Determination of the Density of Toluene in the Range from (293 to 373) K and from (0.1 to 30) MPa[†]

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A hydrostatic balance densitometer with a magnetic suspension coupling has been used to measure the density of liquid toluene in the range from (293 to 373) K and pressures up to 30 MPa. New results of measurements of the density of toluene in the compressed liquid region are presented and compared with literature data. The uncertainty of the present density data is estimated to be within ± 0.01 % across the full temperature and pressure range.

Introduction

Density measurement is a key element of both mass and volume flow rate measurement in the oil industry and as such is fundamental to the commercial operation of facilities. The most widely implemented approach for mass flow measurement is to use a volumetric flowmeter in conjunction with a flow-through, oscillating-tube densitometer. All flowmeters require periodic calibration, and the traceability for this activity within the U.K. is provided through the National Flow Measurement Standard Facilities at TUV NEL under the Engineering and Flow Programme, supported by the National Measurement Office, an Executive Agency of the U.K. Department of Business Innovation and Skills (BIS). The U.K. regulator for petroleum measurement and allocation, now part of the U.K.'s Department of Energy and Climate Change (DECC), had identified a need for research into the performance of commercial densitometers and improvements in the traceability of their calibration.[1]

TUV NEL, the custodians of the U.K. Fluid Density Standards, led a Joint Industry Project (JIP) aimed at providing the oil and gas industry with confidence in densitometer performance, by developing a calibration procedure which links traceably to National Standards.[2] The technical approach involved detailed characterization of industrial densitometers, making use of transfer standard fluids that had been characterized using the TUV NEL Primary Standard Liquid Densitometer.

This paper describes the TUV NEL Primary Standard Liquid Densitometer and presents data for the density of one of the fluids chosen by the JIP as a candidate calibration standard, namely, liquid toluene, in the range from (293 to 373) K and pressures up to 30 MPa.

Experimental Section

As part of previous Flow Programmes, BIS's predecessor, the U.K. Department of Trade and Industry funded the establishment of density standard facilities at TUV NEL.[3] These consist of two primary standard densitometers, one each for liquids and gases. In addition, a facility for the calibration of liquid densitometers (insertion and in-line devices) was also developed.

The TUV NEL Primary Standard Liquid Densitometer is a hydrostatic balance densitometer used in conjunction with a magnetic suspension coupling[3−6] and its associated control unit which were supplied by Rubotherm. The pressure vessel, which contains a quartz sinker that is immersed in the test fluid, the pressure generating and measuring circuit, and the thermostatic bath were all developed and manufactured at TUV NEL.

The temperature of the densitometer is measured by four 25 Ω standard platinum-resistance thermometers attached around the periphery of the pressure vessel which forms the fluid-filled test cell. The vessel is immersed in a temperature-controlled bath, which is stable to within ± 1 mK over its operating range. The total uncertainty in the temperature of the test fluid in the densitometer is assessed as ± 4 mK at a 95 % confidence level.

A differential pressure indicator (DPI) is used to compare the pressure of the test fluid with that of nitrogen from a gas-operated pressure balance. The uncertainty in the measurement of differential pressure is less than 100 Pa. The absolute pressure of the test fluid in the densitometer is obtained from the atmospheric pressure, gas-operated pressure balance, and DPI readings, corrected for temperature effects and pressure heads in the connecting lines as necessary. For pressures between (0.2 and 30) MPa, the uncertainty in calculated total pressure is assessed as less than ± 0.03 % at a 95 % confidence level.

The total uncertainty in the reported measurements of density includes both the uncertainty in the method itself and the contributions from the uncertainty in fluid density arising from uncertainties in temperature and pressure. These can be evaluated from the appropriate partial derivatives obtained from an equation of state fitted to the measured values of density.

Over the full operational range of the facility, the total uncertainty in density is ± 0.015 % at a 95 % confidence level. However, over the limited range investigated here [(293 to 373) K, (0.1 to 30) MPa, (790 to 890) $\text{kg}\cdot\text{m}^{-3}$], the total uncertainty of measurement is within ± 0.010 %.

Principle of Operation. Figure 1 shows the basic design of the magnetic suspension balance and the controlling principle of the magnetic suspension coupling which consists of an electromagnet and a permanent magnet. The electromagnet is attached to the under-pan weighing hook of a commercially available microbalance. Inside the coupling housing, the permanent magnet is connected to the sample load by means of a coupling and decoupling mechanism. The coupling mechanism

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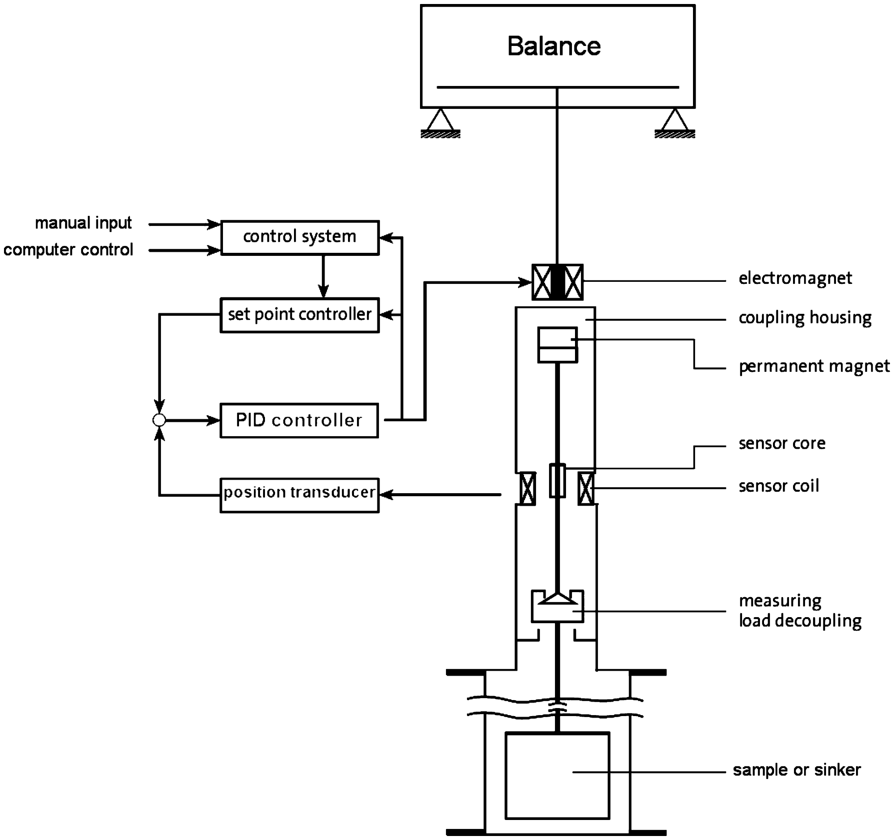

Figure 1. Schematic diagram of the magnetic suspension balance.

allows the weight of the permanent magnet to be tared out. The electronically controlled magnetic suspension coupling transmits the load through the wall of the pressure vessel to the microbalance at ambient conditions.

Control is effected by an electronic unit with position feedback obtained from the sensor coil and core. Using this technique, the measuring or buoyancy force on the permanent magnet and its attachments, including the sample, are transmitted without contact and with negligible error through the walls of the test chamber to the microbalance.

The electronic control unit contains two separate PID controllers: the first, to raise and lower the permanent magnet and its attachments in a controlled way between its rest position and either the "measuring" or "tare" position; and the second, a fast response system, to effect stable position control at the required measuring or tare position. For density measurements, the sample is replaced by a sinker immersed in the fluid under test, as shown in Figure 2. Compensating weights ensure that the balance is always operating near its zero point, thus reducing linearity errors.

In the measuring condition, as indicated in Figure 2, the sinker is directly coupled to the permanent magnet, and buoyancy forces act on all of the freely suspended components. In the tare position, which is a few millimeters below the measuring position, only the permanent magnet, the position sensor, and part of the load decoupling device are freely suspended. Here, the small cage or carrier to which the sinker is attached is seated on an internal support. In this so-called "zero-position", the balance can be tared and calibrated at all times even during a sequence of measurements. The difference in balance readings between the tare and measuring positions determines the buoyancy forces acting on the sinker and its carrier. The volume of the latter is less than 0.4 % of that of the sinker.

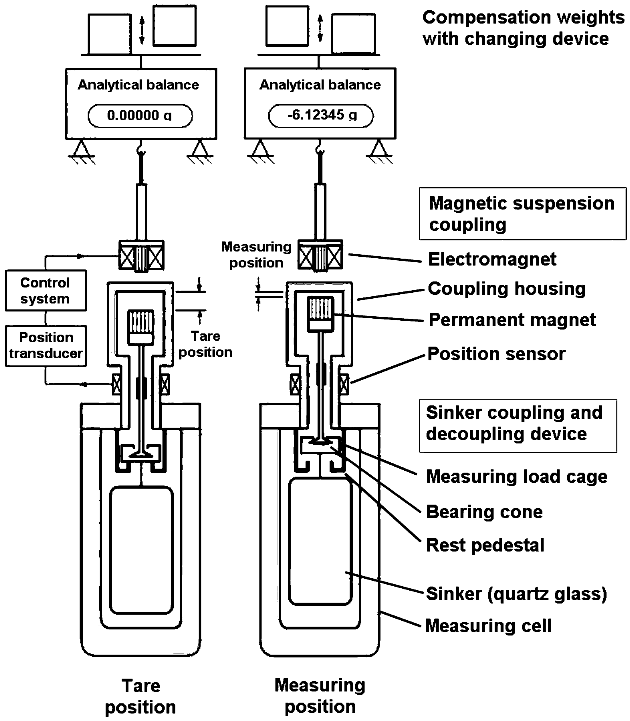

Figure 2. Schematic diagram of magnetic suspension coupling.

The TUV NEL Primary Standard Liquid Densitometer utilizes a single sinker: a solid cylinder of fused quartz with a volume of some 26 cm^3. Only a single sinker needs to be used with liquid systems since the buoyancy forces are considerable, of the order of 25 % to 45 % of the weight of the sinker, and the uncertainties in force measurement are negligibly small. Fluid density is calculated from

$$\rho = \frac{m_S - m_S^*}{V_S(T,P)} \quad (1)$$

where m_S is the true (vacuum) mass of the sinker; m_S^* is its apparent mass (weighed in fluid-filled test cell); and $V_S(T,P)$ is the temperature- and pressure-dependent volume of the sinker.

At each temperature and pressure, a minimum of ten determinations of the apparent mass of the sinker are recorded, and the mean value is used in eq 1. The deviations of the individual values from the mean are a few parts per million.

Sinker Calibration Facility. The major uncertainty associated with this method of measurement arises from the determination of the volume of the sinker and its dilation with temperature and pressure. The volume of the latter is established by careful weighing of the fused quartz sinker and its associated stainless steel suspension in both air and pure water at near ambient conditions.

It was initially thought that sinkers could be calibrated in situ in the densitometers, but experience showed that improved accuracy could be attained by a more direct method of measurement. The sinker and hook are weighed in air at known pressure, temperature, and humidity and again in degassed water of high purity.

A separate facility was developed to calibrate the volumes of the sinker and hook assembly at the selected reference conditions of 293 K and ambient pressure. The equipment used is similar to that required for gravimetric measurements of density at ambient conditions.

A rod hooked to the underside of the pan of a microbalance is connected via a short length of heat-treated nichrome wire of 0.1 mm diameter to the hook. The hook, sinker, and part of the nichrome wire are immersed in the boiled and degassed water contained in a clear Pyrex vessel. That part of the suspension system which is immersed in the water is always maintained at a constant depth beneath the surface. The glass container and components are allowed to cool naturally to room temperature, experience having shown that it was best not to attempt to regulate the temperature of the water in the vessel since any disturbance had a major effect on the repeatability of the measurements. The glass vessel is not insulated in any way and is allowed to stabilize at room temperature in a temperature-controlled room.

After a sinker is loaded onto the hook, a period of a few minutes is allowed before each weight measurement for vibration and convection currents within the vessel to decay. Use of a glass vessel is also important since it allows the operator to determine if the sinkers and assembly are free of bubbles. Each weight determination is repeated up to 20 times, and the temperature of the water after each weighing is accurately recorded using a platinum resistance thermometer.

A number of small influences contribute to the uncertainty in the volume determinations; of these, the uncertainty in the density of air and water is the most significant. The total uncertainty in the density of air at the measurement conditions is assessed as ± 0.15 %, and the uncertainty in the density of pure water of unspecified isotropic composition at ambient conditions is within 20 ppm. Using this apparatus, the volume of the fused quartz cylinder has been established to within 30 ppm, and the vacuum, or true, mass of the sinker has been established to within 3 ppm.

Sinker Dilation. The volumes of the principal components of the densitometer are subject to dilation with both temperature and pressure. The volume of a sinker at absolute temperature T and pressure P can be obtained accurately from its known volume at the specified reference conditions, V_0, from the expression

$$V_S(T,P) = V_0[1 + 3\varepsilon_t(T - T_0)][1 - \kappa_t(P - P_0)] \quad (2)$$

where ε_t, the thermal expansion, and κ_t, the isothermal compressibility, are functions of temperature for each of the individual sinker materials. Literature values[7−10] for the thermal expansion and the isothermal compressibility of fused silica (Heraeus Herasil) and stainless steel were used to develop expressions of these properties covering the working range of the densitometer. The maximum total uncertainty in the dilation of the fused silica artifact due to the combined effects of temperature and pressure is estimated to be within 60 ppm over the operational range of the densitometer. The maximum effective contribution to the uncertainty in the calculation of liquid density arising from the dilation of the suspension cage and hook of the densitometer is around 1 ppm.

Supporting Systems. The densitometer is hung from a horizontally leveled platform mounted on robust aluminum alloy structures. The microbalance is mounted on the platform, and the upper part of the suspension coupling is enclosed in a transparent housing. This can be fed from a dry-air source with a dew point of 193 K to prevent condensation of atmospheric moisture on the upper connecting rods and electromagnets when the densitometer is used at subambient temperatures.

The magnetic-suspension coupling, the housing, and the densitometer are contained in an oil-filled bath positioned beneath the platform. The bath consists of two Dewar vessels mounted concentrically and has provision, in the annular space between each Dewar, for both heating and cooling. Good circulation of the bath fluid, which is contained within the inner Dewar, is provided by a magnetically driven screw impeller mounted in the base of the outer Dewar vessel. The control temperature of the bath is monitored by a 25 Ω standard platinum-resistance thermometer positioned some distance above the screw impeller. The thermometer is monitored through a data acquisition system, and the power inputs to the heating/cooling circuits are adjusted using PID control software. The temperature of the densitometer is measured using four 25 Ω standard platinum-resistance thermometers attached to the body of the densitometer.

The densitometer sinker is housed in a pressure vessel which is connected to the insulating lid of the thermostat. The thermostat is raised to immerse the pressure vessel during measurement runs and can also be lowered to expose the apparatus for disassembly and cleaning. A finned aluminum block is also attached to the pressure vessel to minimize any temperature gradients that may develop along its vertical length.

The temperature stability of the bath is within ± 1 mK over their entire operating range, and the absolute temperature can be set to within a few millikelvins of the desired conditions. The total uncertainty in the temperature of the fluid in the densitometer is estimated to be ± 4 mK.

The densitometer is provided with a sample loading system that enables test fluids to be introduced to the densitometer in a controlled manner. The pressure vessel and connecting pipework can be purged with nitrogen or methane, before being evacuated to very low pressure (∼3 kPa). This ensures that the system is then completely filled by the test fluid, with no vapor space.

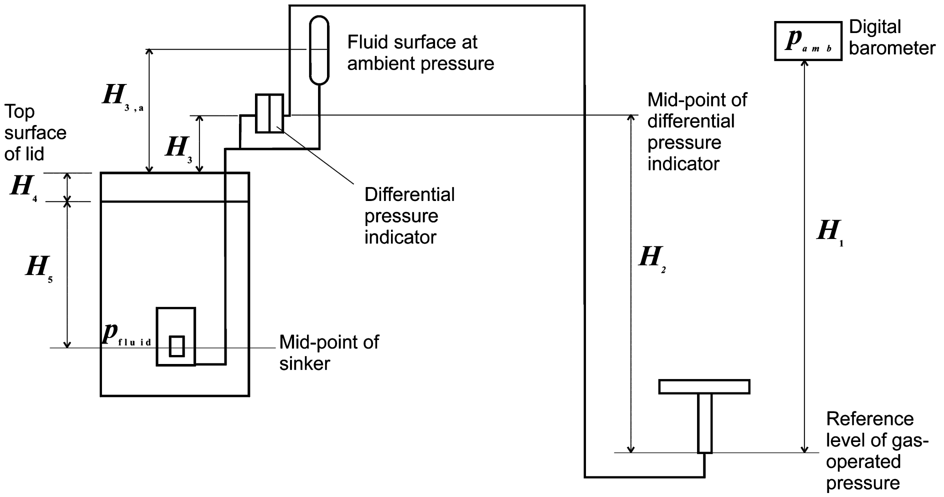

Figure 3. TUV NEL Primary Standard Liquid Densitometer pressure measurement system.

The pressure measurement system is shown schematically in Figure 3. A gas-operated pressure balance of the highest metrology class is used to provide reference gauge pressures accurate to within some 5 parts in 10^5. Atmospheric pressure is measured by means of a calibrated digital barometer accurate to within 30 Pa. The pressure of the fluid under test in the densitometer is obtained with reference to the pressure of nitrogen in the gas-operated balance through a differential pressure indicator (DPI). The uncertainty in the measurement of differential pressure is within 100 Pa. The absolute pressure of the fluid under test in the densitometer is obtained from the atmospheric pressure, gas-operated pressure balance, and DPI readings, corrected for temperature effects and pressure heads in the connecting lines as necessary. The uncertainty in the calculated total pressure of the fluid in the densitometer is assessed as $7 \cdot 10^{-5} \cdot p/\text{MPa} \pm 100$ Pa at a 95 % confidence level.

Fluids. While there is still a degree of debate about the relative merits of pure fluids or mixtures of accurately known composition as transfer standard fluids, for industrial calibration applications, pure fluids offer several advantages. All of the selected transfer standard fluids used in the TUV NEL joint industrial project are single components, thus ensuring that, within the limits of their stated purity, their composition will not change as a function of temperature, pressure, or time, as could be the case for mixtures of hydrocarbons or other fluids. Furthermore, the selected transfer standard fluids are all readily available in sufficient purity from normal laboratory chemical suppliers, thus requiring no further preparation (and hence eliminating potential contamination issues).

Toluene was chosen as one of the potential transfer standard fluids as the density of liquid toluene, and its variation with temperature and pressure are similar to that of typical North Sea crude oils. Furthermore, the density of liquid toluene has been repeatedly measured throughout the temperature and pressure range of relevance to the operation of commercially available densitometers used in the North Sea oil industry. The measurements reported here were performed with HPLC-grade toluene, supplied by Sigma-Aldrich (CHROMASOLV Plus, product number 650579), with a stated purity of > 99.9 %. All the samples were used as received, with no additional purification or processing.

The filling procedure for toluene was done in a number of stages. First, the apparatus was evacuated with a rotary vacuum pump down to a pressure of ~3 kPa and then purged with methane gas to expel any remaining air which might form a vapor bubble in the apparatus and once again evacuated. The toluene was placed in a double-ended metal sample bottle (at ambient conditions) with a valve at each end. A vacuum pump was attached to one end, and the valve was opened to allow the vapor to be drawn off, thus reducing the pressure over the liquid and causing dissolved air to be preferentially removed. The sample bottle was finally attached to the densitometer, and liquid toluene was allowed to enter the measurement volume under the combined action of pressure difference and gravity. This rather involved procedure was adopted because the apparatus did not have a flow-through cell, and it was felt that this was the best way of avoiding the presence of trapped bubbles of noncondensable gas above the liquid surface.

Results

The results obtained for the density, ρ, of toluene along five isotherms between (293 and 373) K, and pressures from (0.58 to 30) MPa, are shown in Table 1.

Over the course of the JIP, several aspects of the TUV NEL Primary Standard Liquid Densitometer were modified. The key differences are described in Table 2, and the corresponding data obtained with these configurations are denoted by a, b, and c in Table 1.

In addition to the changes noted in Table 2, each of the three series of measurements were made on fresh samples of toluene.

All the data in Table 1 were fitted to an equation of the form

$$\rho_{t,p} = 1000 \sum_{i=1}^{13} a(i)\theta^{m(i)}\pi^{n(i)} \tag{3}$$

where θ is the reduced temperature, $\theta = T/100$ for T in °C on ITS90; π is the reduced pressure, $\pi = p/30$ for p in MPa; $a(i)$ are coefficients; and $m(i)$ and $n(i)$ are exponents.

The functional form of eq 3 was chosen on the basis of providing a robust equation that had good extrapolation characteristics at low temperature and pressure (i.e., down to ambient conditions) while also giving the smallest residuals for interpolation over the experimental temperature and pressure range covered in the work. This enables the data to be cast into isothermal, isobaric, or isochoric forms to facilitate comparison with other experimental data. The equation should not be used to extrapolate above the highest temperature (373.15 K) or pressure (30 MPa) of the measurements.

The values obtained for the parameters are listed in Table 3. The (p, ρ, T) surface defined by eq 3 with the parameters listed

Table 1. Experimental Density ρ for Toluene from $T = (293.14$ to $373.37)$ K and $p = (0.58$ to $30.12)$ MPa

p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}
a	T/K = 293.14	a	T/K = 353.05	b	T/K = 373.03
0.58	867.30				
2.08	868.44	2.09	812.26	2.09	792.76
4.08	869.92	4.09	814.44	4.09	795.27
6.08	871.41	6.09	816.57	6.09	797.70
8.08	872.84	8.09	818.63	8.09	800.07
10.08	874.27	10.09	820.66	10.09	802.37
15.09	877.74	15.09	825.54	15.08	807.86
20.09	881.09	20.09	830.16	20.08	813.03
25.09	884.33	25.09	834.54	25.08	817.91
30.09	887.47	30.09	838.72	30.08	822.54
a	T/K = 313.11	a	T/K = 373.03	c	T/K = 293.14
0.59	848.73	0.59	790.76	2.10	868.49
2.09	850.02	2.09	792.70		
4.09	851.70	4.09	795.21		
6.09	853.35	6.09	797.64		
8.09	854.98	8.09	800.00		
10.09	856.57	10.09	802.30	10.11	874.35
15.09	860.44	15.09	807.78	15.11	877.83
20.09	864.16			20.11	881.18
25.09	867.74			25.12	884.42
				30.12	887.56
a	T/K = 333.08	b	T/K = 293.15	c	T/K = 373.37
0.59	829.86				
2.09	831.32	2.08	868.48	2.10	792.38
4.09	833.23	4.08	869.98		
6.09	835.10	6.08	871.45		
8.09	836.93	8.08	872.90		
10.09	838.73	10.08	874.33	10.11	802.04
15.09	843.06	15.08	877.80	15.11	807.56
20.09	847.20	20.08	881.15	20.12	812.74
25.09	851.15	25.08	884.39	25.12	817.63
30.09	854.96			30.12	822.28

Table 2. Experimental Configurations

date	sinker	magnetic suspension controller	pressure separator
a August 2007	gold-plated quartz cylinder	analogue	mercury interface
b April 2008	gold-plated quartz cylinder	digital	mercury interface
c September 2008	unplated quartz cylinder	digital	digital pressure indicator

Table 3. Coefficients of Equation 3

i	$a(i)$	$m(i)$	$n(i)$
1	0.885330	0	0
2	0.0206602	0	1
3	−0.00191999	0	2
4	−0.000166782	0	3
5	−0.0919718	1	0
6	0.0101598	1	1
7	−0.00277892	1	2
8	0.00182826	1	3
9	−0.00128760	2	0
10	0.00735824	2	1
11	−0.00384518	2	2
12	−0.00217362	3	0
13	0.00115831	3	1

in Table 3 describes the whole set of the present results with a standard deviation of 0.003 % within minimum and maximum deviations of −0.006 % and +0.007 %, respectively. The total uncertainty in the measured values of density was assessed as ± 0.008 % at a 95 % confidence level, leading to the values calculated from eq 3 having an uncertainty not exceeding ± 0.010 % across the temperature range from (293 to 373) K at pressures up to 30 MPa.

For the two common isotherms for the three configurations, Figure 4 shows the deviation of each experimental value from the value calculated from eq 3 as a function of pressure. Repeat measurements at corresponding t, p points agree to within ± 0.005 %, i.e., within the assessment of overall uncertainty, suggesting that commercially available HPLC-grade toluene with a stated purity of > 99.9 % can be used as a transfer standard fluid for liquid density without further purification.

Comparisons

Alvelino, Fareleira, and Wakeham[11] used a vibrating-wire device to perform simultaneous measurements of the density and viscosity of toluene (with a stated purity of 99.8 %) at temperatures from (222 to 348) K and pressures up to 80 MPa. At temperatures below 273 K, they estimated the uncertainty in density as ± 0.15 % and ± 0.1 % at higher temperatures. Figure 5 shows the deviations of their experimental data from the values calculated by eq 3 as a function of pressure.

While the values agree to within the quoted uncertainty, there appears to be an offset of about +0.05 % from the values calculated from eq 3. Alvelino, Fareleira, and Wakeham fitted their data to a modified Tait equation[12] and reported that it fit their experimental values with a standard deviation of ± 0.02 % and a maximum deviation not exceeding ± 0.06 %.

Their paper also included a review of several other sets of experimental data obtained by a variety of techniques. The claimed uncertainties for these data sets ranged from ± 0.05 % to ± 0.2 %, and all of the data agreed with their correlation to within ± 0.2 %. Excluding data at the lowest temperature, the average offset of the other experimental data from their correlation is of the order of −0.05 %. Across the temperature and pressure range common with the current work, the agreement is generally within ± 0.1 %, with an average offset of −0.05 %, suggesting that the bulk of the experimental data assessed by Alvelino, Fareleira, and Wakeham[11] lies within ± 0.05 % of the values calculated from eq 3.

More revealing comparisons are with data produced by PTB (Physikalisch-Technische Bundesanstalt, Germany) and NIST (National Institute of Standards and Technology, America) using magnetic suspension densitometers.

As part of an international intercomparison exercise carried out in 1999,[13] PTB made measurements on samples of ultrapure toluene using a magnetic suspension densitometer system similar to the TUV NEL Primary Standard Liquid Densitometer. Unfortunately, at the time of completion of the intercomparison exercise, PTB had not finished their measurement program, and their data have not been published in the open literature. Personal communication[14,15] with PTB has provided the authors of this paper with access to their results.

PTB assessed the overall uncertainty of their experimental data as ± 0.0075 % (at 95 % confidence level) and the uncertainty of values calculated from their fitting equation as ± 0.009 %. The overall uncertainty of the TUV NEL experimental data from the 2007/2008 measurements has been assessed as ± 0.008 % (at 95 % confidence level). An initial comparison showed that across the full temperature and pressure range [(293 to 373) K and from atmospheric pressure up to 30 MPa] the two data sets agreed to within their combined uncertainty, when plotted as a function of pressure. However, when plotted as a function of temperature, there was a small but systematic difference, of the order of 1.25 ppm·K^{-1}.

Weber[15] reported that the vacuum mass of their sinker appeared to be a function of temperature, possibly due to thermal effects on the magnetic coupling system. Further work was therefore undertaken to determine if a similar effect was apparent in the TUV NEL system. Although a shift of −0.3 mg was

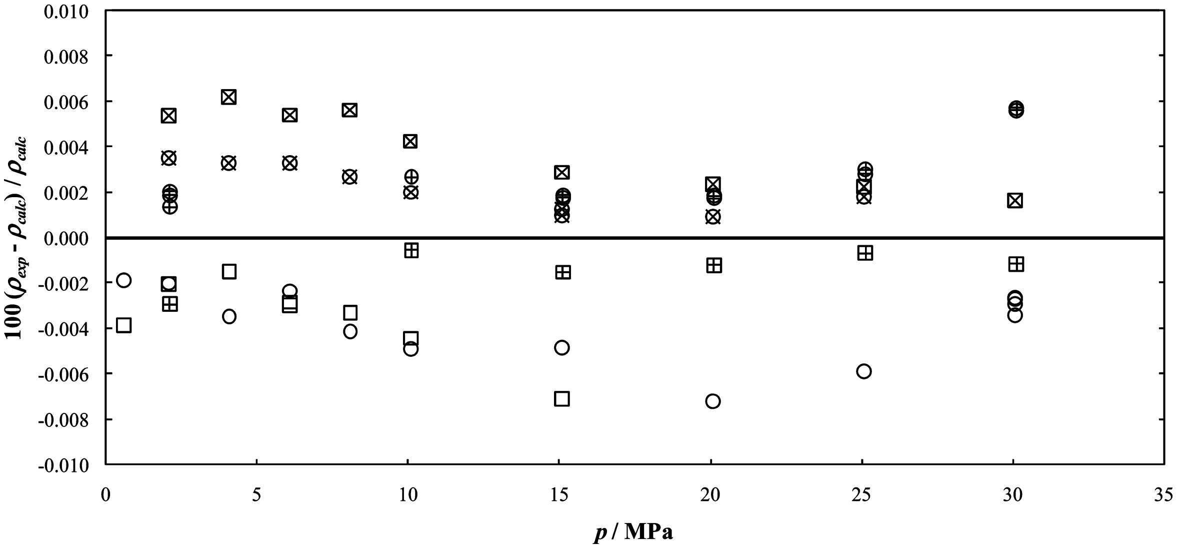

Figure 4. Deviations of experimental densities ρ_{exp} for this work from the correlation of eq 3 ρ_{calc} for the two common isotherms as a function of pressure *p* for the three experimental configurations listed in Table 2. ○, 293.15 K, with experimental configuration a; ⊗, 293.15 K, with experimental configuration b; ⊕, 293.15 K, with experimental configuration c; □, 373.15 K, with experimental configuration a; box with an × inside, 373.15 K, with experimental configuration b; ⊞, 373.15 K, with experimental configuration c.

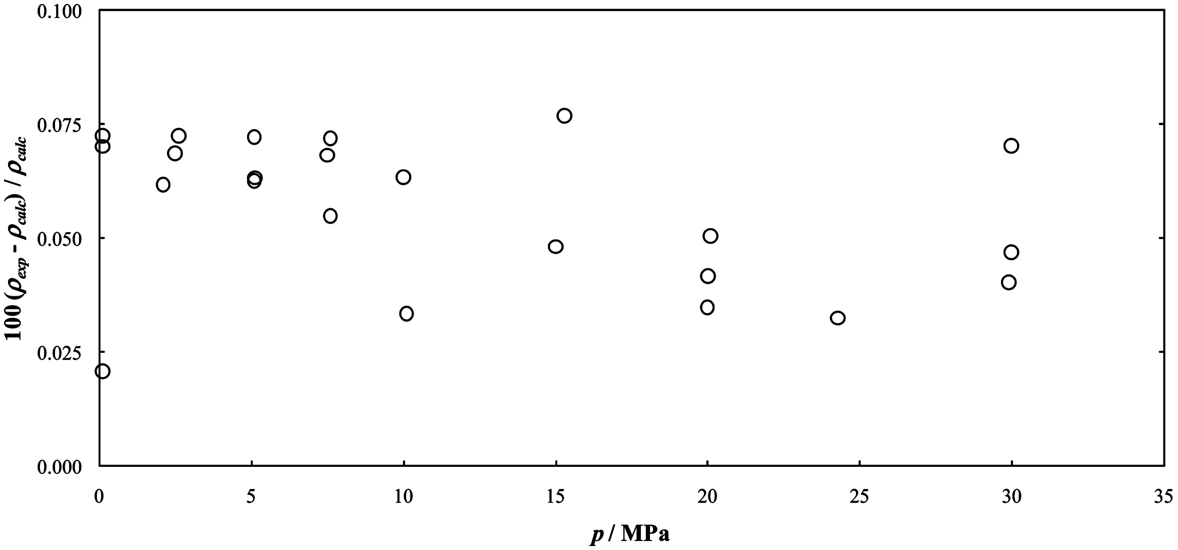

Figure 5. Deviations of Alvelino, Fareleira, and Wakeham[11] experimental densities ρ_{exp} from the correlation of eq 3 ρ_{calc} as a function of pressure *p*.

observed in the vacuum mass between (293 and 373) K, this is of the order of the uncertainty in determining the vacuum mass of the sinker in the sinker calibration facility and an order of magnitude less than that required to account for the difference between the TUV NEL and PTB data.

Further investigation of the temperature measurement system and comparison with the previous TUV NEL data[13] revealed a systematic error affecting calculation of the densitometer temperature due to incorrect coefficients for the four 25 Ω standard platinum-resistance thermometers. However, as the data logging system recorded the raw resistances for these devices, it was possible to retrospectively calculate corrected temperatures. The data reported in Table 1 and the coefficients given in Table 3 are based on the corrected temperature values. On the basis of these revised values, the TUV NEL experimental data from the 2007/2008 measurements and the values from the PTB correlation still agree to within their combined uncertainty across the full temperature and pressure range [(293 to 373) K and from atmospheric pressure up to 30 MPa], with the temperature difference less than 0.5 ppm·K^{-1}.

More recently, McLinden and Splett[16] reported a series of measurements undertaken at the US National Institute of Standards and Technology (NIST) on toluene. This work was made on samples of NIST's Standard Reference Material toluene (with a stated purity of 99.92 %) using a twin-sinker magnetic suspension densitometer. In addition to investigating the effects of air saturation of the fluid, the authors also provided a very comprehensive uncertainty analysis of the data.

For the range of conditions over which the correlation of eq 3 is valid, Figure 6 shows the difference between the NIST experimental data and the values calculated from eq 3. The effect of air saturation can be clearly seen, with an average difference of 0.010 % between air-saturated and degassed densities at corresponding temperatures. There is also a clear systematic difference as a function of temperature. At the maximum temperature and pressure common between the NIST data and

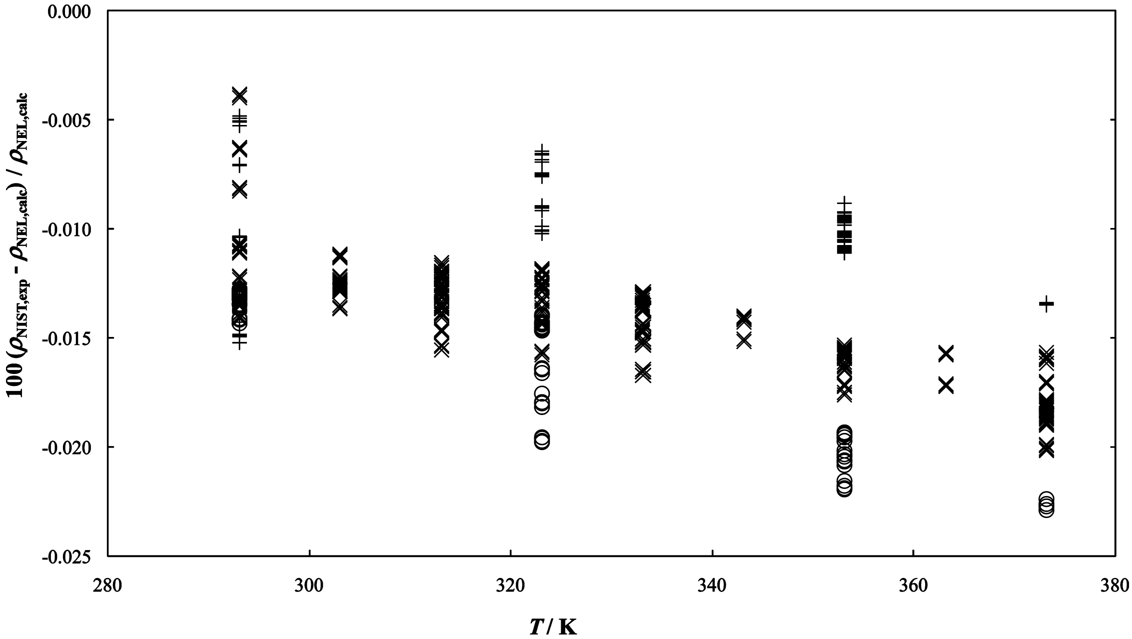

Figure 6. Deviations of NIST experimental densities $\rho_{\mathrm{NIST,exp}}$ from the correlation of eq 3 $\rho_{\mathrm{NEL,calc}}$ as a function of temperature T. +, degassed standard reference material; ×, standard reference material; ○, air-saturated standard reference material.

the present work, the uncertainty of the NIST data is of the order of 0.005 % (at 95 % confidence level), so clearly the two data sets do not agree within their combined uncertainty. However, agreement between the NIST data for their degassed samples and the values calculated from eq 3 is much closer, suggesting that the fluid handling and filling procedure used for the TUV NEL densitometer ensured that samples had very low air content. Furthermore, at any temperature and pressure, the values calculated from eq 3 are always higher than the corresponding NIST experimental values.

Nevertheless, there still remains an absolute difference between the two data sets, in addition to the temperature-dependent difference. These may be due to differences in the purity of the samples or in the design and operation of the densitometers. Although essentially similar to the single-sinker densitometers used by TUV NEL and PTB, in particular with regard to the magnetic coupling system, the NIST densitometer is a twin-sinker design which should reduce errors associated with adsorption onto the surface of the sinker and systematic errors in weighings. In addition, as McLinden and Splett[16] note, uncertainty in sinker volume is the major source of overall fluid density uncertainty for a buoyancy technique. The method used by these authors to determine the volumes of the sinkers in their system, being based on a hydrostatic comparator technique,[17] was also different from that used by TUV NEL and PTB (conventional hydrostatic weighing). Further examination of the sinker calibration procedure employed by TUV NEL and a more detailed examination of the performance of the magnetic coupling system in the TUV NEL densitometer may go some way toward explaining the remaining differences between the data sets.

Conclusions

New results for the density of compressed liquid toluene are presented. The measurements cover a pressure range from (2 to 30) MPa and the temperature range from (293 to 373) K. The results show good agreement with literature data, including those of comparable uncertainty. Furthermore, the reproducibility of the data suggests that commercially available HPLC-grade toluene with a stated purity of ≥ 99.9 % can be used without further purification as a transfer standard fluid for the calibration of industrial densitometers commonly used in fiscal applications throughout the North Sea.

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Literature Cited

(1) Griffin, D. *Solartron Mobrey Densitometer Calibration Issue*. DTI Energy Group, Licensing and Consents Unit, Aberdeen, 2004.
(2) Glen, N. F. *Liquid Densitometer: Traceable Calibration of Liquid Densitometers. A Joint Industry Project Proposal from NEL for the Traceable Calibration of Liquid Densitometers.* Proposal FC03140, TUV NEL Ltd., East Kilbride, February 2005.
(3) Watson, J. T. R.; Ferguson, D.; Ryan, G. National Standard Facilities for the Density of Liquids and Gases at Elevated Pressures. Paper presented at the Density Seminar held in the James Watt Conference Centre, NEL, on 24 October, 1994, in conjunction with the North Sea Flow Measurement Workshop, 1994.
(4) Lösch, H. W. *Entwicklung und Aufbau von neuen Magnetschwebewaagen zurberührungsfreien Messung vertikaler Kräfte*; VDI Fortschritt-Berichte, Reihe 3, Nr. 138: Düsseldorf, 1987.
(5) Lösch, H. W.; Kleinrahm. R.; Wagner, W. *Neue Magnetschwebewaagen fürgravimetrische Messungen in der Verfahrenstechnik*; VDI-GVC Jahrbuch 1994: Düsseldorf, 1994.
(6) Wagner, W.; Brachthauser, K.; Kleinrahm, R.; Lösch, H. W. A New, Accurate Single-Sinker Densitometer for Temperatures from 233 to 523 K at Pressures up to 30 MPa. *Int. J. Thermophys.* **1995**, *16* (2), 399–411.
(7) Rusovic, N.; Goedecke, T. The Thermal Expansion Coefficients of Glassy Quartz and of Alumina Ceramics represented by Gaussian Spline Polynomials. *Z. Metallkd* **1980**, *71* (1), 42–46.
(8) *Quarzglas und Quarzgut. Duckschrift der Fa*; Heraeus Quarzschmelze Q-A1/112.2: Hanau, Germany, 1985.
(9) Kirby, R. K.; Hahn T. A. *American Institute of Physics Handbook*, 3rd ed.; McGraw-Hill: New York, 1972; Chapter 4f.

(10) Trent, H. M.; Stone, D. E.; Beaubien, L. A. *American Institute of Physics Handbook*, 3rd ed.; McGraw-Hill: New York, 1972; Chapter 2e.
(11) Avelino, H. M.T.; Fareleira, J.M. N. A.; Wakeham, W. A. Simultaneous Measurement of the Density and Viscosity of Compressed Liquid Toluene. *Int. J. Thermophys.* **2003**, *24* (2), 323–336.
(12) Dymond, J. H.; Malhotra, R. The Tait Equation: 100 Years On. *Int. J. Thermophys.* **1988**, *9* (6), 941–951.
(13) Watson, J. T. R. *Intercomparison of Density Facilities. Flow Centre Report No 057/2000 produced for the NMSPU*; National Engineering Laboratory: East Kilbride, Glasgow, March 2000.
(14) Wolf, H.; Bettin, H. *Personal communication*. (Physikalisch-Technische Bundesanstalt, 38116 Braunschweig, Germany, January 2009).
(15) Weber, F. Personal communication. January 2009.
(16) McLinden, M. O.; Splett, J. D. A Liquid Density Standard Over Wide Ranges of Temperature and Pressure Based on Toluene. *J. Res. Natl. Inst. Stand. Technol.* **2008**, *113*, 29–67.
(17) Bowman, H. A.; Schoonover, R. M.; Carroll, C. L. The Utilization of Solid Objects as Reference Standards in Density Measurements. *Metrologia* **1974**, *10*, 117–121.

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