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IN-SITU LIQUID DENSITY MEASUREMENT FOR LIQUID COLUMN MANOMETRY

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Abstract:
At PTB, an interferometric liquid column manometer for the pressure measurement up to 2 kPa is under development. Its *in-situ* liquid density measurement is a new approach for those primary pressure standards and makes the use of low-density liquids – low in comparison with the density of mercury, a liquid often used in other standards – possible. Such liquids, here, vacuum oils, offer an excellent sensitivity in length changes against pressure. The liquid density measurement concept is presented, together with the uncertainty estimation.

Keywords: liquid density; liquid column manometer; density standard; hollow sphere; primary pressure standard

1. INTRODUCTION

A liquid column manometer (LCM) realizes the Pascal, the unit of pressure in the International System of Units (SI), by measuring height changes of two liquid columns in a u-shaped tube, when the pressure inside one of the tubes changes. The newly forming equilibrium is developed between the increase in pressure and the gravitational and density driven hydrostatic pressure of the raised liquid column.

Such physics is fundamental and well-known; for the calculation of pressure, all measured input quantities, i.e., the column height, the gravity acceleration, and the liquid density, are SI traceable, which makes such an instrument a primary pressure standard.

This technique is widespread applied, in laboratories of the aircraft industry, accredited calibration laboratories or National Metrology Institutes, in these days usually in the low-pressure range around 0.2 MPa and below and could be used to calibrate force compensated piston gauges, especially in their lower pressure range.

Several older and recent developments [1]-[7] focused on the usage of vacuum oils as manometric liquids instead of mercury [8]-[10], an often used pure and stable but poisonous liquid. Against that, vacuum oils have low liquid densities – which increases the sensitivity of the pressure measurement by a factor of 10 or more, and a low vapour pressure – which makes the measurement of very small absolute pressures possible. But however, they suffer from high thermal volumetric expansion coefficients, gas absorption [2], [6] and possible long-term instability of their density. All these effects would be considered if the liquid density would be known, which means continuously measured. Such an instrument is presented in this paper.

2. IN-SITU LIQUID DENSITY MEASUREMENT BY FLOTATION OF A SOLID DENSITY STANDARD

Any object fully submerged in a liquid at rest is affected only by its weight force F_w and its buoyancy force F_b, and in the object's state of flotation, both forces are opposite and equal, so that they compensate each other. That means $|F_\mathrm{w}| = |F_\mathrm{b}|$ or rather, $\rho_\mathrm{s}\, V_\mathrm{s}\, g = \rho_\mathrm{l}\, V_\mathrm{s}\, g$, together with the density of the liquid ρ_l, the density of the solid object ρ_s, the volume of the solid object V_s and the gravitational acceleration g. Thus, the following simple equation remains:

$$\rho_\mathrm{l}(t,p) = \rho_\mathrm{s}(t,p), \tag{1}$$

also considering the dependence of both densities on the temperature t and the pressure p. For the density of the solid, this dependence $\rho_\mathrm{s}(t,p)$ can be described as follows:

$$\rho_\mathrm{s}(t,p) = \rho_\mathrm{sr}(t_\mathrm{r},p_\mathrm{r})[1-\gamma_\mathrm{s}(t-t_\mathrm{r}) + \kappa_\mathrm{s}(p-p_\mathrm{r})], \tag{2}$$

together with the reference temperature t_r, the reference pressure p_r, the thermal volumetric expansion coefficient γ_s, and the isothermal compressibility κ_s of the solid.

The combination of equation (1) and (2) results into:

$$\rho_\mathrm{l}(t,p) = \rho_\mathrm{sr}(t_\mathrm{r},p_\mathrm{r})[1-\gamma_\mathrm{s}(t-t_\mathrm{r}) + \kappa_\mathrm{s}(p-p_\mathrm{r})], \tag{3}$$

and is valid for the density of the liquid at a temperature t and pressure p, chosen in way that the solid is in a flotation state.

From (3) it can be seen that, under the flotation condition and with a known density of the solid, the density of the liquid in the point of solid standard flotation can be easily derived.

From calibrations, which only need to be repeated every few years, the solid's density can be accurately determined [11]. The solid then acts as a reference standard for an *in-situ* determination of the density of the liquid.

Inside a liquid column manometer, the liquid density needs to be known accurately in the reference pressure level (filling height of the liquid inside the u-tube setup). As at this place an integration of a liquid density measurement based on the flotation principle is hardly realisable, a different place for integration, like the lower end of the u-tube setup, is a good choice. However, the height difference between the level where the density is measured and where it needs to be known makes it necessary to consider the hydrostatic pressure gradient along the liquid, and with this, a vertical gradient in liquid density. In (4), with the compressibility of the liquid κ_l and the difference in the hydrostatic pressures $(p - p_\mathrm{h})$ between the two height levels, the liquid density for the reference pressure level of the manometer is calculated as follows:

$$\rho_\mathrm{l}(t, p_\mathrm{h}) = \rho_\mathrm{sr}(t_\mathrm{r}, p_\mathrm{r})[1 - \gamma_\mathrm{s}(t - t_\mathrm{r}) + \kappa_\mathrm{s}(p - p_\mathrm{r}) - \kappa_\mathrm{l}(p - p_\mathrm{h})], \quad (4)$$

To bring the solid into the flotation state, it is possible to control either temperature t or pressure p, the method then is called temperature-of-flotation (TFM) [12] or pressure-of-flotation method (PFM) [13], respectively.

In general, both methods are possible since the thermal expansion coefficient and the compressibility of liquids are larger than those of solids. For high-level liquid density measurements, the pressure-of-flotation method is commonly preferred, as the pressure can be changed easily and faster than the temperature, e.g., by changing the height of a flexible connected liquid-filed vessel, and with this, the hydrostatic pressure inside the experiment.

For the integration in a liquid column manometer, where pressure is the quantity to be accurately measured and, thus, cannot be used as a freely alterable parameter to control the liquid-solid density equilibrium, the temperature-of-flotation is the only possible method.

In such an application, the liquid density determination can be performed temporally before and after a pressure measurement series, i.e., in the morning and evening, by keeping the flotation temperature t during the pressure measurement series as constant as possible, and with this, the density of the liquid.

3. SOLID DENSITY STANDARD

An adequate solid density standard requires a large volume – as the density of objects with larger volume can be calibrated more precisely [11]; a density similar to the density of the manometric liquid – to be able to be applied in the temperature-of-flotation method; a low thermal volumetric expansion coefficient – as this is an important uncertainty component; and must be non-transparent – to make an optical detection of its flotation condition possible.

The solid density standard (Figure 1), created for the use in the interferometric liquid column manometer, is a nominally 100 cm³ hollow sphere made from Ti6Al4V – a widely used and well machinable alpha-beta phase titanium alloy – offering a low volumetric thermal expansion coefficient and low density of around 4430 kg/m³.

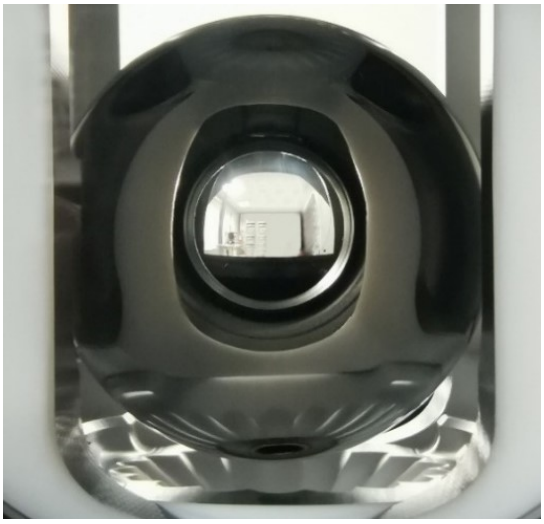

Figure 1: Titanium solid density standard DS1 of PTB and the PTFE centring cage of the density measurement chamber. Inside the centring cage, the density standard holds 5 mm free movement space in each horizontal direction and is presented, when being freely floating in the manometer's liquid, 10 mm above the lower stroke position.

To build a solid density standard of around 830 kg/m³ – the density value of the Edwards 45 liquid used inside the LCM [2] the standard was brought in a thin-walled hollow spherical shape, where all the mass is located next to the outer circumference of the spherical body.

The base body was produced by precision turning of two titanium semi-spherical shells, which were laser welded afterwards. Then, at PTB's Department 5.5 "Scientific Instrumentation", which has great experience in polishing spherical objects,

the sphere was iteratively processed until its final surface finish and target density, – near the density of the liquid, as needed – was reached.

4. DETECTION OF THE FLOTATION STATE

To reach the smallest uncertainty in liquid density, it is necessary to bring the solid density standard in a perfect flotation state without any raising or falling left. Then, the liquid density can be calculated as described in chapter 2. Therefore, a precise temperature control of the bath in the millikelvin to sub millikelvin precision must be used. Cycling the bath's temperature iteratively several times, and with this the whole submerged u-tube setup to find the temperature-of-flotation, usually costs multiple of hours and can be managed the day before and after the pressure measurement or automatically controlled overnight.

However, a first estimation of the flotation temperature can be performed by setting the temperature sufficiently low, so that the density standard arranges itself in the upper stroke position. Then, the temperature of the bath is slightly increased in 10 mK steps, until a slowly down movement of the density standard can be observed. A following decrease of the bath temperature setpoint by -20 mK slows the down movement significantly, so that, after a short period of time, the up and down movement can be reliably controlled by smaller changes of the bath temperature. The density standard is then moving freely without any contact with the upper or lower stroke position. In this situation, an up or down movement can be reproduced within a temperature window of 20 mK, where one must assume that the ideal temperature-of-flotation certainly lays within this temperature window. Such precision in temperature control can already be achieved by precise thermostatic baths without additional modification of the temperature control and starting from stable temperature conditions of the bath, the described procedure usually needs only one to two hours of time. Of course, it also can be performed with a movement of the density standard starting from the lower stroke position.

Helpful for the observation of the flotation state, which is visually detectable through the glass windows of the bath and the density measurement chamber (Figure 2), is a precision levelling telescope, type Ni-2, by Carl Zeiss Jena, Germany. It offers a 32x magnification, together with a plan parallel plate mechanism that allows measuring small height changes within its field of view. Herewith, the height change of the floating density standard can be measured reproducibly within 0.02 mm, offering a precision sufficient to monitor the effect of the temperature regulation lower than 5 mK. With such a high capability to monitor the movement of the solid standard, the next effort will be made to achieve a fine control of the bath temperature, either by an optimization of the control parameters of the bath, or by implementing an external temperature controller.

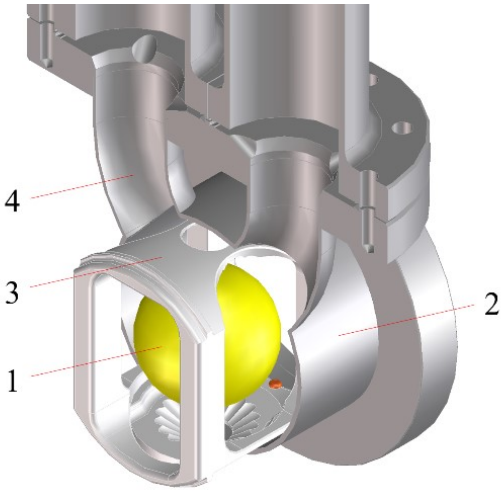

Figure 2: Integration of the liquid density measurement using the temperature-of-flotation method in the liquid column manometer of PTB. Presented as a virtual vertical cut through the stainless-steel body, containing the density standard DS1 (1), the density measuring chamber (2), a PTFE centring cage (3), and the direct hydraulic coupling of the density measurement chamber to the tubes (4).

5. UNCERTAINTY OF THE LIQUID DENSITY DETERMINATION

5.1. Density of the density standard

The density of the hollow titanium sphere was determined in PTB's Workgroup 1.13 "Solid State Density". For the calibration, mass and volume were calibrated separately, whereby the volume measurement was performed by hydrostatic weighing using the Archimedes' principle in pentadecane, whose liquid density is determined *in-situ* by hydrostatic weighing of two silicon samples.

The density was found to be 829.670 kg/m³ for 20 °C with a relative standard uncertainty $u(\rho_{\mathrm{sr}})/\rho_{\mathrm{sr}}$ of 1.6×10^{-6}.

5.2. Temperature of the manometric liquid

The temperature of the liquid inside the u-tube setup is measured with two standard platinum resistance thermometers, positioned in the front and the back next to the density measurement chamber, inside the water filled bath. Following the direct current measurement principle, a temperature bridge of type MKT-50, manufactured by Anton Paar, Austria, is used to measure both temperatures.

The standard uncertainty of the temperature measurement is 3.5 mK.

5.3. Temperature homogeneity and stability of the thermostatic bath that surrounds the u-tube setup

The thermostatic bath, 70 L in usable volume, is of type TV7000DC, manufactured by Tamson Instruments, The Netherlands. It is supported by a cooling bath of type TLC15 of the same manufacturer, which acts as a heat sink, to enable temperature control near room temperature (20 °C).

For the characterisation of the main bath, which later surrounds the density measurement chamber and the u-tube setup, the temperature stability was measured in the vertical centre axis of the bath's inner volume in five distributed levels. There, it was found that the experimental standard deviation of 300 temperature values within 55 min does not exceed 0.5 mK. Within the same five levels, also the temperature distribution was measured at four different places of interest. Fortunately, all temperature values within the bath never deviate more than 1 mK.

5.4. Thermal volume expansion γ_s of the density standard

For the thermal volume expansion coefficient γ_s of the density standard $25.8 \times 10^{-6}\,\mathrm{K}^{-1}$ was chosen [14]. This value is valid for the titanium alloy Ti6Al4V, between 0 °C and 100 °C. Its relative standard uncertainty $u(\gamma_s)/\gamma_s$ was conservatively chosen to 5 % by comparing values of similar titan alloys and covers also the value used for pure titan.

5.5. Compressibility κ_s of the density standard

The isothermal compressibility κ_s for a thin-walled hollow sphere, like the density standard, could be derived analytically and was found to be 0.13 GPa^{-1}. As the titanium material can be assumed to be isotropic, its shell thickness to radius ratio is significantly smaller than 10 % and strains resulting under the influence of pressures are small, then, the material's inner stresses and strains, and with this, the contraction of the sphere under pressure can be described by the theory of elastic plates and shells, where a neglectable variation in the stress field across the material thickness k of the hollow sphere is assumed.

With Young's modulus E and Poisson's ratio ν of the titanium alloy used, and the outer radius r for the isothermal compressibility $\kappa_s = -(\mathrm{d}V/V)/\mathrm{d}p$ it is valid:

$$\kappa_s = \frac{3(1-\nu)}{E}\frac{r}{2k}. \tag{5}$$

Its relative uncertainty was conservatively estimated to 15 % of the calculated value and includes also a 3 % contribution produced by the simplifying assumptions made by the elastic shell theory.

The result is especially important for absolute pressure measurements.

5.6. Deviation from the reference conditions

As the temperature t and the pressure p slightly deviate from the reference condition of the density standard's calibration (t_r, p_r), corrections need to be applied. Because of the uncertain knowledge of the coefficients, for gauge pressure measurements a nearly neglectable, and for absolute pressure measurements a clear contribution to the uncertainty is produced (compare 5.8). This is due to the pressure deviation from the reference value of around 0.1 MPa, which leads into a relative standard uncertainty contribution of around 2×10^{-6}. This contribution would disappear if the calibration of the density standard would be additionally performed under vacuum.

5.7. Deviation from the ideal flotation temperature

Deviations from the ideal flotation temperature occur, when the density standard is not perfectly floating, which means, it is still slowly rising or falling.

This can be caused when the temperature control is not precise and a small deviation from the already perfectly estimated temperature setpoint remains. As mentioned in chapter 4, two measurement points with a slow rising and a slow falling density standard, together with the two corresponding liquid temperatures could be used to locate the flotation temperature in a temperature window of a few millikelvin. The effect caused by a temperature window of 20 mK on the uncertainty of the liquid density determination is included in Table 1.

5.8. Uncertainty of the liquid density determination

Table 1: Uncertainty budget for the determination of the liquid density under gauge pressure measurement conditions, valid in the pressure reference level, containing a significant contribution of the imperfect detection of the flotation temperature.

Source of uncertainty	Uncertainty $\rho_{l,i}$ / (kg/m³)
Density of the standard	0.0013
Thermal expansion of the standard	0.0007
Compressibility of the standard	0.0001
Reference p, t deviation	0.0001
Temperature measurement	0.0021
Temperature inhomogeneity	0.0004
Temperature instability	0.0004
Flotation temperature deviation	0.0035
Combined standard uncertainty	0.0044
Relative combined uncertainty	5.4×10^{-6}

The uncertainty of the liquid density determination needs to be individually estimated for gauge and absolute pressure measurement conditions, differing by the contribution caused by the compressibility of the density standard for the absolute pressure measurement conditions, as described in chapter 5.6.

Uncertainty contributions caused by the hydrostatic pressure difference $(p - p_h)$ are neglectable, even if its correction term is necessary to be applied for the liquid density calculation.

The relative uncertainty in liquid density for absolute pressure measurement conditions, as presented in Table 1 is slightly increased to 5.7×10^{-6}.

Both relative uncertainty values could be seen with the prospect of being shortly reduced by optimizing the flotation process, although for now, they are only slightly higher than the development target of 5×10^{-6}.

6. SUMMARY

Liquid column manometry relies on pure and stable manometer liquids with a known density to enable reliable pressure measurements. For decades, this has typically led into the use of a liquid metal – mercury – which, for absolute pressure measurements, suffers from a vapor pressure that limits the lowest measurable pressure, a low sensitivity for pressure changes due to its high density and is toxicity.

The presented realisation of an *in-situ* liquid density measurement in a liquid column manometer makes the use of other and new liquids possible, in this case a vacuum liquid that solves the above-mentioned restrictions.

Their relative standard uncertainties in liquid density measurement, for both pressure measurement conditions, gauge and absolute pressure, are already reaching satisfying accuracy levels, and will be significantly further reduced after the current predevelopment of the flotation process, with the prospect of achieving relative uncertainty values clearly below the development target of 5×10^{-6}. However, the uncertainties are already low enough to allow the use of this measurement method in the liquid column manometer of PTB for the low-pressure range calibration of force-compensated piston gauges even at this stage.

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