

Force Transmission Errors in Magnetic Suspension Densimeters

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Techniques to determine and compensate for the force transmission error (FTE), including the magnetic effects of the fluid being measured, in magnetic suspension densimeters are presented. For a two-sinker densimeter, the forces on the balance are expressed for each of the weighings comprising a density determination (i.e., the two sinkers plus balance calibration and tare weights). This yields a system of four equations, which are solved for the fluid density, a balance calibration factor, a coupling factor (related to the FTE), and a quantity related to the balance tare. For a single-sinker densimeter, an *in situ* weighing of the sinker in vacuum compensates for the FTE of the apparatus itself. A determination of the fluid-specific effect requires measurements with two different sinkers—analogue to the two-sinker analysis, but with the measurements spread out over time. The apparatus part of the FTE is generally less than ± 20 ppm. Measurements on propane, helium, neon, nitrogen, argon, toluene, and air are analyzed for the fluid-specific effect; this effect is correlated with the magnetic susceptibility of the fluid together with an apparatus constant. With this analysis, the force transmission “error” becomes an effect that can be accounted for rather than a significant source of uncertainty in density measurements carried out with magnetic suspension densimeters.

KEY WORDS: densimeter; density; magnetic susceptibility; magnetic suspension coupling.

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1. INTRODUCTION

The combination of a hydrostatic balance densimeter with a magnetic suspension coupling has yielded the most accurate data for fluid p - ρ - T behavior over wide ranges of temperature, pressure, and density. Wagner and Kleinrahm [1] present a comprehensive review of such instruments, which are broadly divided into single-sinker and two-sinker densimeters. The essential elements of such densimeters are one or two sinkers immersed in the fluid of interest that are weighed by a balance, which is at ambient conditions. A magnetic suspension coupling transmits, to the balance, the weight of the sinkers across a coupling housing, which separates the fluid from the atmosphere. The coupling consists of an electromagnet (in air) and a permanent magnet (in the fluid). The permanent magnet is linked with a lifting device to pick up a sinker for weighing.

With proper design, the efficiency of this force transmission is nearly one, but the coupling will be slightly influenced by nearby magnetic materials, external magnetic fields, and the fluid being measured. These give rise to a “force transmission error” (FTE) that must be accounted for to realize the full accuracy of this technique. The FTE can refer to either the error in a weighing carried out using a magnetic suspension coupling or the error in a density determination arising from magnetic effects. The FTE can be divided into two parts. The first arises from the magnetic characteristics of the apparatus itself. The magnetic susceptibility of the fluid surrounding the magnets also influences the FTE. Because the position of the permanent magnet inside the coupling housing varies as the load on the coupling changes, the distribution of fluid around the magnet varies for the different weighings and this will affect the FTE; this is the “fluid-specific effect.”

Force transmission errors are discussed by Lösch [2] and Wagner and Kleinrahm [1]. The present paper builds upon these studies in the analysis of single-sinker densimeters and presents a new analysis for two-sinker densimeters. Our analysis is largely empirical. An alternate approach is presented by Kuramoto et al. [3]. Their approach is based on a physical model, but it is complex and requires detailed knowledge of the magnetic properties of the apparatus and fluid, which may not be available.

2. TWO-SINKER DENSIMETERS

Kleinrahm and Wagner [4,5] describe the first magnetic suspension densimeter utilizing two sinkers. The magnetic suspension coupling used in the current version of this instrument was developed by Lösch [2], and further developments are described by Lösch et al. [6]. The two sinkers

have (nearly) the same mass, surface area, and surface material, but they are made of materials with different densities (e.g., a gold disk and a gold-plated quartz-glass sphere) so that they have very different volumes. The sinkers are immersed in the fluid of interest, and each is weighed to yield the fluid density ρ :

$$\rho = \frac{(m_1 - m_2) - (W_1 - W_2)}{(V_1 - V_2)}, \quad (1)$$

where m and V are the sinker mass and volume, W is the balance reading, and the subscripts refer to the two sinkers. The use of two sinkers and the differential nature of the measurement largely cancel potential systematic errors associated with nonlinearity of the balance, adsorption onto the surface of the sinkers, and other effects. However, Eq. (1) does not include the force transmission error—it must be modified to yield the correct density.

2.1. Force Transmission Error Analysis

The two-sinker densimeter recently put into operation at NIST [7] has sinkers made of titanium and tantalum with nominal masses of 60 g each and volumes $V_{\text{Ti}} = 13.35 \text{ cm}^3$ and $V_{\text{Ta}} = 3.61 \text{ cm}^3$. It also incorporates two calibration weights that are placed onto the balance pan by small robotic arms. These weights are fabricated of stainless steel. The “calibration weight” has a mass of 59.5 g, and the “tare weight” ($m_{\text{tare}} = 44.3 \text{ g}$) is hollow, so that their volumes (7.48 cm^3) are the same within 0.05%. These additional weights were originally intended to provide an automated balance calibration, but they also allow a determination of the FTE. A schematic diagram of this densimeter is shown as Fig. 1.

A density determination with this instrument involves a total of eight weighings (two weighings each of the four objects) in a symmetrical weighing design: Ta sinker, Ti sinker, calibration weight, tare weight, tare weight (again), calibration weight, Ti sinker, and Ta sinker. During the weighing of the calibration and tare weights, the permanent magnet and “lifting fork” remain in suspension, but both sinkers are on their rests. This is made possible by a relatively new type of magnetic suspension coupling which has two stable states [6] corresponding to the (lifting fork + p-magnet) and the (sinker + lifting fork + p-magnet).

The forces on the balance for the weighing of sinker 1 are summed as follows:

$$W_1 = \alpha \left[\phi \left\{ m_1 + m_{\text{p-mag}} - \rho_{\text{fluid}} (V_1 + V_{\text{p-mag}}) \right\} + (m_{\text{e-mag}} - \rho_{\text{air}} V_{\text{e-mag}}) + W_{\text{zero}} \right], \quad (2)$$

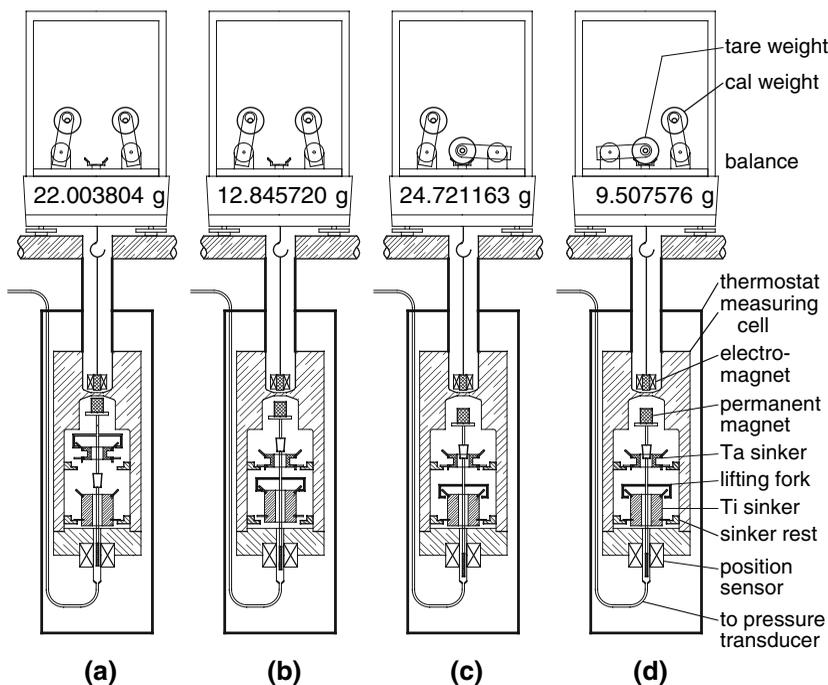


Fig. 1. Schematic of the two-sinker densimeter showing the four weighings; (a) weighing of the tantalum sinker, (b) weighing of the titanium sinker, (c) weighing of the balance calibration weight, and (d) weighing of the balance tare weight; in (c) and (d) both sinkers are on their rests. Balance displays are typical for a fluid density of $941 \text{ kg} \cdot \text{m}^{-3}$. Figure is not to scale.

where

α = balance calibration factor

ϕ = coupling factor

ρ_{fluid} = density of fluid under test

ρ_{air} = density of ambient air (or purge gas) in the balance chamber

V = volume

m = mass

W = balance reading

W_{zero} = balance reading with nothing on the balance pan or weighing hook

subscripts: 1: sinker 1

p-mag: permanent magnet (in fluid), includes lifting fork

e-mag: electromagnet (in air), includes linkage to the balance.

The key assumptions implicit in Eq. (2) are that (a) the force transmitted to the balance by the magnetic suspension coupling is proportional to the suspended load; the proportionality factor, or coupling factor ϕ , is shown below to be directly related to the FTE; (b) all quantities are constant over the time needed for a complete density determination; and (c) the balance reading is linear with the applied load.

The electromagnet and permanent magnet + lifting fork are always weighed, and the W_{zero} is the same for each weighing, so that these can be lumped together:

$$\beta = \phi \{m_{\text{p-mag}} - \rho_{\text{fluid}} V_{\text{p-mag}}\} + (m_{\text{e-mag}} - \rho_{\text{air}} V_{\text{e-mag}}) + W_{\text{zero}}. \quad (3)$$

The separate weighings can thus be written as

$$W_1 = \alpha [\phi \{m_1 - \rho_{\text{fluid}} V_1\} + \beta], \quad (4)$$

$$W_2 = \alpha [\phi \{m_2 - \rho_{\text{fluid}} V_2\} + \beta], \quad (5)$$

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

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

Equations (4) to (7) form a system of four equations in the unknowns α , β , ϕ , and ρ_{fluid} . The two weighings of each object are averaged in this analysis, and the air density ρ_{air} is calculated from the ambient temperature, pressure, and humidity measured in the balance chamber. Equations (6) and (7) are solved for α and β :

$$\alpha = \frac{W_{\text{cal}} - W_{\text{tare}}}{(m_{\text{cal}} - m_{\text{tare}}) - \rho_{\text{air}} (V_{\text{cal}} - V_{\text{tare}})} \text{ and} \quad (8)$$

$$\beta = \frac{W_{\text{cal}}}{\alpha} - (m_{\text{cal}} - \rho_{\text{air}} V_{\text{cal}}). \quad (9)$$

Subtracting Eq. (5) from Eq. (4) yields the fluid density (but includes the coupling factor ϕ):

$$\rho_{\text{fluid}} = \left[(m_1 - m_2) - \frac{(W_1 - W_2)}{\alpha \phi} \right] / (V_1 - V_2). \quad (10)$$

Note that Eq. (10) reduces to Eq. (1) if $\alpha = 1$ and $\phi = 1$. Equation (4) is solved for ϕ ;

$$\phi = \frac{(W_1/\alpha) - \beta}{m_1 - \rho_{\text{fluid}} V_1}. \quad (11)$$

And, finally, the fluid density is given by

$$\rho_{\text{fluid}} = \left[(m_1 - m_2) - \frac{(W_1 - W_2) m_1}{W_1 - \alpha\beta} \right] / \left[(V_1 - V_2) - \frac{(W_1 - W_2) V_1}{W_1 - \alpha\beta} \right]. \quad (12)$$

The key points here are that ρ_{fluid} given by Eq. (12) includes (within the limits of the assumptions stated above) the effects of the force transmission error arising from both apparatus and fluid effects and is, thus, the “true” density, and Eq. (11) gives ϕ at any density, not just in vacuum. The balance factor α drifts slowly with time because of changes in ambient temperature and pressure. The parameter β includes the buoyancy forces on the electromagnet and permanent magnet; it will change with the density of the air and the fluid being measured, but it is constant for a density determination at any given state point.

2.2. Experimental Results

The wide-ranging propane p - ρ - T measurements of McLinden [8] have been analyzed by use of Eqs. (3) to (12). These data cover a temperature range of (265 to 500) K and a density range of (4.5 to 582) $\text{kg} \cdot \text{m}^{-3}$ with pressures up to 36 MPa. The coupling factor, and thus the force transmission error, is a function of the fluid density, as seen in Fig. 2. At zero density (vacuum), $(\phi_0 - 1) = 15.3 \times 10^{-6}$ with $\sigma = 0.9 \times 10^{-6}$. Propane is weakly diamagnetic (specific magnetic susceptibility $\chi_s = -1.10 \times 10^{-8} \text{ m}^3 \cdot \text{kg}^{-1}$ [9]), and the coupling factor decreases with increasing density due to the fluid effects. As with all diamagnetic fluids χ_s for propane is independent of temperature. A linear fit represents the data with a standard deviation of 2.3×10^{-6} . Figure 2 does not show data in the immediate vicinity of the critical point ($T_{\text{crit}} \approx 369.9 \text{ K}$; $\rho_{\text{crit}} \approx 220 \text{ kg} \cdot \text{m}^{-3}$). Near the critical point, the compressibility of the fluid is large, leading to significant vertical density gradients in the cell. Because the position of the permanent magnet varies significantly between the sinker weighings and the weighings of the calibration weights, the assumption that the forces lumped into the parameter β are the same for all the weighings is not valid. This effect is discussed further by McLinden [8].

A similar analysis of the measurements on air reveals very different results, Fig. 3. These measurements were made on the ternary mixture (0.78111 mole fraction nitrogen + 0.20969 oxygen + 0.00920 argon) and cover a temperature range of (250 to 460) K, densities of (25 to 435) $\text{kg} \cdot \text{m}^{-3}$ with pressures up to 38 MPa [10]. Oxygen is strongly paramagnetic,

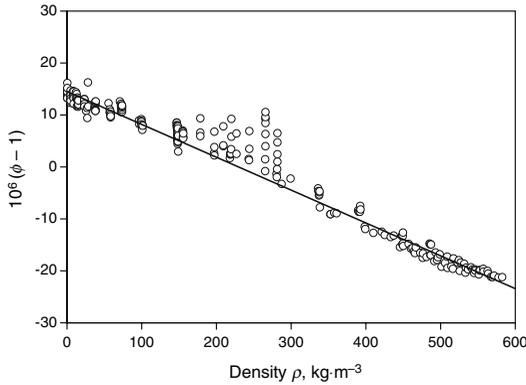


Fig. 2. Coupling factor ϕ as a function of density ρ for propane measured in the two-sinker densimeter: \circ data; — linear fit of the data.

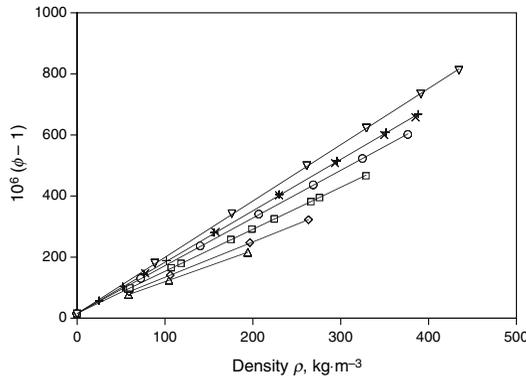
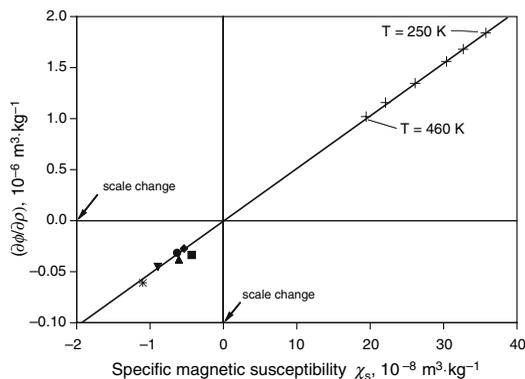


Fig. 3. Coupling factor ϕ as a function of density ρ for air measured in the two-sinker densimeter at various temperatures and at pressures up to 38 MPa: ∇ 250 K; $*$ 273 K (2 series); \circ 293 K; \square 340 K; \diamond 400 K; \triangle 460 K; — linear fits of the data at the various temperatures.

and, like all paramagnetic substances, its specific magnetic susceptibility is inversely proportional to temperature. Davis [11] recommends the value $\chi_s = 134.0 \times 10^{-8} \text{ m}^3 \cdot \text{kg}^{-1}$ for pure oxygen at 293.15 K. The specific magnetic susceptibility of our air sample is thus $\chi_s = 35.7 \times 10^{-8} \text{ m}^3 \cdot \text{kg}^{-1}$ at 250 K and $\chi_s = 19.1 \times 10^{-8} \text{ m}^3 \cdot \text{kg}^{-1}$ at 460 K. The FTE of the apparatus ($\phi_0 - 1$) is nearly the same as for propane (15.0×10^{-6} with $\sigma = 0.5 \times 10^{-6}$), but the coupling factor ϕ increases with density and is also a function of temperature. The slope ($\partial\phi/\partial\rho$) for air is 16–30 times greater than that for propane, and of the opposite sign.

Table I. Slope of the Coupling Factor ($\partial\phi/\partial\rho$) as a Function of the Temperature and Specific Magnetic Susceptibility χ_s of the Fluid

Fluid	Temperature (K)	χ_s ($10^{-8} \text{ m}^3 \cdot \text{kg}^{-1}$)	$(\partial\phi/\partial\rho)$ ($10^{-6} \text{ m}^3 \cdot \text{kg}^{-1}$)
Helium	223.15–323.15	−0.635	−0.0317
Neon	293.15–429.75	−0.434	−0.0337
Nitrogen	250.00–500.00	−0.538	−0.0274
Argon	234.32–505.08	−0.608	−0.0382
Propane	265.00–500.00	−1.10	−0.0609
Toluene	213.15–473.16	−0.895	−0.0452
Air	250.00	35.74	1.841
	273.16	32.66	1.681
	293.15	30.38	1.560
	340.00	26.11	1.374
	400.01	22.09	1.157
	460.02	19.12	1.020

**Fig. 4.** Slope of the coupling factor ($\partial\phi/\partial\rho$) as a function of the specific magnetic susceptibility χ_s of the fluid: ● helium; ■ neon; ◆ nitrogen; ▲ argon; * propane; ▼ toluene; + air at $T=(250 \text{ to } 460) \text{ K}$; — linear fit of the data.

Most fluids are weakly diamagnetic, and ϕ displays a behavior similar to that seen with propane. Helium, neon, nitrogen, argon, and toluene have also been measured in the NIST two-sinker densimeter; these data are reported elsewhere [7, 10, 12]. The slope ($\partial\phi/\partial\rho$) for these fluids is given in Table I and plotted as a function of χ_s in Fig. 4; it is directly proportional to the specific magnetic susceptibility of the fluid.

These results clearly demonstrate that the coupling factor can be divided into apparatus and fluid-specific contributions; ϕ_0 is the value of ϕ in vacuum, and it is the apparatus contribution. Furthermore, ϕ is proportional to the fluid density and the magnetic susceptibility of the fluid so that

$$\phi = \phi_0 + \varepsilon_\rho \frac{\chi_s}{\chi_{s0}} \frac{\rho_{\text{fluid}}}{\rho_0}, \quad (13)$$

where $\rho_0 = 1000 \text{ kg} \cdot \text{m}^{-3}$ and $\chi_{s0} = 10^{-8} \text{ m}^3 \cdot \text{kg}^{-1}$ are reducing constants and ε_ρ is an apparatus-specific constant. (It is equal to 51.7×10^{-6} for the NIST two-sinker densimeter.)

2.3. Effect of FTE on Density for a Two-Sinker Densimeter

The magnitude of the FTE on density may be obtained by subtracting Eq. (10) from the same equation, but with $\phi = 1$:

$$\Delta\rho = \rho_{(\phi=1)} - \rho_{\text{fluid}} = \frac{1}{(V_1 - V_2)} \left[\frac{(W_1 - W_2)}{\alpha\phi} - \frac{(W_1 - W_2)}{\alpha} \right]. \quad (14)$$

In other words, $\Delta\rho$ would be the error in the density if the FTE were not compensated for. If ($m_1 \approx m_2$), Eq. (14) can be rearranged to give

$$\frac{\Delta\rho}{\rho_{\text{fluid}}} \approx \phi - 1. \quad (15)$$

Combining Eqs. (13) and (15) gives the result,

$$\frac{\Delta\rho}{\rho_{\text{fluid}}} = (\phi_0 - 1) + \varepsilon_\rho \frac{\chi_s}{\chi_{s0}} \frac{\rho_{\text{fluid}}}{\rho_0}. \quad (16)$$

From Eq. (16) one readily sees that the apparatus portion of the FTE for a two-sinker densimeter contributes a constant relative error to the density. The magnitude of $(\phi_0 - 1)$ is typically $\pm 20 \times 10^{-6}$ or less, or about $\pm 1.2 \text{ mg}$ for sinkers of 60 g mass. The coupling housings are usually made of a copper beryllium alloy or a copper chromium zirconium alloy. Most housings are slightly diamagnetic and have a $(\phi_0 - 1)$ up to $+20 \times 10^{-6}$. A few housings are slightly paramagnetic with $(\phi_0 - 1)$ as large as -20×10^{-6} . For the NIST two-sinker densimeter, it is about $+15 \times 10^{-6}$. The fluid-specific effect is directly proportional to the fluid density and the specific magnetic susceptibility of the fluid. For most fluids, this effect will be small (e.g., -29 ppm for propane at $500 \text{ kg} \cdot \text{m}^{-3}$). But for air at 273 K and 35 MPa (where $\rho = 388 \text{ kg} \cdot \text{m}^{-3}$), the fluid effect is $+0.065\%$; pure oxygen

at the same temperature and pressure (where $\rho = 496 \text{ kg} \cdot \text{m}^{-3}$) would have a fluid effect of approximately +0.37%.

The above analysis requires weighings of separate balance tare and calibration weights. For two-sinker densimeters lacking this feature (but still allowing a “tare” weighing where both sinkers are decoupled from the balance), the balance calibration factor can be determined separately, either manually with standard masses or by using the built-in calibration function available on some balances. The balance factor would then be

$$\alpha = 1/(1 - \rho_{\text{air}}/\rho_{\text{cal}}) \quad (17)$$

or about 1.00015 for a typical sea-level air density of $1.2 \text{ kg} \cdot \text{m}^{-3}$ and a stainless steel calibration mass having a density of $8000 \text{ kg} \cdot \text{m}^{-3}$. The factor β would be given by a “tare” weighing with both sinkers decoupled from the balance. The balance can also be tared at this state, and then the factor β is zero. The fluid density and coupling factor ϕ are then given by Eqs. (11) and (12) at each state point.

3. SINGLE-SINKER DENSIMETERS

An Archimedes-type density measurement combined with a magnetic suspension coupling was first described by Beams and Clarke in 1962 [13]. In this system the sinker was made of an iron alloy and was itself levitated by several solenoid coils; the buoyancy force on the sinker was determined from the coil current needed to suspend the sinker. The modern design utilizing a non-magnetic sinker, separate coupling, and an independent balance for the weighings was first developed by Brachthäuser et al. [14] in 1993. A single-sinker densimeter is considerably simpler compared to a two-sinker instrument, and this has led to a range of general purpose and specialized instruments. Several of these are reviewed by Wagner and Kleinrahm [1]. However, this flexibility comes with an increased sensitivity to force transmission errors, and this demands careful attention to achieve the full accuracy of which these instruments are capable.

3.1. Force Transmission Error Analysis

For a single-sinker densimeter, two weighings are carried out, and (making the same assumptions as above) the forces on the balance for the two weighings are

$$W_1 = \alpha \left[\phi \left\{ m_s + m_{\text{p-mag}} - \rho_{\text{fluid}} (V_s + V_{\text{p-mag}}) \right\} + m_{\text{e-mag}} + m_{\text{c1}} - \rho_{\text{air}} (V_{\text{e-mag}} + V_{\text{c1}}) + W_{\text{zero}} \right] \quad (18)$$

and

$$W_2 = \alpha \left[\phi \left\{ m_{p\text{-mag}} - \rho_{\text{fluid}} V_{p\text{-mag}} \right\} + m_{e\text{-mag}} + m_{c2} - \rho_{\text{air}} (V_{e\text{-mag}} + V_{c2}) + W_{\text{zero}} \right], \quad (19)$$

where the subscript *s* refers to the sinker, and *c1* and *c2* refer to compensation weights, which have masses chosen to give approximately the same total balance loading for each weighing (i.e., $(m_{c2} - m_{c1}) \approx m_s$). The fluid density is obtained by subtracting Eq. (19) from (18):

$$\rho_{\text{fluid}} = \frac{\phi m_s + (m_{c1} - m_{c2}) - (W_1 - W_2)/\alpha - \rho_{\text{air}} (V_{c1} - V_{c2})}{\phi V_s}. \quad (20)$$

The compensation weights are typically made of different materials, so that $V_{c1} \approx V_{c2}$ and the air buoyancy term is zero. If the balance is tared when the sinker is on its rest, the balance reading W_2 is zero. The balance factor α is obtained by a separate calibration. Recognizing that m_s/V_s is the density of the sinker, Eq. (20) can be rearranged to

$$\rho_{\text{fluid}} = \rho_s + \frac{1}{\phi} \frac{(m_{c1} - m_{c2}) - (W_1 - W_2)/\alpha}{V_s}. \quad (21)$$

Equations (20) and (21) give the “true” fluid density, but they include the unknown coupling factor ϕ . Setting $\phi = 1$ and subtracting Eq. (21) from the result gives the error in the density if the FTE were not compensated for:

$$\Delta\rho = \rho_{(\phi=1)} - \rho_{\text{fluid}} = (\rho_s - \rho_{\text{fluid}}) (1 - \phi) \quad \text{or} \quad (22)$$

$$\frac{\Delta\rho}{\rho_{\text{fluid}}} = (\phi - 1) \left(1 - \frac{\rho_s}{\rho_{\text{fluid}}} \right). \quad (23)$$

The two-sinker analysis above demonstrated that the coupling factor can be divided into apparatus and fluid-specific effects. ϕ_0 is obtained by weighing the sinker in vacuum. It can be determined from Eq. (20) with ($\rho_{\text{fluid}} = 0$):

$$\phi_0 = \frac{-(m_{c1} - m_{c2}) + (W_1 - W_2)/\alpha}{m_s}. \quad (24)$$

Combining Eqs. (13) and (23) yields

$$\frac{\Delta\rho}{\rho_{\text{fluid}}} = (\phi_0 - 1) \left(1 - \frac{\rho_s}{\rho_{\text{fluid}}} \right) + \varepsilon_\rho \frac{\chi_s}{\chi_{s0}} \left(\frac{\rho_{\text{fluid}}}{\rho_0} - \frac{\rho_s}{\rho_0} \right). \quad (25)$$

The first term on the right-hand side of Eq. (25) represents the error in density arising from the apparatus effect $\Delta\rho_0$, and the second term represents the fluid-specific effect $\Delta\rho_{\text{fse}}$. The apparatus effect should always be compensated for through the use of ϕ_0 . To compensate also for the fluid-specific effect in a single-sinker densimeter, Eqs. (13) and (20) are combined;

$$\rho_{\text{fluid}} = \frac{\phi_0 m_s + (m_{c1} - m_{c2}) - (W_1 - W_2)/\alpha}{V_s} \frac{1}{\phi_0} + \frac{\varepsilon_\rho}{\phi_0} \frac{\chi_s}{\chi_{s0}} \left(\frac{\rho_s}{\rho_0} - \frac{\rho_{\text{fluid}}}{\rho_0} \right) \rho_{\text{fluid}}. \quad (26)$$

This expression gives the “true” fluid density in terms of measured or known quantities, except that ρ_{fluid} is required to compute $\Delta\rho_{\text{fse}}$, and ε_ρ must be determined. Since $\Delta\rho_{\text{fse}}$ is a small correction, it is sufficient to use the approximate density given by Eq. (20) with ($\phi = \phi_0$) in the second term on the right-hand side of Eq. (26). The determination of the apparatus constant ε_ρ is discussed in the next section.

The coupling factor at zero density ϕ_0 is also a weak function of temperature. The reason is that, even with a constant load, the vertical position of the permanent magnet will change with temperature due to the decreasing strength of the magnetic field with increasing temperature. Thus, it is important that the value of ϕ_0 be checked before and/or after the density measurements on each isotherm by weighing the sinker in vacuum. Equation (24) actually yields the quantity $(\phi_0 m_s)$, and it is not possible to determine if the sinker mass has changed. But unless the sinker has experienced severe corrosion or mechanical damage due to a severe shock, its mass should be very nearly constant and the vacuum measurement will yield ϕ_0 . The value of ϕ_0 has its most significant effect on the quantity $(\phi_0 m_s)$ in Eq. (26); the effect on the factor $1/\phi_0$ will be a very small correction.

3.2. Determination of the Fluid-Specific Effect for a Single-Sinker Densimeter

The apparatus-specific constant ε_ρ , which accounts for fluid effects, may be estimated by measuring a fluid at the same temperature, pressure, and density at different times using two different sinkers. Equation (25) is applied to density determinations using sinkers 1 and 2 with densities $\rho_{s,1}$ and $\rho_{s,2}$ (for example, a silicon sinker with $\rho_{s,1} = 2329 \text{ kg} \cdot \text{m}^{-3}$ and a tantalum sinker with $\rho_{s,2} = 16670 \text{ kg} \cdot \text{m}^{-3}$):

$$\frac{\Delta\rho_{\text{fse},1}}{\rho_{\text{fluid},1}} = -\varepsilon_\rho \frac{\chi_s}{\chi_{s0}} \left(\frac{\rho_{s,1}}{\rho_0} - \frac{\rho_{\text{fluid},1}}{\rho_0} \right) \text{ and} \quad (27)$$

$$\frac{\Delta\rho_{\text{fse},2}}{\rho_{\text{fluid},2}} = -\varepsilon_{\rho} \frac{\chi_s}{\chi_{s0}} \left(\frac{\rho_{s,2}}{\rho_0} - \frac{\rho_{\text{fluid},2}}{\rho_0} \right), \quad (28)$$

where $\rho_{\text{fluid},i}$ is the “true” fluid density measured with sinker i . If $\rho_{\text{fluid},1} \approx \rho_{\text{fluid},2}$, subtracting Eq. (27) from Eq. (28) and solving for ε_{ρ} gives

$$\varepsilon_{\rho} = \frac{\chi_{s0}}{\chi_s} \left(\frac{\rho_0}{\rho_{s,2} - \rho_{s,1}} \right) \left(\frac{\Delta\rho_{\text{fse},1} - \Delta\rho_{\text{fse},2}}{\rho_{\text{fluid}}} \right). \quad (29)$$

For the ρ_{fluid} term in the denominator of Eq. (29), it is sufficient to use an approximate value of the fluid density (e.g., that given by Eq. (20) with $\phi = \phi_0$). The $\Delta\rho_{\text{fse},1}$ and $\Delta\rho_{\text{fse},2}$ are the differences between the densities measured with the two sinkers and corrected for the apparatus effect (i.e., Eq. (20) with $\phi = \phi_0$) and the “true” fluid densities. Taking the difference between $\Delta\rho_{\text{fse},1}$ and $\Delta\rho_{\text{fse},2}$ will cancel out ρ_{fluid} , except that the measurements with sinker 1 and sinker 2 will typically be at slightly different temperatures and pressures (and thus densities). This complication is resolved by referencing the experimental values to the densities predicted by an equation of state evaluated at the experimental temperatures and pressures:

$$\frac{\Delta\rho_{\text{fse},1} - \Delta\rho_{\text{fse},2}}{\rho_{\text{fluid}}} = \frac{\rho_{1,\phi=\phi_0} - \rho_{\text{EOS}}(T_1, p_1)}{\rho_{\text{EOS}}(T_1, p_1)} - \frac{\rho_{2,\phi=\phi_0} - \rho_{\text{EOS}}(T_2, p_2)}{\rho_{\text{EOS}}(T_2, p_2)}. \quad (30)$$

The equation of state density ρ_{EOS} also cancels out of Eq. (30), except for the small difference due to any difference between (T_1, p_1) and (T_2, p_2) ; thus, the equation of state does not need to be particularly accurate. In this way, the fluid-specific effect can be compensated for if the specific magnetic susceptibility of the fluid is known.

A simpler approach to estimate the apparatus-specific constant ε_{ρ} is possible for those applications where an approximation of the fluid-specific effect is acceptable. The density of pure oxygen would be measured near $p = 0.1$ MPa and $T = 293.15$ K. (Higher pressures would give more accurate results, but measurements on high-pressure oxygen are dangerous. This should be attempted only if the densimeter is suitable for use with oxygen and all components are rigorously cleaned of all hydrocarbons.) The corresponding fluid-specific effect is described by the second term on the right-hand side of Eq. (25);

$$\frac{\Delta\rho_{\text{fse}}}{\rho_{\text{fluid}}} = \frac{\rho_{\phi=\phi_0} - \rho_{\text{EOS}}}{\rho_{\text{EOS}}} = \varepsilon_{\rho} \frac{\chi_s}{\chi_{s0}} \left(\frac{\rho_{\text{EOS}}}{\rho_0} - \frac{\rho_s}{\rho_0} \right), \quad (31)$$

where $\rho_{\phi=\phi_0}$ is the density determined by Eq. (20) with $\phi = \phi_0$, and ρ_{EOS} is the “true” density of oxygen at the experimental conditions given by a

reliable equation of state (such as [15], which is accurate to about 0.02% at these conditions). Rearranging Eq. (31) gives ε_ρ ;

$$\varepsilon_\rho = \left[\frac{\rho_{\phi=\phi_0} - \rho_{\text{EOS}}}{\rho_{\text{EOS}}} \right] / \left[\frac{\chi_s}{\chi_{s0}} \left(\frac{\rho_{\text{EOS}}}{\rho_0} - \frac{\rho_s}{\rho_0} \right) \right], \quad (32)$$

where $\chi_s = 134.0 \times 10^{-8} \text{ m}^3 \cdot \text{kg}^{-1}$ for pure oxygen at 293.15 K. If, for example, the fluid specific effect determined in this way was $(\Delta\rho_{\text{fse}}/\rho_{\text{EOS}}) = -1.56\%$ using a silicon sinker ($\rho_s = 2329 \text{ kg} \cdot \text{m}^{-3}$), the apparatus-specific constant would be $\varepsilon_\rho = 50 \times 10^{-6}$ with an uncertainty of about $\pm 10 \times 10^{-6}$. To check this result, the density of pure nitrogen should be measured at the same temperature and pressure as the oxygen measurement and also at pressures high enough so that the uncertainty in the measurement is minimized. The densities determined by Eq. (26) using $\chi_s = -0.538 \times 10^{-8} \text{ m}^3 \cdot \text{kg}^{-1}$ for nitrogen and ε_ρ determined by Eq. (32) should agree with the “true” density of nitrogen (given by an accurate equation of state, e.g., [16]) within the uncertainty of the measurements. The low-pressure measurement provides a check on the low-density performance of the densimeter, and thus the accuracy of the oxygen density at $p = 0.1 \text{ MPa}$. The higher-pressure measurements provide a check on the value of ε_ρ .

3.3. Effect of FTE on Density for a Single-Sinker Densimeter

Comparing Eqs. (15) and (23) and Eqs. (16) and (25) reveals that the force transmission error has a fundamentally different character for single-sinker and two-sinker instruments. For a two-sinker instrument, the apparatus portion of the FTE has a small relative (constant percentage) effect, while for a single-sinker densimeter this term contributes an absolute error to the density, which is proportional to $(\rho_s - \rho_{\text{fluid}})$. This demonstrates that for single-sinker instruments the sinker density should be as near as practical to the fluid density (e.g., a silicon or quartz-glass sinker or even a hollow sinker of stainless steel might be preferred over a relatively low-density metal like titanium). The fluid-specific FTE for both types of densimeter contribute relative errors in density that are proportional to the density and magnetic susceptibility of the fluid. The single-sinker equation includes a term which is proportional to $(\chi_s \rho_s)$, which is not present for a two-sinker-instrument. This term adds an additional constant relative error to the density, and it arises from the different positions for the permanent magnet for the sinker and tare weighings. (For a two-sinker densimeter, the position of the permanent magnet is nearly the same for the weighings of

the two sinkers.) Note that since $\rho_s > \rho_{\text{fluid}}$, the sign of the overall fluid-specific effect will be opposite for the two types of densimeter.

For a single-sinker densimeter the effect of the FTE is most pronounced at low densities. For example, with a 60 g sinker of silicon $V_s = 25.76 \text{ cm}^3$, and if a FTE of 1.2 mg were not taken into account, the error in density would be $0.047 \text{ kg} \cdot \text{m}^{-3}$. For a liquid density of $1000 \text{ kg} \cdot \text{m}^{-3}$, this would be 0.0047%, but for a gas at $50 \text{ kg} \cdot \text{m}^{-3}$ the error would be 0.093%. For a 60 g titanium sinker $V_s = 13.31 \text{ cm}^3$, and the corresponding errors would be $0.090 \text{ kg} \cdot \text{m}^{-3}$, 0.0090%, and 0.18%.

The use of ϕ_0 obtained by a vacuum weighing of the sinker together with Eq. (20) will compensate for the FTE of the apparatus, and this comprises the majority of the FTE except for strongly paramagnetic fluids. However, to obtain the highest accuracy from a single-sinker densimeter, the fluid-specific effect must also be taken into account. However, this correction is required only where densities of the highest accuracy are required. For example, the error for methane ($\chi_s = -1.36 \times 10^{-8} \text{ m}^3 \cdot \text{kg}^{-1}$ [9]) can be estimated by Eq. (25) to be less than +164 ppm for a silicon sinker ($\rho_s = 2329 \text{ kg} \cdot \text{m}^{-3}$) and less than +316 ppm for a titanium sinker ($\rho_s \approx 4500 \text{ kg} \cdot \text{m}^{-3}$). Most fluids have magnetic susceptibilities less than that of methane, and thus the errors due to the fluid-specific effect will be even smaller.

3.4. Single-Sinker Results

The single-sinker densimeter developed by Brachthäuser et al. [14] at the Ruhr-Universität Bochum in the early 1990s covers a temperature range of (233 to 523) K at pressures up to 30 MPa. A sinker of quartz glass was used with $V_s \approx 26.5 \text{ cm}^3$, $m_s \approx 60 \text{ g}$, and $\rho_s \approx 2200 \text{ kg} \cdot \text{m}^{-3}$. This instrument has been used to measure comprehensive p - ρ - T properties on important pure fluids, including argon, nitrogen, methane, carbon dioxide, ethene, ethane, and sulfur hexafluoride. It is also briefly described by Wagner and Kleinrahm [1]. The coupling housing of this densimeter is slightly paramagnetic ($\phi_0 - 1) = -8 \times 10^{-6}$. The apparatus constant for the fluid specific effect is $\varepsilon_\rho = 36 \times 10^{-6}$ [1]. It was determined by Klimeck [17] from measurements on methane at 293.15 K using the quartz-glass sinker and, in a separate set of measurements, a tantalum sinker. In the current version of this instrument a new magnetic suspension coupling (including new magnets and a new coupling housing) has been implemented; its constant for the fluid specific effect is $\varepsilon_\rho = 44 \times 10^{-6} \pm 6 \times 10^{-6}$ [18]. This result demonstrates that the apparatus effects must be determined for each densimeter and also if a given densimeter undergoes a major modification.

The coupling factor at zero density ϕ_0 is affected by small changes in the alignment of the magnets. A change of ± 0.5 mm in the vertical position of the permanent magnet with respect to the coupling housing can result in a change in ϕ_0 of up to $\pm 10 \times 10^{-6}$. Since the positions of the permanent magnet and the electromagnet are interdependent, a change in the position of the electromagnet will cause a corresponding change in the position of the permanent magnet. Moreover, a change of ± 0.5 mm in the vertical position of the permanent magnet would also cause a change in the apparatus constant, $\varepsilon_\rho = 44 \times 10^{-6}$, of up to about $\pm 15 \times 10^{-6}$. Thus, it is important that the position of the electromagnet be the same for all measurements, in particular for the experiments with the different sinkers used to determine ε_ρ .

Densities measured with this single-sinker densimeter display excellent agreement with densities measured on a two-sinker instrument where overlapping data exist. For example, the nitrogen p - ρ - T comparisons presented by Span et al. [16] reveal average differences between the single-sinker and two-sinker results of 40 ppm or less. Thus, with careful measurements and the necessary calibrations, a single-sinker densimeter can yield p - ρ - T data nearly as accurate as those from a two-sinker densimeter.

The NIST *two*-sinker densimeter allows a further examination of the FTEs in *single*-sinker densimeters. Its “two-position” coupling allows the data for either sinker to be analyzed as if this two-sinker densimeter were a single-sinker instrument. This allows a direct comparison of single-sinker densities with the (presumably “correct”) two-sinker values at exactly the same temperature and pressure state points.

The correction for the fluid-specific effect was determined by applying Eqs. (29) and (30) to the measurements on propane, toluene, and air. In principle, ε_ρ can be determined from a single pair of measurements using two sinkers of different densities, but, of course, a more accurate ε_ρ will be obtained by averaging the results of many measurements on several fluids. Figure 5 summarizes the results. The solid line represents the value $\varepsilon_\rho = 51.7 \times 10^{-6}$ obtained from the two-sinker analysis (i.e., Fig. 4). The propane data show considerable scatter at low densities; for $\rho > 100 \text{ kg} \cdot \text{m}^{-3}$, they yield an average $\varepsilon_\rho = 56.0 \times 10^{-6}$, with $\sigma = 5.0 \times 10^{-6}$, which is slightly high compared to the two-sinker value. The values of ε_ρ determined from the toluene data are in excellent agreement with the two-sinker value (average $\varepsilon_\rho = 51.6 \times 10^{-6}$, with $\sigma = 1.8 \times 10^{-6}$). The values of ε_ρ determined from the air measurements are remarkably consistent, even at low densities. They are in excellent agreement with the two-sinker value (average $\varepsilon_\rho = 52.4 \times 10^{-6}$, with $\sigma = 0.8 \times 10^{-6}$). This result should not be surprising: the fluid-specific effect is much larger for air than any of the other fluids considered, so that the “signal-to-noise ratio” is larger. These results

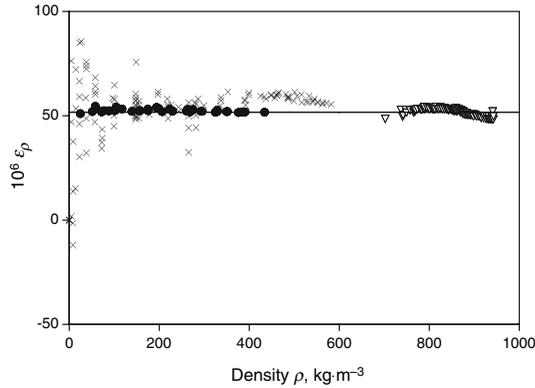


Fig. 5. Apparatus constant ε_ρ for the fluid-specific effect for several fluids: \times propane; ∇ toluene; \bullet air; — $\varepsilon_\rho = 51.7 \times 10^{-6}$ determined from the two-sinker analysis.

suggest measurements on an oxygen-containing mixture (e.g., a “standard air” mixture of accurately known composition) for the determination of ε_ρ .

Figure 6 shows a comparison of “single-sinker” densities with the two-sinker propane data of McLinden [8]; for clarity in the figure, only a subset of the data is shown. The densities were first calculated with Eq. (20) with no corrections for the FTE (i.e., $\phi = 1$). The relative error in density becomes large at low densities, and the errors for the tantalum sinker ($\rho_{\text{Ta}} = 16670 \text{ kg} \cdot \text{m}^{-3}$) are substantially larger than those for the titanium sinker ($\rho_{\text{Ti}} = 4507 \text{ kg} \cdot \text{m}^{-3}$). Including the correction for ϕ_0 results in a nearly constant relative error in the propane density. Finally, the densities corrected for the fluid-specific effect (using $\varepsilon_\rho = 51.7 \times 10^{-6}$ determined for this instrument in the two-sinker analysis above) are shown for the Ti sinker data. For $\rho > 100 \text{ kg} \cdot \text{m}^{-3}$, these densities have an average difference of just 1.2 ppm, but the scatter is large with $\sigma = 47.3 \text{ ppm}$. This again demonstrates that a single-sinker densimeter is capable of uncertainties only slightly higher than a two-sinker densimeter. It is interesting to note that the errors with no FTE correction are smaller at high densities than those with only the ϕ_0 correction, and the error goes through zero at a density of about $275 \text{ kg} \cdot \text{m}^{-3}$. This is not a general result and will depend on the specific magnetic susceptibility of the fluid and whether the coupling housing is paramagnetic or diamagnetic.

These results emphasize the increased sensitivity to force transmission errors at low fluid densities, the importance of correcting for ϕ_0 , and the desirability of low-density sinkers. They also demonstrate that the

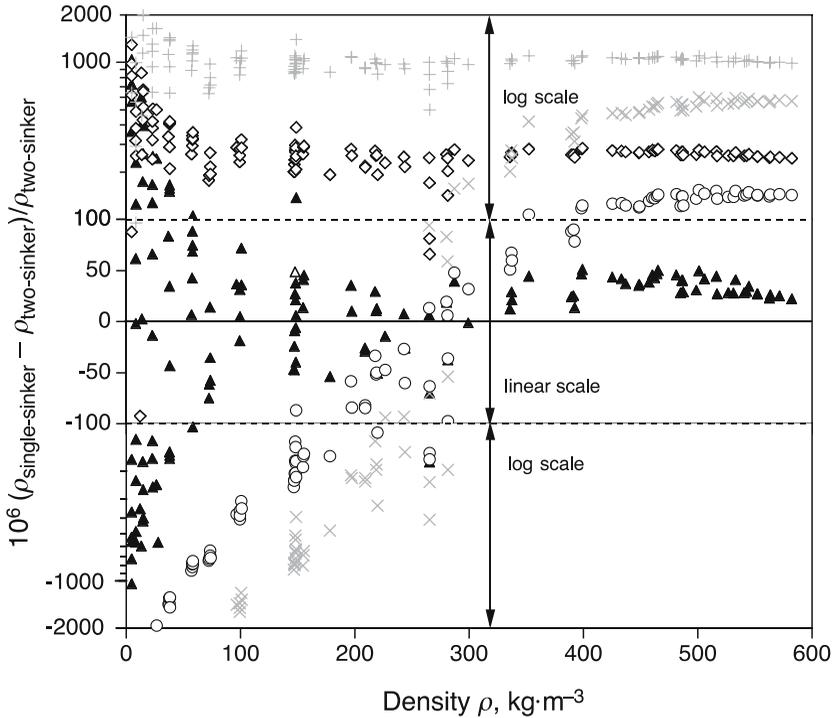


Fig. 6. Comparison of propane densities analyzed as single-sinker data with different corrections for the force transmission error: Ta sinker: \times no corrections ($\phi=1$), $+$ apparatus correction only ($\phi=\phi_0$); Ti sinker: \circ no corrections ($\phi=1$), \diamond apparatus correction only ($\phi=\phi_0$); \blacktriangle including fluid effects (Eq. (26)).

fluid-specific effect can be compensated for in a single-sinker densimeter. The present data illustrate these points, but we emphasize that the exact magnitude of the errors and corrections will be fluid and apparatus specific.

4. CONCLUSIONS

We have developed a quantitative analysis of the force transmission errors in hydrostatic balance densimeters utilizing magnetic suspension couplings. The FTE comprises contributions from the apparatus itself and from the fluid being measured. For two-sinker densimeters that have balance tare and calibration weights in addition to the sinkers, a new analysis allows the determination of a “coupling factor” (which is related to the FTE) at any density. This analysis fully compensates for the FTE and

allows measurements on strongly paramagnetic fluids. However, even with no compensation, the FTE in a two-sinker densimeter is small (on the order of a few tens of ppm), except for measurements on strongly paramagnetic fluids.

For single-sinker densimeters, the force transmission errors can be substantially larger. Compensation for the FTE must be made to avoid significant errors. We have refined earlier analyses for this type of instrument. The relative errors in density are largest at low fluid densities and with a sinker of high density. The apparatus portion of the FTE can be determined with a simple experiment in vacuum. This correction should always be applied. The fluid-specific FTE can be estimated by measurements of one or more fluids using two different sinkers. This experiment, though tedious, yields an apparatus constant that can be applied to compensate for the magnetic effects of any other fluid with a known magnetic susceptibility. With this analysis, the uncertainty in density for a single-sinker instrument can approach that of a two-sinker instrument, except at very low densities.

With the appropriate analysis, the force transmission “error” becomes an *effect* that can be calculated and compensated for rather than a source of significant error in density measurements.

REFERENCES

1. W. Wagner and R. Kleinrahm, *Metrologia* **41**:S24 (2004).
2. H. W. Lösch, *Entwicklung und Aufbau von neuen Magnetschwebewaagen zur berührungsfreien Messung vertikaler Kräfte*, Fortschr.-Ber. VDI, Reihe 3, No. 138 (VDI-Verlag, Düsseldorf, 1987).
3. N. Kuramoto, K. Fujii, and A. Waseda, *Metrologia* **41**:S84 (2004).
4. R. Kleinrahm and W. Wagner, *Entwicklung und Aufbau einer Dichtemeßanlage zur Messung der Siede- und Taudichten reiner fluider Stoffe auf der gesamten Phasengrenzkurve*, Fortschr.-Ber. VDI, Reihe 3, No. 92 (VDI-Verlag, Düsseldorf, 1984).
5. R. Kleinrahm and W. Wagner, *J. Chem. Thermodyn.* **18**:739 (1986).
6. H. W. Lösch, R. Kleinrahm, and W. Wagner, *Chem.-Ing.-Tech.* **66**:1055 (1994).
7. M. O. McLinden and C. Lösch-Will, *J. Chem. Thermo.* **39**:507 (2007).
8. M. O. McLinden, submitted to *J. Chem. Eng. Data*.
9. D. R. Lide, ed., *CRC Handbook of Chemistry and Physics*, 85th Ed., (CRC Press, Boca Raton, Florida, 2004).
10. M. O. McLinden, *unpublished data*, National Institute of Standards and Technology, Boulder, Colorado, U.S.A. (2006).
11. R. S. Davis, *Metrologia* **35**:49 (1998).
12. M. O. McLinden, *Meas. Sci. Technol.* **17**:2597 (2006).
13. J. W. Beams and A. M. Clarke, *Rev. Sci. Instrum.* **33**:750 (1962).
14. K. Brachthäuser, R. Kleinrahm, H. W. Lösch, and W. Wagner, *Entwicklung eines neuen Dichtemeßverfahrens und Aufbau einer Hochtemperatur-Hochdruck-Dichtemeßanlage*, Fortschr.-Ber. VDI, Reihe 8, No. 371 (VDI-Verlag, Düsseldorf, 1993).

15. W. Wagner and K. M. de Reuck, *International Thermodynamic Tables of the Fluid State—9, Oxygen* (Blackwell Scientific Publishing, Oxford, 1987).
16. R. Span, E. W. Lemmon, R. T. Jacobsen, W. Wagner, and A. Yokozeki, *J. Phys. Chem. Ref. Data* **29**:1361 (2000).
17. J. Klimeck, *Weiterentwicklung einer Ein-Senkörper-Dichtemessanlage und Präzisionsmessungen der thermischen Zustandsgrößen von Kohlendioxid, Argon, Stickstoff und Methan*, (Dissertation, Ruhr-Universität Bochum, Germany, 1997).
18. M. Richter, D. Sommer, and R. Kleinrahm, *personal communication*, Lehrstuhl für Thermodynamik, Ruhr-Universität Bochum, Germany (2007).