Int J Thermophys (2010) 31:698–709
DOI 10.1007/s10765-010-0702-3

Force Transmission Error Analysis for a High-Pressure Single-Sinker Magnetic Suspension Densimeter

Diego E. Cristancho · Ivan D. Mantilla · Saquib Ejaz · Kenneth R. Hall · Gustavo A. Iglesias-Silva · Mert Atilhan

Received: 16 May 2009 / Accepted: 5 January 2010 / Published online: 23 January 2010

Abstract The magnetic suspension densimeter (MSD) is a sophisticated, state-of-the-art device that provides extremely accurate results for density measurements. The MSD uses a magnetic technique to couple a mass inside a measurement cell with an external mass balance for mass measurement. This article presents a force transmission error (FTE) analysis for a high-pressure, single-sinker MSD. Due to the magnetic working principle of the apparatus, magnetic properties of the high-pressure cell and external magnetic fields affect the measurements slightly. For the analysis, McLinden et al. suggest making measurements using two different sinkers, a titanium sinker and a copper sinker, having the same mass. The measurements cover densities for methane, ethane, carbon dioxide and nitrogen over the temperature range from 265 K to 450 K ($\pm$5 mK stability) up to 180 MPa (uncertainty of 0.01 % full scale: 200 MPa). Comparing and manipulating the measurements permit determination of apparatus and fluid specific effects that contribute to the FTE. For this MSD, the apparatus effect is about 200 ppm, which effectively masks any fluid specific effect. A comprehensive analysis of the FTE produces a uniform deviation for density values of about 0.05 % at 2σ across the full range of pressure.

D. E. Cristancho · I. D. Mantilla · S. Ejaz · K. R. Hall (✉)
Artie McFerrin Department of Chemical Engineering, Texas A&M University,
College Station, TX 77843-3122, USA
e-mail: krhall@tamu.edu

G. A. Iglesias-Silva
Departamento de Ingeniería Química, Instituto Tecnológico de Celaya,
38010 Celaya, Guanajuato, México

M. Atilhan
Chemical Engineering Department, Qatar University, 2713 Doha, Qatar

Keywords Densimeter · Force transmission error · High pressure · Magnetic suspension coupling

1 Introduction

Magnetic suspension densimeters (MSD) yield very accurate p–ρ–T data. An MSD utilizes the Archimedes principle, and consists of a pressurized cell with an internal sinker that experiences a buoyancy force when the cell contains a fluid. A magnetic suspension coupling system transmits the change in its apparent weight to a high-precision balance. Knowledge of the apparent weight of the sinker and its properties allows determination of accurate densities for the fluid. The general features of this apparatus appear in [1] and [2], and the specific details of the present instrument appear in [3–6].

The force transmission error (FTE) is a significant source of uncertainty in this technique. The FTE is the error caused by the magnetic behavior of the cell, the suspension coupling, and the measured fluid that leads to inaccuracies in the transmitted force measured at the high-precision balance. Different approaches exist to estimate and compensate for the FTE [7,8]. Kano et al. [7] have proposed an analysis based upon a magnetostatic study of the MSD suspension. This analysis accounts for all the magnetic, gravitational, and buoyancy forces during the measuring process. Unfortunately, this approach requires a detailed knowledge of both the magnetic and geometric properties of the MSD and the fluid, which are not always available. McLinden et al. [8] have developed an empirical analysis applicable to both two- and single-sinker MSDs. In their analysis, they attribute the FTE to two different sources. One is the error introduced by the MSD, the *"apparatus effect"* that accounts for error caused by the magnetic characteristics of the densimeter cell and the suspension coupling. In principle, the apparatus effect is available from vacuum measurements of the sinker mass. The other source of error, the "*fluid-specific effect*," depends upon the magnetic properties of the fluid.

McLinden et al. [8] present a detailed explanation of each of the different sources of error and a mathematical model for its determination. The mathematical model results from force balances during the different measurements steps in the MSD. For a single-sinker MSD, they suggest performing experiments using two different sinkers to determine unknowns in the mathematical model. They applied their technique to the single-sinker densimeter developed by Brachthäuser and coworkers [2]. The results show different values for the apparatus effect for each densimeter version, and they conclude, "*the apparatus effect must be determined for each densimeter*." An additional important result in their analysis is that "*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*" presuming the two-sinker densimeter data are correct.

Rubotherm Präzisionsmesstechnik GmbH manufactured our single-sinker MSD designed to work at pressures up to 200 MPa over a temperature range of 193 K to 523 K. We have used this apparatus to measure densities of mixtures similar to natural gas as well as for low- and high-pressure densities for pure components [3–6]. The FTE

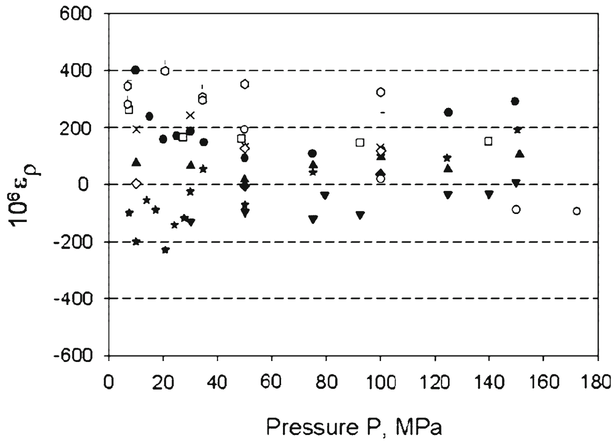

Fig. 1 Apparatus constant calculations based upon experimental data measured in the high-pressure single-sinker MSD; Nitrogen: • 265 K, ▲ 298 K, * 350 K; Carbon dioxide: ▼ 310 K, ♦ 350 K; Methane: - 305 K, ı 340 K, ⬡ 400 K; Ethane: × 298 K, ∘ 350 K, □ 400 K, ◇ 450 K

analysis for this apparatus uses the principles of McLinden et al. [8], but not exactly the same procedure because of peculiarities in this MSD (thicker cell wall causing a higher apparatus contribution to the FTE). Scatter in the apparatus constant for this MSD determined from the McLinden et al. [8] approach is apparent in Fig. 1. The apparatus constant (i.e., a measure of the fluid-specific effect) results have an average value of (55.5 ± 211.5) ppm. The 55.5 ppm is essentially the same as determined by McLinden et al. [8] for their apparatus. This result leads to a slightly different approach to quantify and compensate for this source of error.

2 Force Transmission Error Analysis

Figure 2 presents the operation of the single-sinker MSD. The (a) position is the balance tare; the (b) position weighs the permanent magnet (pm); and the (c) position weighs the permanent magnet and the sinker. In all positions, the electromagnet (em) is weighed. The forces on the balance are

$$w_1 = \alpha \left\{\phi \left[m_{\text{pm}} - \rho_{\text{f}} V_{\text{pm}}\right] + m_{\text{em}} + m_{\text{c1}} - \rho_{\text{a}} \left(V_{\text{em}} + V_{\text{c1}}\right) + w_{\text{zero}}\right\} \quad (1)$$

$$w_2 = \alpha \left\{\phi \left[m_{\text{s}} + m_{\text{pm}} - \rho_{\text{f}} \left(V_{\text{s}} + V_{\text{pm}}\right)\right] + m_{\text{em}} + m_{\text{c2}} - \rho_{\text{a}} \left(V_{\text{em}} + V_{\text{c2}}\right) + w_{\text{zero}}\right\} \quad (2)$$

$$w_2 - w_1 = \alpha \left\{\phi \left[m_{\text{s}} - \rho_{\text{f}} V_{\text{s}}\right] + m_{\text{c2}} - m_{\text{c1}} - \rho_{\text{a}} \left(V_{\text{c1}} - V_{\text{c2}}\right)\right\}, \quad (3)$$

where α is the balance calibration factor, ϕ is the coupling factor, ρ_{f} is the fluid density, ρ_{a} is the density of the purge gas in the balance chamber (nitrogen), V is the sinker volume, m is the mass, w is the balance reading, and w_{zero} is the balance reading with nothing on the balance pan or weighing hook. The subscripts are: 1 denotes balance position 1, pm the permanent magnet and includes the lifting device, em the

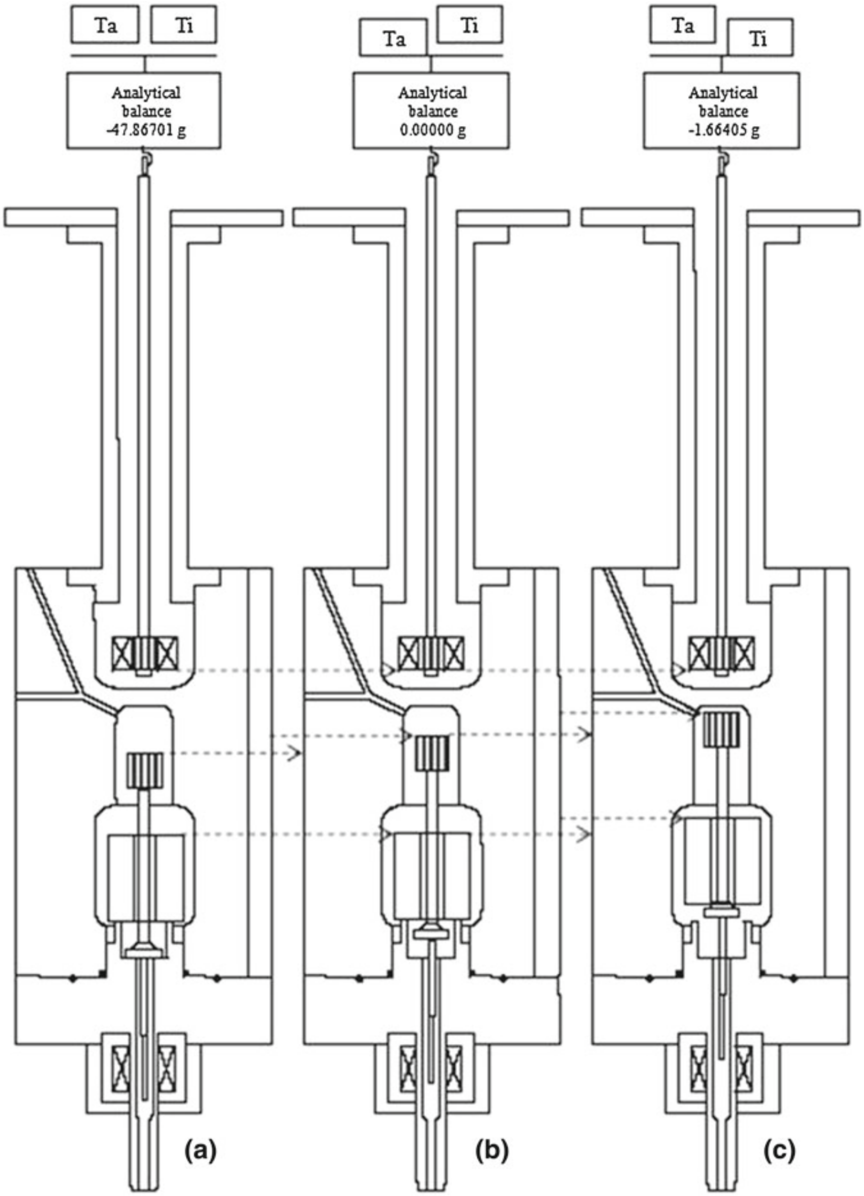

Fig. 2 Operation of the single-sinker MSD: (**a**) suspension control (SC) 'off', Ti and Ta both raised, (**b**) SC 'on'; zero position (ZP), Ta lowered, Ti raised, and (**c**) measuring position, SC 'on', Ta raised, Ti lowered

electromagnet and includes linkage to the balance, c1 compensation weight 1 (tantalum), and c2 compensation weight 2 (titanium). The balance calibration factor α is determined by a separate calibration using standard weights. As $V_{c2} \approx V_{c1}$ and ρ_a is small,

$$w_2 - w_1 = \alpha \{\phi [m_s - \rho_f V_s] + (m_{c2} - m_{c1})\}. \tag{4}$$

The coupling factor, ϕ, represents the correction to the force balance in the MSD caused by the FTE. For a measurement of vacuum in the cell, $\rho_f = 0$ and

$$(w_2 - w_1)_0 = \alpha \{\phi_0 m_s + (m_{c2} - m_{c1})\}. \tag{5}$$

Here, ϕ_0 accounts for the apparatus effect of the FTE. Combining Eqs. 4 and 5,

$$\rho_f = \rho_s \left(1 - \frac{\phi_0}{\phi}\right) + \frac{(w_2 - w_1)_0 - (w_2 - w_1)_f}{\phi \alpha V_s} \tag{6}$$

and, from Eq. 4,

$$\rho_f = \rho_s + \frac{(m_{c2} - m_{c1}) - (w_2 - w_1)_f / \alpha}{\phi V_s}. \tag{7}$$

Equations 6 and 7 are equivalent. Now, assuming that

$$\rho_f = \rho_{\phi=1} + \Delta\rho_{\text{FTE}} \tag{8}$$

and postulating that

$$\rho_f = \rho_{\phi=1} + \Delta\rho_{\text{ApparatusEffect}} + \Delta\rho_{\text{FluidEffect}}, \tag{9}$$

it is possible to rewrite Eq. 9 as

$$\rho_f = \rho_{\phi=\phi_0} + \Delta\rho_{\text{FluidEffect}}, \tag{10}$$

where

$$\rho_{\phi=\phi_0} \equiv \rho_{\phi=1} + \Delta\rho_{\text{ApparatusEffect}}, \tag{11}$$

which basically corrects the raw density data with the apparatus effect. One important detail is that, although the true fluid density ρ_f appears in two terms, the right-hand side of Eq. 7 does not change. Density measurements performed on different fluids with two different sinkers (copper and titanium) determine the coupling factor using Eqs. 7 and 10. Now, assuming

$$\Delta\rho_{\text{FluidEffect}}(T_1, P_1) \cong \Delta\rho_{\text{FluidEffect}}(T_2, P_2) \tag{12}$$

when (T_1, P_1) and (T_2, P_2) are nearly the same values for the same fluid, it is possible to combine Eqs. 7 and 10 for both titanium and copper sinkers;

$$\rho^{\mathrm{s1}}_{\phi=\phi_0}(T_1, P_1) + \Delta\rho_{\mathrm{FluidEffect}}(T_1, P_1) = \rho_{\mathrm{s1}} + \frac{(m_{\mathrm{c2}} - m_{\mathrm{c1}}) - (w_2 - w_1)^{\mathrm{s1}}_{\mathrm{f}}/\alpha}{\phi V_{\mathrm{s1}}} \tag{13}$$

$$\rho^{\mathrm{s2}}_{\phi=\phi_0}(T_2, P_2) + \Delta\rho_{\mathrm{FluidEffect}}(T_2, P_2) = \rho_{\mathrm{s2}} + \frac{(m_{\mathrm{c2}} - m_{\mathrm{c1}}) - (w_2 - w_1)^{\mathrm{s2}}_{\mathrm{f}}/\alpha}{\phi V_{\mathrm{s2}}} \tag{14}$$

where s1 and s2 denote sinker 1 (titanium) and sinker 2 (copper). Finally, Eqs. 13 and 14 using the assumption of Eq. 12 provide ϕ:

$$\phi = \frac{(m_{\mathrm{c2}} - m_{\mathrm{c1}})\left(\frac{1}{V_{\mathrm{s2}}} - \frac{1}{V_{\mathrm{s1}}}\right) - \frac{1}{\alpha}\left[\frac{(w_2-w_1)^{\mathrm{s2}}_{\mathrm{f}}}{V_{\mathrm{s2}}} - \frac{(w_2-w_1)^{\mathrm{s1}}_{\mathrm{f}}}{V_{\mathrm{s1}}}\right]}{\left[\rho^{\mathrm{s2}}_{\phi=\phi_0} - \rho^{\mathrm{s1}}_{\phi=\phi_0}\right] - [\rho_{\mathrm{s2}} - \rho_{\mathrm{s1}}]}. \tag{15}$$

Equation 15 is the expression to determine the FTE from the two sinkers experiments.

3 Experimental

Performing the two sinkers experiments required collecting data for four pure compounds (methane, ethane, carbon dioxide, and nitrogen) up to 180 MPa at temperatures ranging between 265 K and 400 K. Methane and nitrogen came from Scott Specialty Gases having a grade of Ultra High Purity with mole fractions of 99.99 % and 99.9995 %, respectively. Ethane and CO_2 came from Matheson Tri Gas with mole fractions of 99.95 % and 99.999 %, respectively. The titanium sinker mass and volume were 30.39159 g and 6.741043 cm^3, and the copper sinker mass and volume were 30.398939 g and 3.403268 cm^3 (determined using the apparatus and procedure described by McLinden and Splett [9]). Patil et al. [3,4] described the single-sinker MSD, and additional modifications to expand the range of measured temperature appeared in [5,6]. The Platinum resistance thermometer (PRT) (Minco Products Model S1059PA5X6) has been calibrated at fixed temperature points defined by ITS-90 and by a calibrated PRT traceable to NIST. The temperature stability was ±5 mK, and the uncertainty of the PRT was 2 mK with respect to the triple point of water [5]. Two Digiquartz® transducers (40 MPa and 200 MPa) from Paroscientific Inc. were used to measure pressure. The uncertainty for these transducers was 0.01 % of full scale or 0.004 MPa and 0.02 MPa, respectively.

4 Results and Analysis

The two sinkers experiment, reported in Table 1, cover several temperatures for pressures up to 180 MPa. All the data are at similar pressure and temperature conditions

Table 1 Two sinkers experiment temperatures

Fluid	Copper–titanium sinkers (K)
N_2	265
	298
	350
CO_2	310
	350
CH_4	305
	340
	400
C_2H_6	298
	400
	450

Table 2 Characteristic parameters for the MSD

Calibration factor α	1.00015
Ti sinker mass (g)	30.39159
Cu sinker mass (g)	30.398939
Ti compensation mass (g)	11.23311
Ta compensation mass (g)	41.61804

for both sinkers to justify Eq. 12. Tables 2 and 3 contain samples of raw data for independent verifications. Additional data for all the fluids to validate the FTE results will appear in future publications with their respective analyses. The deviations for the raw densities (densities without FTE compensation) compared to densities calculated with equations of state [10–13] as implemented in NIST REFPROP 8.0 [14] appear in Figs. 3 and 4. The data have considerable deviations in the low-pressure range. This reflects the observation that the FTE affects the low-pressure densities to a greater extent as suggested by McLinden et al. [8].

Equations 7 and 15 determine both $\rho_{\phi=\phi_0}$ and the coupling factor, ϕ, for the copper and titanium sinkers. The determined value for the apparatus effect is $(\phi_0 - 1) = (189 \pm 16)$ ppm for the set of experiments. This value corresponds to a correction of about 5.17 mg for our vacuum measurement. The apparatus contribution, ϕ_0, from the FTE for our high-pressure, single-sinker MSD is higher than any reported by McLinden et al. [8]. This result occurs because our cell design has thick walls for higher pressures, and it is diamagnetic (beryllium copper). It is important to note that the high fluctuations in the apparatus contribution to the FTE are products of the two sinkers experiment. Changing the sinkers introduces a considerable amount of uncertainty into the experiment. For example, ϕ_0 depends on exact alignment and relative position of e-magnet, p-magnet, etc.; the disassembly and reassembly required for two sinkers experiment will result in slightly different positions. This fact is one of the most serious difficulties when performing the two sinkers experiment, and it is more serious for the high-pressure, single-sinker MSD.

Table 3 Experimental data sample

	T (Cu) (K)	P (Cu) (MPa)	T (Ti) (K)	P(Ti) (MPa)	$(w_2 - w_1)$ Cu (g)	$(w_2 - w_1)$ Ti (g)	Vol Cu sinker (cm^3)	Vol Ti sinker (cm^3)	$(w_2 - w_1)0$ Cu (g)	$(w_2 - w_1)0$ Ti (g)
N_2	264.810	19.993	264.808	20.003	−0.82470	−1.66061	3.397588	6.734622	0.01924	0.01228
N_2	264.827	29.966	264.829	29.978	−1.13350	−2.27223	3.397295	6.733934	0.01924	0.01228
N_2	264.827	100.461	264.823	100.437	−2.06436	−4.11584	3.395220	6.729075	0.01924	0.01228
CO_2	310.017	124.778	310.008	124.812	−3.87540	−7.69887	3.402602	6.735684	0.01964	0.01222
CH_4	338.070	20.683	338.082	20.687	−0.42490	−0.86576	3.411074	6.748006	0.01945	0.01256
CH_4	338.068	34.492	338.066	34.473	−0.64800	−1.30632	3.410663	6.747088	0.01945	0.01256
CH_4	399.993	50.005	400.001	50.037	−0.6771	−1.36279	3.420964	6.756778	0.01948	0.01268
C_2H_6	349.997	150.000	349.985	149.940	−1.76760	−3.52220	3.409012	6.741189	0.01955	0.01235

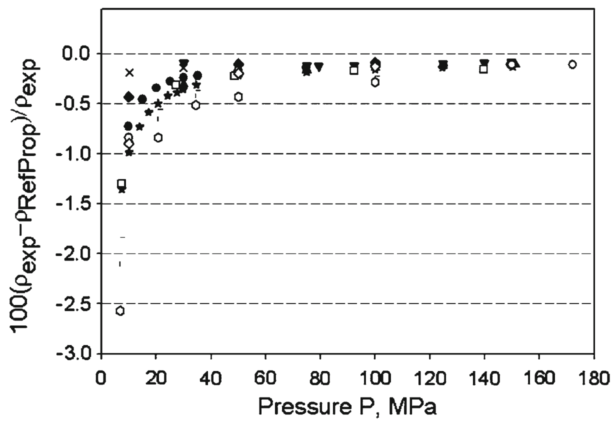

Fig. 3 Titanium sinker raw densities ($\phi = 1$) deviations; Nitrogen: • 265 K, ▲ 298 K, ⋆ 350 K; Carbon dioxide: ▼ 310 K, ♦ 350 K; Methane: - 305 K, ı 340 K, ⬡ 400 K; Ethane: × 298 K, ∘ 350 K, □ 400 K, ◊ 450 K

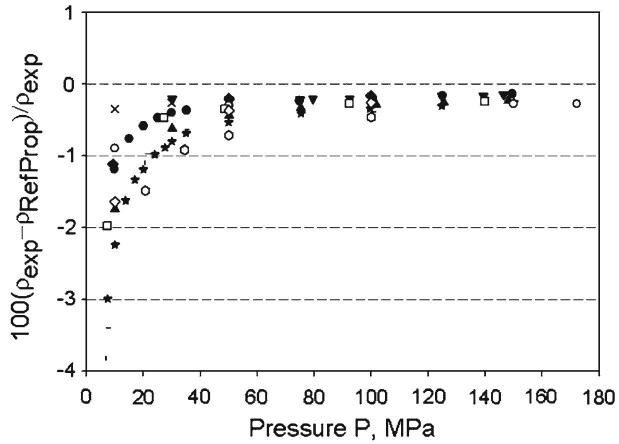

Fig. 4 Copper sinker raw densities ($\phi = 1$) deviations; Nitrogen: • 265 K, ▲ 298 K; Carbon dioxide: ▼ 310 K, ♦ 350 K; Methane: - 305 K, ı 340 K, ⬡ 400 K; Ethane: × 298 K, ∘ 350 K, □ 400 K, ◊ 450 K

Figure 5 presents ($\phi - \phi_0$) as a function of pressure. This plot reveals two important characteristics of our FTE: (1) the coupling factor is essentially independent of pressure and (2) the fluctuations of ($\phi - \phi_0$) are larger than the fluid contribution effect. These observations indicate that the fluid contribution to the FTE is negligible and that the assumption of the FTE is independent of temperature and pressure does not introduce significant uncertainty. This does not mean that the fluid specific effect does not exist, but the apparatus contributions mask its effect. Thus, the experiments on this apparatus compensate only for the apparatus effect. However, the 16 ppm fluctuation in ϕ_0 agrees with the fluctuations of the data when compared to the equations

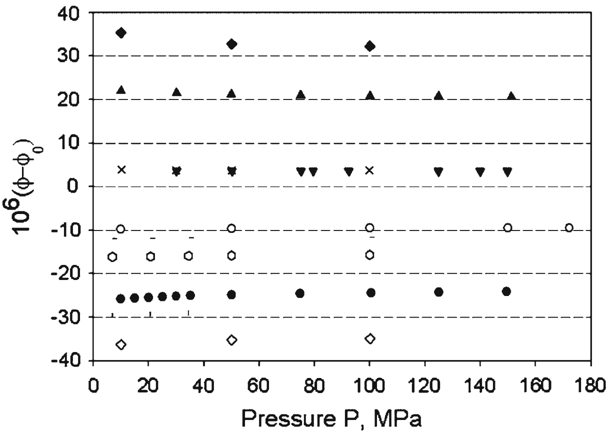

Fig. 5 $(\phi - \phi_0)$ values for the two sinkers experiment: Nitrogen: • 265 K, ▲ 298 K; Carbon dioxide: ▼ 310 K, ♦ 350 K; Methane: - 305 K, ı 340 K, ⬡ 400 K; Ethane: × 298 K, ∘ 350 K, ◇ 450 K

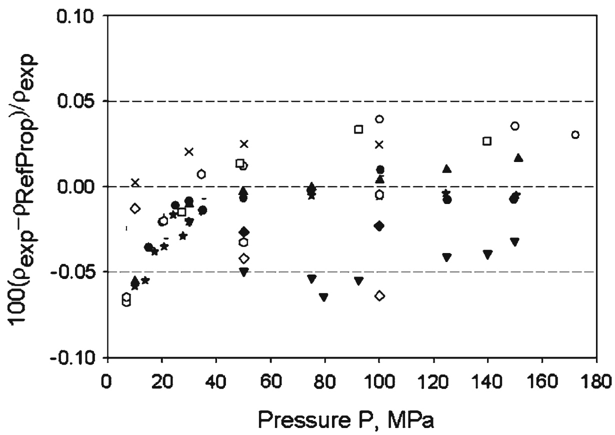

Fig. 6 Titanium sinker corrected density deviations; Nitrogen: • 265 K, ▲ 298 K, * 350 K; Carbon dioxide: ▼ 310 K, ♦ 350 K; Methane: - 305 K, ı 340 K, ⬡ 400 K; Ethane: × 298 K, ∘ 350 K, □ 400 K, ◇ 450 K

of state implemented in NIST REFPROP 8.0 for the different fluids [10–14]. Figure 6 illustrates this behavior.

Figure 6 also indicates that the experimental data for pure compounds lie within a 2σ deviation band of 0.05 %. Higher deviations exist at pressures below 7 MPa caused by the intrinsic characteristics of the high-pressure, single-sinker MSD and its ancillary equipment. However, the low-pressure data fall within the experimental uncertainty at low pressure.

An additional experimental observation is that the data measured with the copper sinker have higher deviations compared to the equations of state than the densities measured with the titanium sinker as is apparent in Fig. 7. This effect is caused by the differences between the sinker densities and the fluid densities. The density of copper is almost twice that of titanium (8905.54 $kg \cdot m^{-3}$ and 4508.44 $kg \cdot m^{-3}$, respectively).

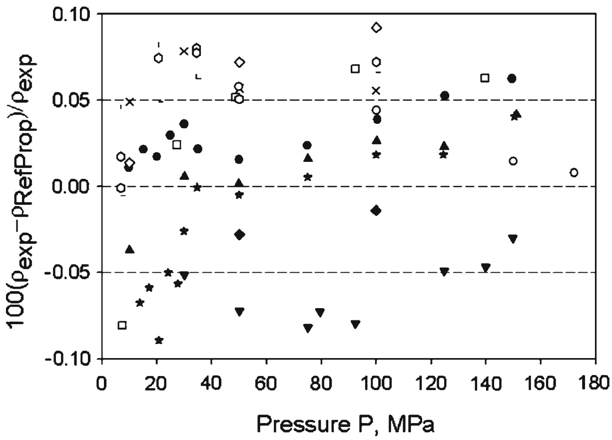

Fig. 7 Copper sinker corrected density deviations; Nitrogen: ● 265 K, ▲ 298 K, * 350 K; Carbon dioxide: ▼ 310 K, ◆ 350 K; Methane: - 305 K, ı 340 K, ⬡ 400 K; Ethane: × 298 K, ○ 350 K, □ 400 K, ◇ 450 K

Better experimental accuracy would result if the density of the sinker were closer to the fluid density. McLinden et al. [8] and Wagner and Kleinrahm [1] also reach this conclusion.

5 Conclusions

This article has reported the FTE analysis for the high-pressure, single-sinker MSD in our laboratory. The analysis consists of comparing densities measured at similar conditions using two different sinkers, copper and titanium, as suggested by McLinden et al. [8]. The apparatus effect is the overwhelming contributor to the FTE having a value of approximately 189 ppm. Compensation of the density measurements using this analysis leads to a 2σ deviation band of 0.05 % compared to RefProp 8.0.

Acknowledgments We gratefully acknowledge support for this work from the Jack E. & Frances Brown Chair endowment and from the Texas Engineering Experiment Station.

References

1. W. Wagner, R. Kleinrahm, Metrologia **41**, S24 (2004)
2. W. Wagner, K. Brachthäuser, R. Kleinrahm, H.W. Lösch, Int. J. Thermophys. **16**, 399 (1995)
3. P. Patil, S. Ejaz, M. Atilhan, D. Cristancho, J.C. Holste, K.R. Hall, J. Chem. Thermodyn. **39**, 1157 (2007)
4. P.V. Patil, Commissioning of a magnetic suspension densitometer for high-accuracy density measurements of natural gas mixtures. Ph.D. Thesis, Texas A&M University, College Station, TX (2005)
5. S. Ejaz, High-accuracy P–ρ–T measurements of pure gas and natural gas like mixtures using a compact magnetic suspension densimeter. Ph.D. Thesis, Texas A&M University, College Station, TX (2007)
6. M. Atilhan, High-accuracy P–ρ–T measurements up to 200 MPa between 200 K to 500 K using a single sinker magnetic suspension densitometer for pure and natural gas like mixtures. Ph.D. Thesis, Texas A&M University, College Station, TX (2005)
7. Y. Kano, Y. Kayukawa, K. Fujii, K. Sato, Meas. Sci. Technol. **18**, 659 (2007)

8. M.O. McLinden, R. Kleinrahm, W. Wagner, Int. J. Thermophys. **28**, 429 (2007)
9. M.O. McLinden, J.D. Splett, J. Res. Natl Inst. Stand. Technol. **113**, 29 (2008)
10. R. Span, E.W. Lemmon, R.T. Jacobsen, W. Wagner, A. Yokoseki, J. Phys. Chem. Ref. Data **26**, 1361 (2000)
11. R. Span, W. Wagner, J. Phys. Chem. Ref. Data **25**, 1509 (1996)
12. U. Setzmann, W. Wagner, J. Phys. Chem. Ref. Data **20**, 1061 (1991)
13. D. Bücker, W. Wagner, J. Phys. Chem. Ref. Data **35**, 205 (2006)
14. E.W. Lemmon, M.L. Huber, M.O. McLinden, NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties-REFPROP, Version 8.0. National Institute of Standards and Technology, Standard Reference Data Program, Gaithersburg, MD (2007)