, has a rough surface and has different surface characteristics ( $\gamma_{1,2,3} \neq \gamma_4$ ).

By solving equations 2–7 the six unknowns of interest (namely,  $\alpha$ ,  $\beta$ ,  $\rho_{\text{fluid}}$ ,  $\gamma_{1,2,3}$ ,  $\gamma_4$  and  $\Phi$ ) can be calculated. For the determination of the change in mixture composition, the total amount of adsorbed mass has to be calculated. Therefore, the amount of adsorbed mass on the walls of the measuring cell and on the surface of the sinker changing device has to be estimated. Since the measuring cell is gold-plated (like sinkers 1, 2 and 3) and the sinker changing device is made of stainless steel (like sinker 4),

the adsorbed mass on these surfaces can be estimated by equation (9). A VLE equation of state for the mixture of interest calculates  $\rho_{\text{condensate}}$  and the composition of the condensed phase  $x_{i,\text{condensate}}$  by assuming that the condensed material is at the same pressure as the vapor phase and in equilibrium with it. By combining the total amount of adsorbed mass, the composition  $x_{i,\text{condensate}}$  and the density  $\rho_{\text{condensate}}$  of the condensate, the composition of the remaining vapor phase can be calculated through a mass balance.

### 3.3. Apparatus design

A detailed cut away view of the four-sinker densimeter and its measuring cell is shown in Figure 2.



**Figure 2** Left: Detailed cut away view of the four-sinker densimeter. Right: Magnified view of the measuring cell and measuring cell plate.

The four sinks are located inside the measuring cell. The two density sinks are located at the top of the cell, while the two sorption sinks are located at the bottom of the measuring cell. Each sink is weighed by lowering them one-at-a-time onto the suspension rod by actuators employing a shape memory alloy (SMA).

The magnetic suspension coupling is a key component of the weighing system. It allows the contactless weighing of the sinkers, which are immersed in the fluid of unknown density, with the balance. Furthermore, the magnetic suspension coupling separates the fluid sample (which may be at high pressure and temperature) from the balance, which is at ambient conditions. The magnetic suspension coupling consists of a permanent magnet, an electromagnet and a position sensor. The permanent magnet is located inside the upper part of the measuring cell plate, while the electromagnet is attached to the under-pan weighing hook of the balance and is located outside the fluid sample. To connect the sinkers to the balance, a suspension rod for the sinkers is attached to the permanent magnet.

The measuring cell is made of copper and has an inner volume of 632 cm<sup>3</sup>; it is attached to the measuring cell plate. The measuring cell shield and thermostat ring are directly attached to the measuring cell and include an electrical heater as well as cooling tubes. The temperature of the measuring cell is measured with a 25  $\Omega$  standard platinum resistance thermometer (SPRT, model: 162D, Rosemount Aerospace, USA) and a thermometry bridge (model: Super Thermometer 1595A, Fluke Calibration, USA). To measure any vertical temperature gradient along the measuring cell wall, a second SPRT is installed near the bottom of the cell. The inner surfaces of the measuring cell are gold plated to achieve a smoother surface finish and thus to reduce sorption effects.

The measuring cell plate is made of Inconel 625 and acts also as the lower part of the housing of the magnetic suspension coupling. The coupling housing, which is made of almost-non-magnetic copper-beryllium, is connected to the base plate of the balance hood by a tube. To control the temperature of the sample inside the coupling housing, a ring thermostat including electrical heaters and cooling tubes is attached to the coupling housing (see figure 2, left view).

The measuring cell plate is suspended by three thin stainless-steel tubes from the intermediate plate, which, in turn, is suspended from the base plate. Similar to the measuring cell plate, a temperature controlled shield is directly attached to the intermediate plate. An insulation cylinder, which is evacuated, surrounds the core apparatus.

For accurate measurements, precise temperature control is required. A refrigerated bath circulator (model: Proline Kryomat RP 3090CW, Lauda, Germany) is used to cool the apparatus to temperatures as low as 193.15 K. The power of the electrical heaters is controlled with programmable temperature controllers (model: PTC 10, Stanford Research Systems, USA). The pressure of the fluid is accurately measured with three absolute pressure transducers (model: 2300A-101-CE, max. 2.07 MPa; 31K-101-CE, max. 6.9 MPa; 43K-101-CE, max. 20.7 MPa, Paroscientific, USA), which are located inside a fully automated gas-dosing system and are constantly heated to  $T \approx 373.15$  K to prevent condensation of the sample.

For the investigation of dew-point densities, measurements will be carried out along isotherms with increasing pressure. The measurements will start in the homogeneous gas phase, at about 80 % of the dew-point pressure, and will go up to the dew point and into the two-phase region. An equilibration time of approximately 60 minutes will be required upon changing the pressure, and then a complete measurement sequence will require approximately 20 minutes.

#### **4. Conclusions and outlook**

After a detailed study of the influence of sorption phenomena in the homogeneous gas phase and in particular close to the dew line, a novel apparatus, to accurately determine dew-point densities, has been developed and designed. This new densimeter applies the well-established two-sinker density measurement principle in combination with two additional sinkers, to also allow the quantification of sorption phenomena on the sinker surfaces. The combined data analysis given by the two density sinkers and the two sorption sinkers will also yield information about the change in mixture composition due to sorption effects.

For commissioning and performance testing the new instrument, measurements with nitrogen, propane and carbon dioxide will be carried out. These pure fluids are well investigated, and the low uncertainties in density calculation with the respective equations of state [10-12] are well suited to validate the results obtained with the four-sinker densimeter. We will then focus on the study of binary mixtures.

As a major result, understanding and quantifying sorption phenomena close to the dew line represents an advance in the state of the art in thermodynamic property measurements of fluid mixtures. The resulting high-accuracy dew-point densities will enable significant improvements to mixture models.

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