Selection and characterization of liquids for a low pressure interferometric liquid column manometer

Sven Ehlers [a,*], Jens Könemann [a], Oliver Ott [a], Henning Wolf [a], Janez Šetina [b], Andreia Furtado [c], Wladimir Sabuga [a]

[a] Physikalisch-Technische Bundesanstalt (PTB), Bundesallee 100, 38116 Braunschweig, Germany
[b] Institute of Metals and Technology (IMT), Lepi pot 11, 1000 Ljubljana, Slovenia
[c] Instituto Português da Qualidade (IPQ), Rua António Gião 2, 2829-513 Caprica, Portugal

A B S T R A C T

At PTB, the development of a new primary interferometric liquid column manometer for measurement of absolute and gauge pressures in the range up to 2 kPa is an ongoing project. For measurements in this pressure range, liquids with a low density are advantageous because of a better pressure resolution determined through differential column height measurements. In addition, low vapor pressure is a precondition for an accurate measurement of absolute pressure. The choice of liquid is crucial for the accuracy of the new instrument. This paper discusses the effect of liquid properties such as vapor pressure, density, viscosity, surface tension and gas absorption capacity on the performance of the micromanometer. Seven liquids – all oils used in vacuum applications (vacuum oils) – representing different classes of chemical compounds were analyzed in respect to their viscosity, density, thermal expansion and compressibility. Detailed investigations were performed on three liquids out of seven to determine their density versus gas saturation, ab- and desorption kinetics and surface tension, as well as the wettability of the micromanometer's materials. Results of the measurements and recommendations for the use of the liquids are presented.

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1. Introduction

To measure pressures below a few kilopascals, liquid column manometry is the most appropriate choice. Within the scope of the EMPIR joint research project "pres2vac" conducted by 16 European national metrology institutes (NMIs), universities and companies [1], a new oil-based U-tube interferometric micromanometer is being developed as a primary standard of absolute and gauge pressure for the pressure range from 1 Pa to 2 kPa [2]. The liquid manometry method relies strongly on a comprehensive knowledge of the liquid density, and also requires that the liquid has certain further properties in order to achieve optimal performance of the manometer. A common solution is the usage of mercury as a manometric liquid because its density and thermal expansion are well known [3–6] and stable. However, apart from its toxicity, the greatest disadvantage of its use in measurement of low absolute pressure is its high vapor pressure and very high density

and, consequently, a low sensitivity of the column height to pressure changes.

Oils have been considered as an alternative to mercury and have been used in the micromanometers of several NMIs [7–11]. Although they have several advantages when compared with mercury, oils suffer from the high instability of their density, which can change mostly due to gas solubility by up to 10^{-4} relative [8]. In [12], this problem is partially solved by a study of gas-in-oil absorption/desorption at variable pressure. An essential reduction in the uncertainty can be achieved if the oil density is measured *in situ* by state-of-the-art techniques [13,14]. This concept is used in the new interferometric micromanometer. Even though the density of the oil can be monitored, it is favorable to have the density changes be as low as possible. This as well as other properties, whose role in the pressure measurement is discussed below, make a search for the best suitable oil an important task in the realization of the micromanometer.

In the following, a theoretical analysis of oil properties for the operation of the micromanometer is presented, possible oil candidates are selected and the results of the experimental investigation on several types of selected oils are presented.

* Corresponding author.
E-mail address: sven.ehlers@ptb.de (S. Ehlers).

2. Theoretical aspects of working fluid properties

Several properties of a manometric liquid, such as vapor pressure, density dependence on temperature, pressure and gas saturation, viscosity and capillary properties, have an effect on the performance of the liquid column manometer and on the achievable uncertainty.

2.1. Vapor pressure

When operating the liquid-column manometer in absolute mode, the vapor pressure of the working fluid should be as low as possible, in order to achieve a sufficiently low residual pressure, to avoid non-equilibrium conditions and to minimize local pressure gradients in the reference column. To have no significant effect on the target uncertainty, the vapor pressure should be lower than the expected standard uncertainty of the lowest measurable absolute pressure by one to two orders of magnitude. In this particular case, it should be less than 0.1 mPa.

2.2. Density and density-affecting quantities

In a liquid column manometer, a change in pressure p is proportional to the change of the column height difference h being the measured quantity. The sensitivity coefficient dh/dp is inversely proportional to the product of the gravity acceleration g and liquid density ρ:

$$\frac{dh}{dp} = \frac{1}{\rho \cdot g} \tag{1}$$

Here, a liquid with a lower density is advantageous for achieving a higher sensitivity. However, the idea of using fluids with a very low density to maximize the sensitivity to pressure chances is limited, in particular, due to geometric and thermal restrictions. For a pressure range up to 2 kPa, a tolerated density interval between 700 kg/m^3 and 1500 kg/m^3 would allow a column height difference of 14 cm to 30 cm.

Inside the manometer, the hydrostatic pressure as well as the pressure to be measured act on the working fluid. As liquid density is a function of pressure, the liquid compressibility needs to be considered. A typical value for the compressibility of vacuum oils is around 1×10^{-6} kPa^{-1}. As the pressure distribution along the liquid columns is known, this effect can be corrected.

A typical thermal expansion coefficient of vacuum oils is near 1×10^{-6} mK^{-1}. As this value is quite high, spatial and temporal temperature differences can have a noticeable effect on the fluid density. This creates a demand for thorough temperature stabilization and homogenization of the apparatus within 3 mK. Unique thermostatic baths and temperature controllers, mostly used for high level density determination, are reported to reach temperature stability in the μK scale over hours [13]. Such devices seem to be a promising approach to measure and control the liquid density sufficiently, although, additional effects, e.g. vibrations, must be considered. Moreover, to apply corrections to density due to residual temperature differences along the micromanometer columns or due to a difference in temperature during the density and pressure measurement (e.g., when the density is measured outside the micromanometer using an oscillation-type density meter), the thermal expansion coefficient of the liquid must be accurately known.

Inside the micromanometer, the free surfaces of the columns' fluid are in direct contact with the pressure-transmitting gas medium in the measurement column, and with the vacuum in the absolute mode or with the air in the gauge mode in the reference column. It is expected that, with increasing pressure in the measuring column, gas will be absorbed by the fluid and may also desorb into vacuum in the reference column, as well in the measurement column when the pressure later decreases. In [15], a density decrease is reported for a wide set of alkanes of around 70 ppm to 130 ppm (1 ppm = 10^{-6}) when saturated with air or nitrogen at a pressure of around 0.1 MPa. For initially degassed bis(2-ethylhexyl) sebacate vacuum oil brought into contact with nitrogen for 2 h, a density decrease of over 40 ppm was observed in [12]. Data on gas absorption and desorption kinetics for other vacuum oils is not very clear and therefore has to be determined.

2.3. Viscosity

When pressure in the micromanometer changes, the liquid columns inside the U-tube begin to move until equilibrium is achieved between the hydrostatic pressure and the new pressure difference.

This involves the whole mass of the liquid in the U-tube; the time to reach the required level of equilibrium (a perfect equilibrium would require an infinitely long time) will depend, in addition to the U-tube geometry and the liquid density, on the liquid viscosity. An ideal non-viscous working fluid would produce a continuous harmonic oscillation inside the tube with a constant frequency ω_0. For a viscous fluid, the columns' height deviation from their equilibrium position x is described by Eq. (2),

$$\ddot{x} + 2\beta\dot{x} + \omega_0^2 x = 0, \tag{2}$$

in which the frequency ω_0 and the damping parameter β depend on the fluid's dynamic viscosity η and density ρ, the U-tube liquid column total length l and the column diameter d:

$$\omega_0 = \sqrt{2g/l}, \tag{3}$$

$$\beta = 16\eta / \left(\rho d^2\right) \tag{4}$$

Depending on the fluid properties and the U-tube geometry, the fluid movement will show an underdamped oscillation at $\omega_0 > \beta$, a critically damped oscillation at $\omega_0 = \beta$ or an overdamped oscillation at $\omega_0 < \beta$. In the underdamped process, the amplitude of the columns height difference oscillation, expressed in the unit of pressure, reduces with time t according to

$$\delta p = \Delta p \cdot e^{-\beta t} \times \cos(\omega t), \tag{5}$$

where Δp is the initial pressure change in the micromanometer and $\omega = (\omega_0^2 - \beta^2)^{0.5}$ is the frequency of the underdamped oscillation. In the overdamped process, $\omega = (\beta^2 - \omega_0^2)^{0.5}$ is the oscillation frequency and the deviation from the pressure equilibrium δp is given by:

$$\delta p = \Delta p \cdot e^{-\beta t} \times \left[\frac{(\beta + \omega)}{2\omega} e^{t\omega} - \frac{(\beta - \omega)}{2\omega} e^{-t\omega} \right] \tag{6}$$

For use in the micromanometer, a critically damped oscillation is preferable, as the equilibrium is reached in the least amount of time. This case is described by:

$$\delta p = \Delta p \cdot e^{-\beta t} \times (1 + \beta t) \tag{7}$$

For density ranging from 700 kg/m^3 to 1500 kg/m^3, the dynamic viscosity should lie between 830 mPa·s and 1790 mPa·s to fulfill conditions of the critically damped oscillation. This estimation is valid for a column diameter of 6 cm and a total U-tube length of 0.7 m. Flow restrictions like valves or flanges can easily shift the values because of the quadratic contribution of the column diameter d. Nevertheless, for the defined conditions calculations show that within the density range from 700 kg/m^3 to 1500 kg/m^3 and