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2 *cis*-1,3,3,3-tetrafluoroprop-1-ene (R1234ze(Z)) and
3 *trans*-1-chloro-3,3,3-trifluoropropene (R1233zd(E))

4 R. Romeo^{a,*}, P.A. Giuliano Albo^a, S. Lago^a, J. S. Brown^b

5 ^a*Istituto Nazionale di Ricerca Metrologica, Strada delle Cacce 91, 10135*

6 ^b*Department of Mechanical Engineering, The Catholic University of America, 620*
7 *Michigan Ave., NE, Washington, DC 20064, USA*

8 **Abstract**

In this work, liquid phase densities of two fourth generation refrigerants, *cis*-1,3,3,3-tetrafluoroprop-1-ene R1234ze(Z) and *trans*-1-chloro-3,3,3-trifluoropropene R1233zd(E), are measured. The densities have been measured using a vibrating tube densimeter over the temperature range from (273.15 to 333.15) K for pressures up to 30 MPa. For both fluids, the expanded uncertainty at a confidence level of 95% in the density measurements is estimated to be 0.07% over the entire T - p range measured.

9 *Keywords:* density, R1234ze(Z), R1233zd(E), high pressure

10 **1. Introduction**

11 In recent years, the interest in new working fluids, e.g. refrigerants, is growing
12 due to regulations being adopted and implemented to tackle global warming
13 as established by the Kyoto Protocol (1997). This fourth generation of refrigerants
14 (Calm, 2008), in addition to needing to possess attributes such as low
15 toxicity, low flammability, short atmospheric lifetime, and near-zero ozone depleting
16 potential (ODP), must also possess low or ultra-low global warming
17 potential (GWP) UNEP (2014).

18 The refrigerant *cis*-1,3,3,3-tetrafluoroprop-1-ene, i.e. HFO-1234ze(Z), is a
19 hydrofluoroolefin which has zero ODP, an atmospheric lifetime of 10 days and
20 a 100-year time horizon GWP lower than 6 (Akasaka et al., 2014). The refrigerant
21 *trans*-1-chloro-3,3,3-trifluoropropene, i.e. HCFO-1233zd(E), is a hydrochloro-
22 fluorolefin which has a near-zero ODP, an atmospheric lifetime of 26
23 days, and a GWP lower than 7 (Orkin et al., 2014). Thus, these two fluids
24 hold promise as two possible candidates as substitutes for previous generation
25 refrigerants. Despite this fact, the open literature contains few experimental
26 data of the thermodynamic properties for these refrigerants. Regarding density,
27 Kayukawa et al. (2012) measured compressed liquid and saturated liquid density
28 of R1234ze(Z) in the temperature range from (310 to 420) K for pressures up to

*Corresponding author

29 5 MPa. Higashi et al. (2013) and Tanaka et al. (2013) performed the same type
 30 of measurements from (360 to 432) K up to 6 MPa and from (310 to 410) K
 31 up to 5 MPa, respectively. The compressed liquid density of R1234ze(Z) was
 32 also measured by Fedele et al. (2014) from (283 to 363) K for a much wider
 33 pressure range than previously considered, that is, up to 35 MPa. Regarding
 34 R1233zd(E), currently there are only two published papers presenting experi-
 35 mental density data: measurements carried out by Mondéjar et al. (2015) over
 36 the temperature range from (215 to 444) K for pressures up to 24.1 MPa and
 37 by Tanaka (2016) from (328 to 443) K for pressures up to 10 MPa.

38 Therefore, in this paper, we wish to add to the publicly available literature a
 39 number of experimental compressed liquid density measurements for R1234ze(Z)
 40 and R1233zd(E), and in doing so extend the temperature and pressure ranges
 41 beyond those previously considered. The measurements were performed using
 42 a commercial vibrating tube densimeter over the temperature range (273.15 to
 43 333.15) K for pressures up to 30 MPa.

44 2. Experimental section

45 Vibrating-tube densimeters are widely used for accurate measurements of
 46 fluids both in the gaseous and liquid phases, finding applications both in research
 47 and in industry. Some of the most attractive characteristics of these densimeters
 48 are their high precision, operational simplicity and the small amount of sample
 49 volume required to make the measurements. The working principle of vibrating-
 50 tube densimeters is based on measuring the mechanical resonant frequency of
 51 a U-tube, filled with the sample fluid, when it is excited by a piezoelectric
 52 external transducer coupled with the measurement cell. The oscillation periods,
 53 corresponding to the value of a resonant frequency, are directly correlated to the
 54 value of the sample density, which depends mainly on the working temperature
 55 and pressure. Therefore, the vibrating tube densimeter consists of a glass (to
 56 measure at atmospheric pressure) or metallic (to measure at high pressure) U-
 57 shaped capillary tube, with a volume of a few cubic centimeters, isolated in a
 58 thermostatic test cell. The tube is filled with the sample of interest and vibrates
 59 perpendicular to its plane by means of a piezoelectric transducer. The period,
 60 τ , of the harmonic oscillation of the tube can be directly related to the density,
 61 ρ , of the fluid contained in the tube by:

$$\rho(T, p) = A(T, p) \cdot \tau^2(T, p) - B(T, p) \quad , \quad (1)$$

62 where A and B , both of which are dependent on temperature and pressure, are
 63 characteristic parameters of the instrument, defined as

$$A = \frac{K(T, p)}{4\pi^2 V(T, p)} \quad ; \quad B = \frac{M_0}{V(T, p)} \quad , \quad (2)$$

64 where K is the tube stiffness, V is the tube inner volume and M_0 is the evacuated
 65 tube mass.

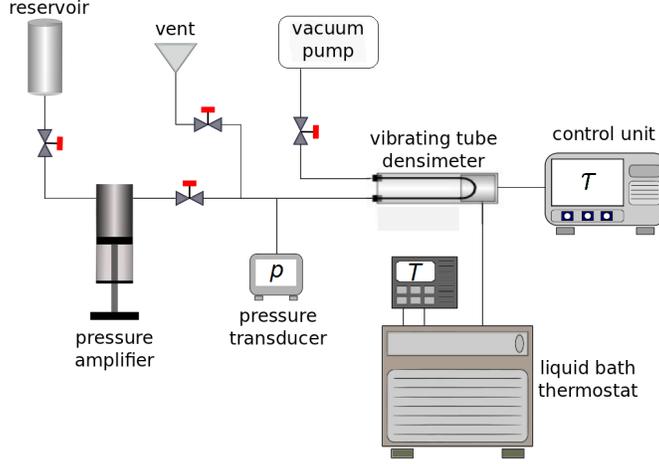


Figure 1: Schematic representation of the experimental apparatus used in this work.

66 The experimental apparatus for density measurements is schematically shown
 67 in Fig. 1. It mainly consists of an Anton Paar DMA 512P vibrating tube densi-
 68 meter connected to an Anton Paar DMA 5000 densimeter, used as a counter
 69 unit. The temperature of the measurement cell, which contains the vibrating
 70 tube, is thermostatically controlled by a liquid bath. The sample temperature
 71 is measured using a PT100 platinum resistance thermometer coupled with a
 72 thermometer readout resulting in an expanded uncertainty of 0.01 K. Details of
 73 the experimental apparatus are provided in Giuliano Albo et al. (2013).

74 2.1. Calibration procedure

75 In order to characterize and determine the instrument parameters defined
 76 in Eq. 2, the vibrating periods of two reference fluids of known density need
 77 to be measured. In order to simplify the calibration procedure, the period is
 78 usually measured in an evacuated tube and one charged with water. Following
 79 this procedure, the unknown density can be obtained through the relation

$$\rho(T, p) = \rho_w(T, p) \frac{\tau^2(T, p) - \tau_0^2(T)}{\tau_w^2(T, p) - \tau_0^2(T)}, \quad (3)$$

80 where τ , τ_w , τ_0 are the measured periods related to the oscillation of the tube
 81 filled with the sample, i.e., evacuated and charged with water. For the present
 82 work, the calibration of the vibrating tube densimeter was performed using
 83 water as the reference fluid while calibrating in a vacuum. The oscillation
 84 period of pure water was measured in the temperature range from (273.15 to
 85 333.15) K, along 6 isotherms, and for pressure from (1 to 30) MPa, i.e., the same
 86 thermodynamic states over which the refrigerants are measured. The water
 87 densities used in the formula are the values provided by the reference equation

88 of state of Wagner and Pruss (2002), which has a maximum uncertainty of
 89 0.003% over the T - p range considered.

90 *2.2. Uncertainty*

In order to estimate the expanded uncertainty of density, it was considered as a function of pure water density ρ_w , vibrating periods τ , τ_w , τ_0 , temperature T and pressure p :

$$\rho = \rho(\rho_w, \tau, \tau_w, \tau_0, T, p) \quad (4)$$

Consequently, propagation of uncertainty as shown below was carried out in order to estimate the relative uncertainty of the water density

$$\frac{u(\rho)}{\rho} = \left[\left(\frac{\partial \rho}{\partial \rho_w} \right)^2 u^2(\rho_w) + \left(\frac{\partial \rho}{\partial \tau} \right)^2 u^2(\tau) + \left(\frac{\partial \rho}{\partial \tau_w} \right)^2 u^2(\tau_w) + \left(\frac{\partial \rho}{\partial \tau_0} \right)^2 u^2(\tau_0) + \left(\frac{\partial \rho}{\partial T} \right)^2 u^2(T) + \left(\frac{\partial \rho}{\partial p} \right)^2 u^2(p) \right]^{0.5} . \quad (5)$$

91 The uncertainty in the reference water density is from Wagner and Pruss
 92 (2002) and is provided above. For the vibrating period, the uncertainty is 0.1 μ s,
 93 corresponding to the repeatability of ten readings at each measuring point.
 94 The uncertainty of the calibrated PT100 resistance thermometer is 0.03 K. The
 95 pressure transducer uncertainty is 0.03 MPa. The relative uncertainty in the
 96 density measurements of density is calculated using Eq. 5 with a coverage factor
 97 of 2. The resulting uncertainty is 0.07% at the confidence level of 95%. Table
 98 1 provides the sources and associated uncertainties contributing to the density
 99 uncertainty. Table 1 demonstrates that the major contributor to the density
 100 uncertainty results from uncertainties in the vibrating period measurements.

Table 1: Density uncertainty budget.

Uncertainty source	Relative magnitude %
water density	0.004
oscillation period	0.070
temperature	0.001
pressure	0.001
Estimated overall uncertainty ($k=2$)	0.07

101 **3. Density results**

102 The experimental densities presented in this paper were calculated using
 103 Eq. 3. However, it should be pointed out that there are multiple ways that
 104 one could analyze the measurements taken with a vibrating tube densimeter.
 105 Particularly, in several papers such as ones by Fedele et al. (2014), Bouchot

106 and Richon (2001), Outcalt and McLinden (2007) or Comuñas et al. (2008), the
 107 authors use different fitting functions to correlate the experimental values or
 108 to calculate the densities. For example, in Comuñas et al. (2008) the function
 109 used to calculate the densities comes from considering that both instrument
 110 parameters A and B are pressure dependent; whereas the method presented
 111 herein considers the parameter B to be pressure independent. Regardless, the
 112 differences between the two approaches have been confirmed to be negligible by
 113 the present authors.

114 3.1. R1234ze(Z) density results

115 R1234ze(Z) in the compressed liquid state was measured over the pressure
 116 range from (1 to 30) MPa, along five isotherms: (273.15, 283.15, 293.15, 313.15,
 117 333.15) K. Since the densimeter calibration was carried out using water as
 118 the reference fluid, the 273.15 K isotherm consists of only the data at 25 MPa
 119 and 30 MPa. The density values at each measured temperature and pressure
 120 are reported in Table 2. Figure 2 shows a plot of the experimental densities
 121 calculated by Eq. 3 as a function of pressure along the five isotherms.

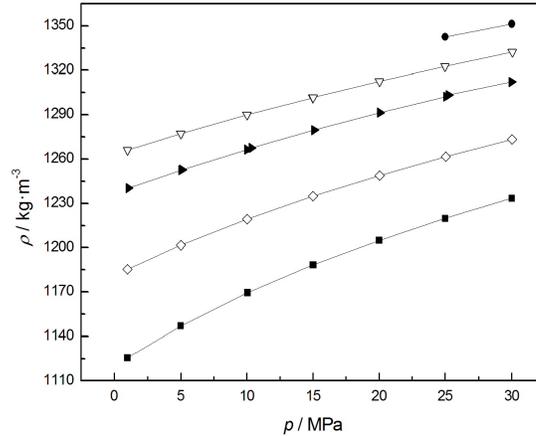


Figure 2: R1234ze(Z) compressed liquid densities as a function of pressure: (●), $T = 273.15$ K; (▽), $T = 283.15$ K; (▴), $T = 293.15$ K; (◇), $T = 313.15$ K; (■), $T = 333.15$ K.

122 The experimental results were compared with the fundamental equation of
 123 state for R1234ze(Z) developed by Akasaka et al. (2014), even though it was
 124 developed without access to experimental liquid density data.

125 Fig. 3 reports the deviations of the experimental values from the equation
 126 of state (zero line) as a function of pressure. Although the declared validity of
 127 the Akasaka equation is for pressures up to 6 MPa, Fig. 3 shows deviations over
 128 the entire pressure range considered herein. Considering that the equation has

Table 2: Experimental R1234ze(Z) density ρ at temperature T and pressure p .

T/K	p/MPa	$\rho/\text{kg}\cdot\text{m}^{-3}$
273.154	25.00	1342.58
273.145	30.01	1351.38
283.148	1.00	1266.05
283.151	5.01	1277.22
283.149	10.01	1290.00
283.153	15.00	1301.59
283.153	15.01	1301.63
283.148	20.02	1312.54
283.151	24.99	1322.61
283.153	30.05	1332.32
293.146	1.08	1240.34
293.154	5.05	1252.39
293.143	5.11	1252.83
293.153	10.03	1266.48
293.147	10.35	1267.52
293.148	15.09	1279.66
293.147	20.07	1291.49
293.153	25.08	1302.24
293.150	25.26	1303.34
293.150	30.00	1312.22
313.156	1.00	1185.36
313.154	1.02	1185.46
313.152	5.01	1201.61
313.152	10.03	1219.29
313.150	15.01	1234.80
313.150	20.04	1248.91
313.151	25.05	1261.67
313.153	30.03	1273.33
333.148	1.00	1125.59
333.156	5.00	1146.91
333.150	10.06	1169.46
333.152	15.00	1188.23
333.152	15.03	1188.32
333.151	20.00	1204.91
333.152	25.00	1219.84
333.151	30.00	1233.41

¹²⁹ a stated uncertainty of 0.2% for liquid density, most of the measurements are
¹³⁰ in agreement with Akasaka's equation.

¹³¹ Furthermore, the densities presented herein were also compared with the
¹³² measurements carried out by Fedele et al. (2014), also using a vibrating tube

133 densimeter, for temperatures from (283 to 363) K for pressures up to 35 MPa.
 134 The deviations of our results from Fedele et al. densities are shown in Fig. 4.
 135 The deviations systematically increase as the pressure increases, but considering
 136 the uncertainty declared by Fedele et al. (2014) (maximum uncertainty of 0.07%)
 137 all the experimental data are in agreement.

138 From the period measurements, the densities were also calculated following
 139 the method used in Comuñas et al. (2008), in order to compare the two different
 140 methods. Figure 5 presents the deviations of the densities using the two meth-
 141 ods: most of the deviations are lower than the uncertainty, demonstrating that
 142 there is no major difference between the two methods at low pressures, with
 143 just three data points at the higher pressures (25 MPa and 30 MPa) deviating
 144 up to about 0.1%.

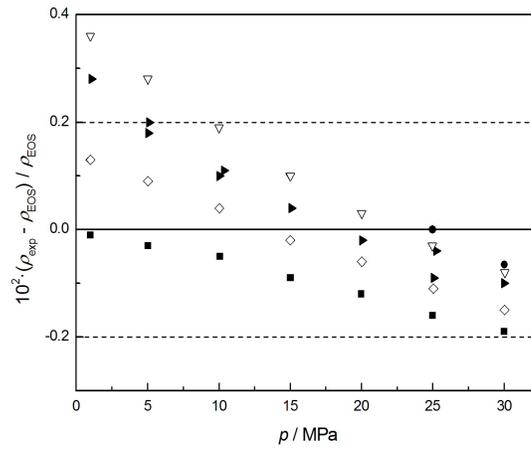


Figure 3: Deviations of R1234ze(Z) experimental densities from the fundamental equation of state of Akasaka et al. (2014) as a function of pressure: (●), $T = 273.15$ K; (▽), $T = 283.15$ K; (▶), $T = 293.15$ K; (◇), $T = 313.15$ K; (■), $T = 333.15$ K; the dashed lines represent the stated uncertainty of Akasaka et al. liquid density.

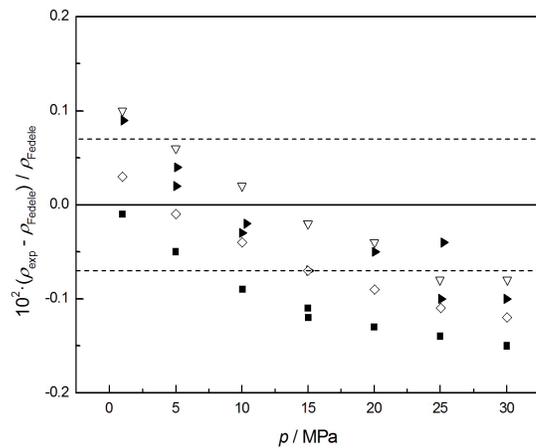


Figure 4: Deviations of R1234ze(Z) experimental densities from the measurements of Fedele et al. (2014) as a function of pressure: (∇), $T = 283.15$ K; (\blacktriangleright), $T = 293.15$ K; (\diamond), $T = 313.15$ K; (\blacksquare), $T = 333.15$ K; the dashed lines represent the maximum uncertainty of Fedele et al. densities.

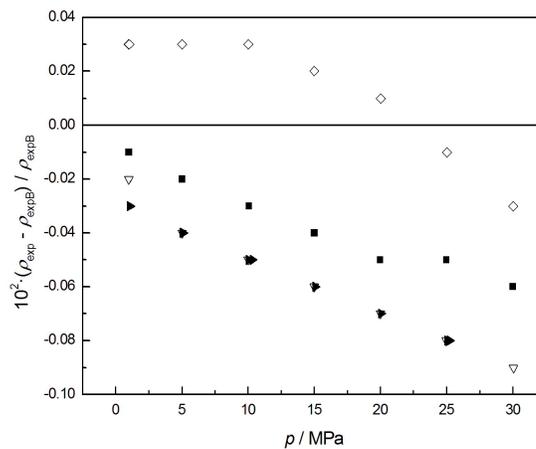


Figure 5: Deviations of R1234ze(Z) experimental densities from the experimental values calculated by the B pressure dependent method as a function of pressure: (∇), $T = 283.15$ K; (\blacktriangleright), $T = 293.15$ K; (\diamond), $T = 313.15$ K; (\blacksquare), $T = 333.15$ K.

145 *3.2. R1233zd(E) density results*

146 The compressed liquid density of R1233zd(E) was measured along five isotherms
 147 (274.15, 283.15, 293.15, 313.15, 333.15) K for pressures from (1 to 25) MPa. In
 148 Table 3, the experimental density values at each measured temperature and
 149 pressure are reported, while Fig. 6 shows R1233zd(E) densities as a function of
 150 pressure along the five isotherms. The experimental results were compared to
 151 the fundamental equation of state developed by Mondéjar et al. (2015). Fig. 7
 152 provides the deviations of the experimental values from the equation of state
 153 (zero line) as a function of pressure. Figure 7 shows that all the deviations are
 154 within $\pm 0.06\%$, demonstrating that all the measurements are in good agreement
 155 with the existing equation.

156 The density of R1233zd(E) was also calculated by using the B pressure
 157 dependent method, and the results are compared with the densities obtained by
 158 Eq. 3. The deviations between the two methods are shown in Fig. 8, with all
 159 the deviations being lower than 0.08%. Similar to the case of R1234ze(Z), the
 160 larger deviations correspond to the higher pressures.

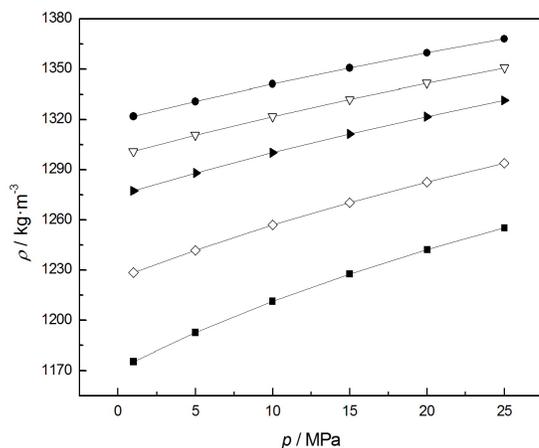


Figure 6: R1233zd(E) compressed liquid densities as a function of pressure: (●), $T = 274.15$ K; (▽), $T = 283.15$ K; (▶), $T = 293.15$ K; (◊), $T = 313.15$ K; (■), $T = 333.15$ K.

Table 3: Experimental R1233zd(E) density ρ at temperature T and pressure p .

T/K	p/MPa	$\rho/\text{kg}\cdot\text{m}^{-3}$
274.150	1.00	1321.95
274.147	5.00	1330.84
274.151	10.00	1341.16
274.150	15.00	1350.75
274.149	20.01	1359.73
274.149	25.00	1368.12
283.154	1.00	1301.12
283.148	5.00	1310.73
283.150	10.00	1321.78
283.147	15.01	1332.07
283.148	20.00	1341.64
283.153	25.01	1350.73
293.152	1.00	1277.44
293.151	5.04	1288.16
293.149	10.02	1300.25
293.151	15.01	1311.40
293.152	20.01	1321.80
293.151	25.00	1331.52
313.152	1.00	1228.52
313.152	4.99	1241.96
313.151	10.00	1257.00
313.150	15.00	1270.49
313.152	20.01	1282.69
313.147	25.00	1293.96
333.149	1.00	1175.46
333.151	5.00	1192.70
333.152	10.00	1211.40
333.152	15.00	1227.66
333.146	20.04	1242.27
333.147	25.01	1255.26

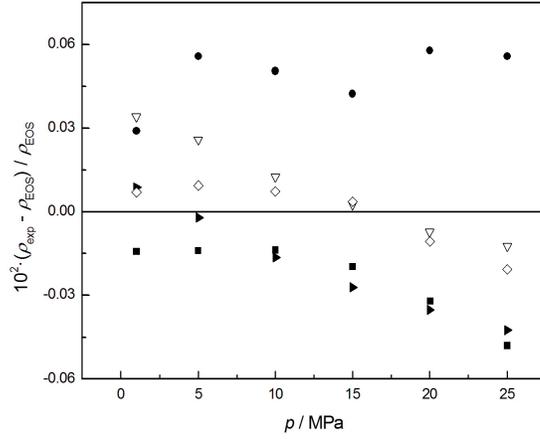


Figure 7: Deviations of R1233zd(E) experimental densities from the fundamental equation of state of Mondéjar et al. (2015) as a function of pressure: (●), $T = 273.15$ K; (▽), $T = 283.15$ K; (▶), $T = 293.15$ K; (◇), $T = 313.15$ K; (■), $T = 333.15$ K.

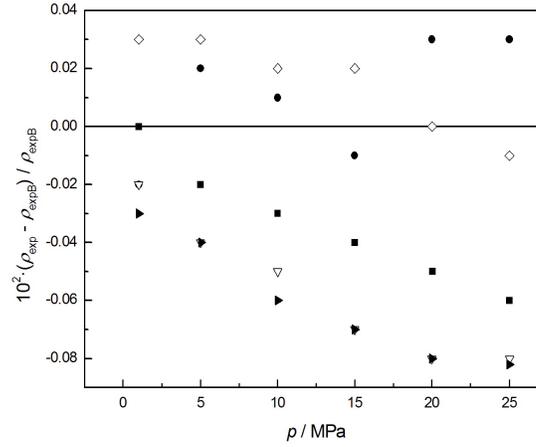


Figure 8: Deviations of R1233zd(E) experimental densities from the experimental values calculated by the B pressure dependent method as a function of pressure: (●), $T = 273.15$ K; (▽), $T = 283.15$ K; (▶), $T = 293.15$ K; (◇), $T = 313.15$ K; (■), $T = 333.15$ K.

161 4. Conclusion

162 Since there is on-going and growing interest in environmentally-friendly, al-
163 ternative refrigerants possessing low and ultra-low GWP values and the need
164 for additional measured data of these fluids, this paper places in the publicly
165 available literature density measurements of R1234ze(Z) and R1233zd(E).

166 The density measurements were taken using a vibrating tube densimeter
167 (Anton Paar 512P) over the temperature range from (273.15 to 333.15) K and
168 for pressures from (1 to 30) MPa with an expanded uncertainty of 0.07% at the
169 95% confidence level.

170 The measured densities of R1234ze(Z) were compared with the fundamental
171 Helmholtz equation of state of Akasaka et al. (2014). Although the equation is
172 valid for pressures only up to 6 MPa, it is in good agreement with the experimen-
173 tal data reported herein. In addition, the measured values were also compared
174 with the measured densities of Fedele et al. (2014), with both datasets demon-
175 strating good agreement over the entire T - p range. The experimental densities
176 of R1233zd(E) were also compared with the dedicated fundamental Helmholtz
177 equation of state of Mondéjar et al. (2015), demonstrating good agreement with
178 the experimental data reported herein.

179 In this work the density results were calculated using two different density
180 functions: the first considered one of the instrument's fitting parameters to be
181 pressure dependent and the second method considered it to be pressure inde-
182 pendent. Since the measurements were carried out at pressures up to 30 MPa,
183 the two methods resulted in differences that were negligible.

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