

Traceable Calibration of Liquid Densitometers

Norman Glen, TUV NEL Ltd

Douglas Griffin, Department for Business, Enterprise and Regulatory Reform

1 INTRODUCTION

Density measurement is a key element of both mass and volume flowrate 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 and a densitometer. All flowmeters require periodic calibration and traceability within the UK is provided through the Flow Programme. All commercial densitometers also require periodic calibration. In 2004 the Aberdeen-based Energy Resources Development Unit of DTI's Energy Group identified a need for research into practical methods for in-situ calibration of densitometers, as well as a greater understanding of the effects on densitometer performance of variations in product density, pressure and temperature.

This is particularly important as more and more operators are involved in smaller field developments tied back to other operators' platforms, feeding third-party pipeline infrastructures. In addition, as more HTHP fields come on stream, more densitometers will be operating at temperatures and pressures significantly different from those currently used as the reference conditions for calibration.

TUV NEL, the custodians of the UK Fluid Density Standards, are leading 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. Fourteen operators, a densitometer manufacturer and the UK oil and gas regulator (part of the Department for Business, Enterprise and Regulatory Reform) have joined the project.

The key task of the JIP is the detailed characterisation of densitometers in well-controlled conditions, making use of accurately-characterised transfer standard fluids that cover the density and viscosity ranges which are encountered across the full temperature and pressure range of operation of UK offshore oil facilities.

This paper describes the technical approach being used and presents initial results.

2 BACKGROUND

The most widely implemented approach for mass flow measurement is to use a volumetric flowmeter and a densitometer. In this case, the uncertainty in mass flow measurement is dependent equally on the uncertainty in volumetric flowmeter measurement and in densitometer measurement. The calculation of volume flow rate however also requires a knowledge of the density since it is necessary to reduce the measurements of volume throughput to standard conditions. It can therefore be seen that density measurement, volumetric and mass flow measurement are of equal importance.

The essential requirements of a density measurement system are that:-

- Calibrations should only be carried out using instruments that form part of a calibration chain traceable to national standards.
- Densitometers should be checked and calibrated regularly at temperatures and pressures corresponding to actual operational conditions.

All commercial densitometers, for use on gases or liquids, operate on an oscillatory principle and as such are not independent of other fluid properties. However, the theory of such methods is not rigorously established and even with careful design it is not possible to uncouple fully the effects of density from the other physical properties of the calibration fluids. To maximise the accuracy attainable with such densitometers, it is necessary to calibrate them against reference fluids with similar physical characteristics (such as speed of sound and viscosity).

It has been accepted industry practice to quote a calibration at only a single reference temperature (generally 20°C) and apply correction factors to account for the influence of temperature and pressure on both the calculated density and its uncertainty. However, recent work has raised a number of issues with regard to the whole calibration process, in particular when a densitometer is operated at a temperature different from the reference temperature. This has significant implications for fields operating in common transportation systems, where the mass allocations are based on densitometer readings.

3 OSCILLATORY DENSITOMETER THEORY

All commercial liquid density transducers operate on the same general principle. The manufacturers generally model the instruments as a simple spring mass oscillator system comprising the vibrating test section and the fluid contained in it, totally disregarding hydrodynamic effects. As the liquid density changes it in turn changes the total vibrating mass, which is then detected by a change in the resonant frequency. For a simple system, the resonant frequency f is given by:

$$f = \frac{1}{2\pi} \sqrt{\frac{K}{M}} \quad (1)$$

where K is the stiffness and M is the mass of the element (M_1) plus the mass of the fluid (M_2).

If K , M and V_f (the volume of fluid in the test section) are constant then equation 1 can be written in terms of density ρ as

$$\rho = K_0 + \frac{K_2}{f^2} \quad (2)$$

where $K_0 = -M_1/V_f$ and $K_2 = K/4\pi^2V_f$, or, in terms of oscillation period τ ,

$$\rho = K_0 + K_2\tau^2 \quad (3)$$

In recognition that equation 1 is only a first approximation to the actual behaviour of an oscillating tube filled with liquid [1], equation 3 is normally modified by the inclusion of a linear term K_1 , giving an empirical expression of the form

$$\rho = K_0 + K_1\tau + K_2\tau^2 \quad (4)$$

At any given temperature t and pressure p the three constants in equation 4 can be determined by calibrating the device with three fluids of known density. To ensure the highest accuracy this should be undertaken across the full operational temperature and pressure range, thus requiring a knowledge of the density of each calibration fluid at the corresponding conditions. Accepted practice however has been to calibrate at one reference temperature (normally 20°C) at atmospheric pressure to determine the coefficients at those conditions and then apply correction terms to account for the effects of operation at other temperatures and elevated pressure. The correction terms are of the form

$$\rho_t = \rho_0 \{1 + K_a(t - t_0)\} + K_b(t - t_0) \quad (5)$$

where ρ_0 is the density at the reference calibration temperature t_0 and

$$\rho_{t,p} = \rho_T \{1 + K_c(p - p_0) + K_d(p - p_0)^2\} + \{K_e(p - p_0) + K_f(p - p_0)^2\} \quad (6)$$

At the time of manufacture, the coefficients in equations 5 and 6 are determined for each instrument and these temperature and pressure coefficients are provided for use by the operator. For example, Emerson Process Management calibrate each Solartron 7835 densitometer using three fluids to cover the full operating density range of the instrument (300 to 1100kgm⁻³). Each instrument is calibrated at 20°C and 60°C, followed by a separate pressure calibration at pressures which cover the specified pressure range of the instrument.

Whilst the procedures used by manufacturers to obtain instrument coefficients at the time of manufacture ensure that these coefficients are as accurate as possible, this will not necessarily be the case following recalibration, unless similar procedures are followed. Within the UK the majority of industrial densitometers are recalibrated by third-party calibration laboratories. Current practice is to calibrate each instrument in a test rig using three fluids at atmospheric pressure and a reference pressure. In practice this means that the range of pressures and temperatures at which the instruments are

normally calibrated is limited to near ambient conditions but many densitometers, particularly those used in offshore applications, operate under high pressure, high temperature conditions.

The density of each test fluid is typically measured by two in-line transfer standard densitometers that are periodically calibrated using fluids of accurately known density. From at least 1986 accepted practice was to check the temperature coefficients (K_a and K_b in equation 5) of the transfer standard densitometers using air and then apply corrections for use with other calibration fluids and assume that no systematic bias was introduced. However, a note issued by the Licensing and Consents Unit of DTI's Energy Group in 2004 [2] summarising a review carried out by industry, found that there was a small but systematic 'offset error' when a densitometer is operated at a temperature different from the reference temperature. The offset error was corrected in 2004 by the use of revised temperature coefficients.

Although the magnitude of the particular offset error identified by the manufacturer and reported by DTI seemed small, $0.014\text{kg m}^{-3}\text{ K}^{-1}$, a number of UK Continental Shelf fields operate with measuring stations at temperatures approaching 100°C . For a field producing 50,000 barrels per day the mis-measurement at the platform would be of the order of 25,000 barrels per annum. A similar effect will occur at the on-shore terminal. If the oil from a number of fields has been fed in to a common pipeline the allocation to each field is based on the 'measured' mass fed in by each. Clearly the actual mis-allocations will depend on the temperatures of each off-shore measuring station, the flow rates and the temperature of the on-shore measurements but could easily run to 10s of thousands of barrels per annum for each field. The mismeasurement on condensate fields will be greater than that for oilfields, as the relative error in density measurement is greater for lower-density product; in addition, condensate production tends to be at relatively high temperatures. Taken over the whole of the UK production, mis-allocation errors arising from this effect alone could run to several million pounds per annum and possibly hundreds of millions over a 20 year period.

In addition to this specific point, the review raised a number of issues with regard to the whole calibration process and the calculation methodology. TUV NEL have been aware for many years of the influence of other fluid properties (primarily viscosity and speed of sound) on the operation of oscillatory densitometers and sponsored work to investigate these effects [3,4]. For liquids, this clearly demonstrated the coupling between density and viscosity: it is possible to optimise a vibrating element to respond to either density or viscosity as a first-order effect but the other property is always present as a second-order effect. Accurate characterisation, and calibration, of oscillatory densitometers therefore requires knowledge of the effects of temperature and pressure on a number of fluid properties across the full operational range of the device. Furthermore, a complete characterisation of a vibrating tube densitometer would also require to investigate additional effects including fluid velocity, torque loading, mounting misalignment etc.

4 TECHNICAL APPROACH

As part of previous Flow Programmes, DTI funded the establishment of density standard facilities at TUV NEL [5]. 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 original concept for the TUV NEL Industrial Densitometer Calibration Facility for the calibration of liquid densitometers envisaged that the facility would be directly linked to the TUV NEL Primary Standard Densitometer for liquids. Whilst this has the merit that the fluid in the densitometer under calibration is the same as that in the Primary Standard Densitometer and at identical conditions, thus minimising the uncertainty in the fluid density, it has a number of practical drawbacks. In particular, the time required for the Primary Standard Densitometer to reach equilibrium and make a measurement is substantially longer than the time required in the Industrial Densitometer Calibration Facility. In addition, the task of cleaning the Primary Standard Densitometer is time-consuming, particularly if it has been filled with difficult fluids such as heavy oils.

In view of these considerations, a better approach is to use stable, accurately characterised transfer standard fluids. As noted in Section 3, there is a coupling between fluid density and viscosity in an oscillatory densitometer and hence the chosen fluids must cover the density and viscosity ranges which are encountered across the full temperature and pressure range of operation of UK offshore oil facilities.

To be considered for use as true transfer standard fluids, fluids must either be single components or stable mixtures of known composition. Such fluids have the advantage that once their PVT behaviour has been established (using the TUV NEL Primary Standard Densitometer) they can then be used in any other (transfer) facility without further characterisation, thus providing much closer traceability to primary standards.

4.1 The TUV NEL Primary Standard Liquid Densitometer

The TUV NEL Primary Standard Liquid Densitometer is based on the buoyancy method using the Archimedes' principle. This involves measuring the weight of an object of known mass and volume in the test fluid at the conditions of measurement. The weight, W , of an object of mass m and volume V in a fluid is given to a first approximation by the equation:

$$W/g = m - V\rho \quad (7)$$

from which the density, ρ , of the fluid can be expressed as:

$$\rho = [(W/g) - m]/V \quad (8)$$

The operating range of the densitometer is from -40 to 150°C across the pressure range from 0.1 to 30MPa.

4.1.1 Magnetic-Suspension Coupling System

The standard object is not coupled directly to the microbalance. Instead, as shown in see Figure 1, the microbalance is indirectly connected by a magnetic-suspension coupling to the standard object which is located within the measurement chamber. The coupling comprises an electromagnet, a permanent magnet, a sensor core and coil and a device for coupling and decoupling the standard object. The electromagnet, which is hooked to the underside of the balance pan, maintains the permanent magnet and its attachments within the measurement chamber in a freely suspended state. 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 standard object, are transmitted without contact and with negligible error through the walls of the test chamber to the microbalance at ambient conditions.

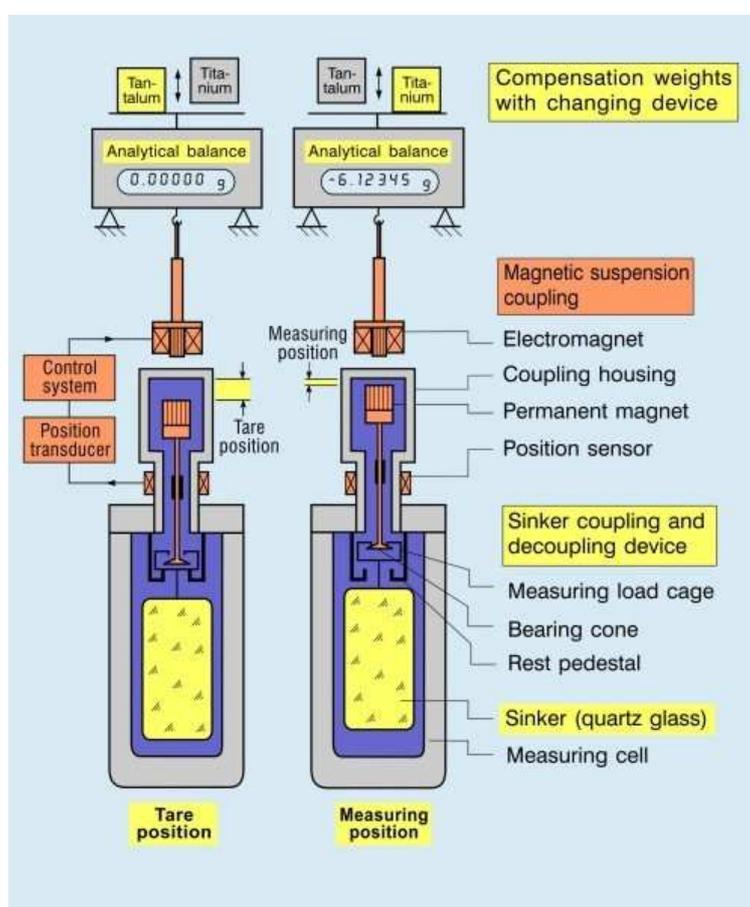


Figure 1 Magnetic-suspension coupling
(a) tare position, (b) measuring position

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 'zero-point' position; and the second, a fast response system, to effect stable position control at the required 'measuring' or 'zero-point' position. In the 'measuring' condition, as indicated in Figure 1b, the standard

object is directly coupled to the permanent magnet and buoyancy forces act on all of the freely suspended components. In the 'zero-point' position, which is a few millimetres below the 'measuring' position, only the permanent magnet (Figure 1a), the position sensor and part of the load decoupling device are freely suspended. Here the small cage or carrier to which the standard object 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 'zero-point' and 'measuring' positions determines the buoyancy forces acting on the standard object and its carrier. The volume of the latter is less than 0.4% of that of the standard object.

Only force measurements are involved in the density determination, both in the calibration of the standard objects and in the measurement process. The accuracy and repeatability of the magnetic-suspension coupling is readily confirmed by weighing standard masses alternately on the balance pan and hung from the coupling.

The densitometer utilises a single sinker: a gold-plated solid cylinder of fused quartz with a volume, V , of some 24 cm³. This sinker is coupled by a thin stainless steel rod to a simple mechanical linking mechanism then to a microbalance via other thin rods and an electronically controlled magnetic-suspension coupling. This coupling, as outlined in the previous section, transmits the load from the sinker inside the pressure vessel to the microbalance at ambient conditions without any direct contact. To measure the density, the sinker is alternatively coupled to, and detached from, the simple mechanical coupling and the resulting differential force, the buoyancy-force ΔF , is measured with a microbalance (resolution $\sim 10 \mu\text{g}$). From these force measurements, the density of the liquid at the temperature and pressure of measurement can be obtained from an equation of the form:

$$\rho = (\Delta F/g)/V_{t,p} \quad (9)$$

For liquids 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. The sinker is gold-plated to eliminate electrostatic forces and since the test liquid fills the densitometer completely the force measurements are free from the effects of surface tension.

The major uncertainty associated with this method of measurement arises from the determination of the volumes of the sinker and the small stainless steel carrier. The volumes are obtained by careful weighing in air and in pure water at around 20°C and ambient pressure. The relative uncertainty in the combined sinker and carrier volume at the reference conditions is assessed at less than 30 ppm. Taken together with the uncertainties resulting from the thermal expansion and the compression of the sinker, force determination, and temperature and pressure measurement, this leads to a total uncertainty in fluid density of 0.015% across the full operating range of the densitometer.

4.1.2 Dilation of Sinker

The volumes of the principal components of the densitometer are subject to dilation with both temperature and pressure. The volume of the sinker at absolute temperature t and pressure p can be obtained accurately from its known volume at the specified reference conditions, V_{ref} , from the expression:

$$V_{t,p} = V_{ref} \left[1 + 3\varepsilon_t(t - t_{ref}) \right] \left[1 - \kappa_t(p - p_{ref}) \right] \quad (10)$$

where ε_t the thermal expansion, and
 κ_t the isothermal compressibility,

are functions of temperature for each of the individual sinker materials. 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 57 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 single-sinker densitometer is around 1 ppm.

4.1.3 Supporting Systems

The densitometer is hung from a horizontally levelled platform mounted on a robust aluminium alloy structure. The microbalance is mounted above the platform and the upper part of the suspension coupling is enclosed in a transparent housing which is fed from a dry-air source with a dew-point of -80°C. The latter prevents condensation of atmospheric moisture on the upper connecting rods and electromagnets when the densitometer is used at sub-ambient temperatures. The magnetic-suspension coupling, its 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 is provided by magnetically-driven screw impellers mounted in the base of the outer dewar vessel. The control temperature of the bath is monitored by a 25 ohm standard platinum-resistance thermometer positioned some distance above the screw-impeller. The thermometer is monitored through a data acquisition system by a control computer 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 ohm standard platinum-resistance thermometers attached to the body of the densitometer.

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

The densitometer is provided with a circuit for filling and evacuation. A gas-operated pressure balance of the highest metrology class is used to provide reference gauge pressures accurate to within 5 parts in 10^5 . Atmospheric pressure is measured by means of a calibrated digital barometer accurate to within 20 Pa.

The pressure of the test fluid in the densitometer is obtained with reference to the pressure of nitrogen in the gas-operated balance through a mercury manometer separator. The uncertainty in the measurement of differential pressure is within 100 Pa.

As shown in Figure 2 and equations 11 to 13, the absolute pressure of the test fluid in the densitometer is obtained from the atmospheric pressure, gas-operated pressure balance and mercury manometer separator, corrected for temperature effects and pressure heads in the connecting lines as necessary. The uncertainty in the calculated total pressure is assessed as $7 \cdot 10^{-5} p \pm 100$ Pa.

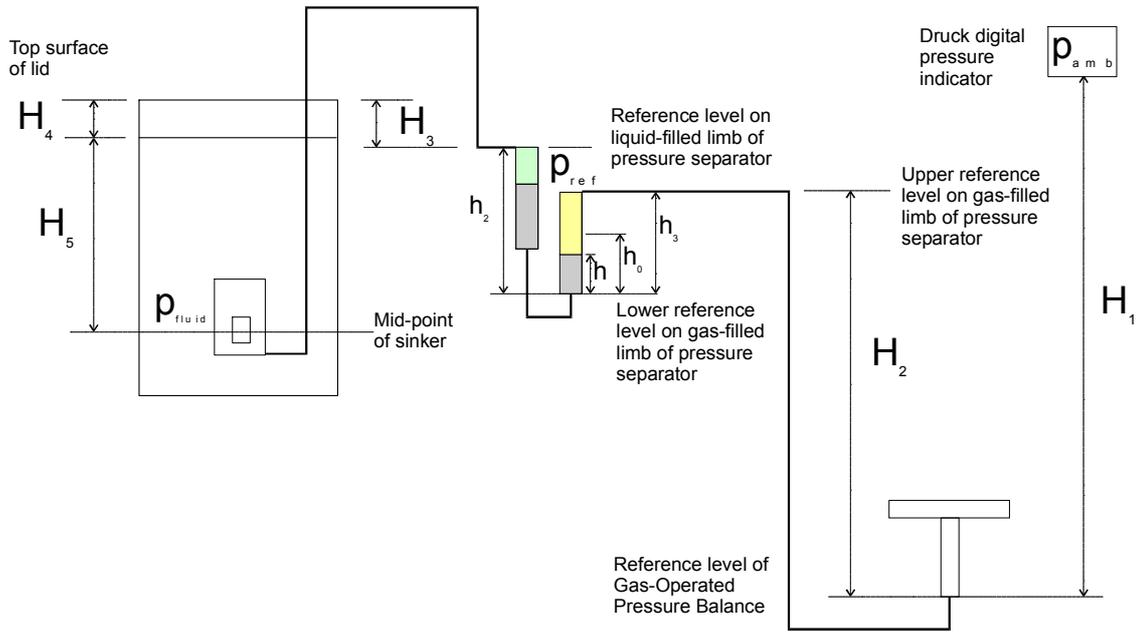


Figure 2 Schematic of pressure circuit for primary standard liquid densitometer

$$p_{ref} = \{p_{amb,pri} + g \cdot \rho_{air}(p_{amb,pri}, t_{amb,pri}) \cdot H_1\} + \{p_{stand} + g \cdot \rho_{N_2}(p_{stand}, t_{amb,pri}) \cdot H_2\} \quad (11)$$

$$p_{fluid} = p_{ref} + dp_{sep} + \{g \cdot \rho_{fluid}(p_{ref}, t_{amb,pri}) \cdot H_3 + g \cdot \rho_{fluid}(p_{ref}, t_{lid}) \cdot H_4 + g \cdot \rho_{fluid}(p_{ref}, t_{bath}) \cdot H_5\} \quad (12)$$

$$dp_{sep} = g \cdot \{\rho_{N_2}(p_{ref}, t_{amb,pri}) \cdot (h_3 - h) + 2 \cdot \rho_{Hg}(t_{amb,pri}) \cdot (h - h_0) + \rho_{fluid}(p_{ref}, t_{amb,pri}) \cdot (2 \cdot h_0 - h - h_2)\} \quad (13)$$

4.1.4 Densitometer Performance

As part of an international intercomparison exercise carried out in 1999 [6], the TUV NEL Primary Standard Liquid Densitometer was used to measure the density of a sample of ultra-pure toluene. As discussed in Section 4.3, one of the fluids chosen as a transfer standard was toluene, allowing a comparison with the previous data. Figures 3 and 4 show examples of the stability of weighing the sinker at various conditions for the 1999 and 2007 measurements respectively.

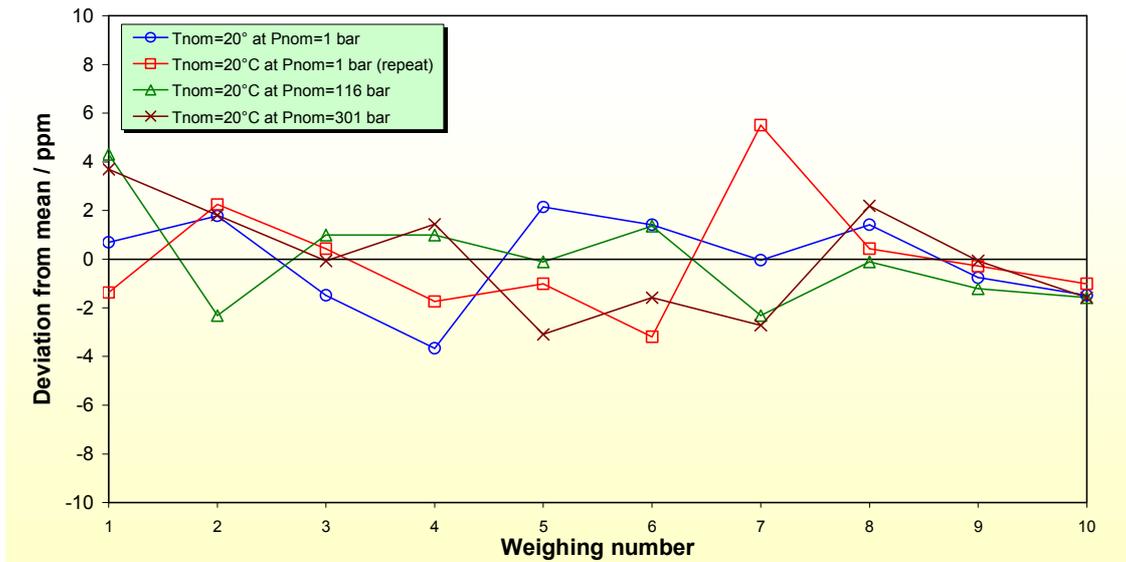


Figure 3 Example of weighing stability, toluene sample, 1999

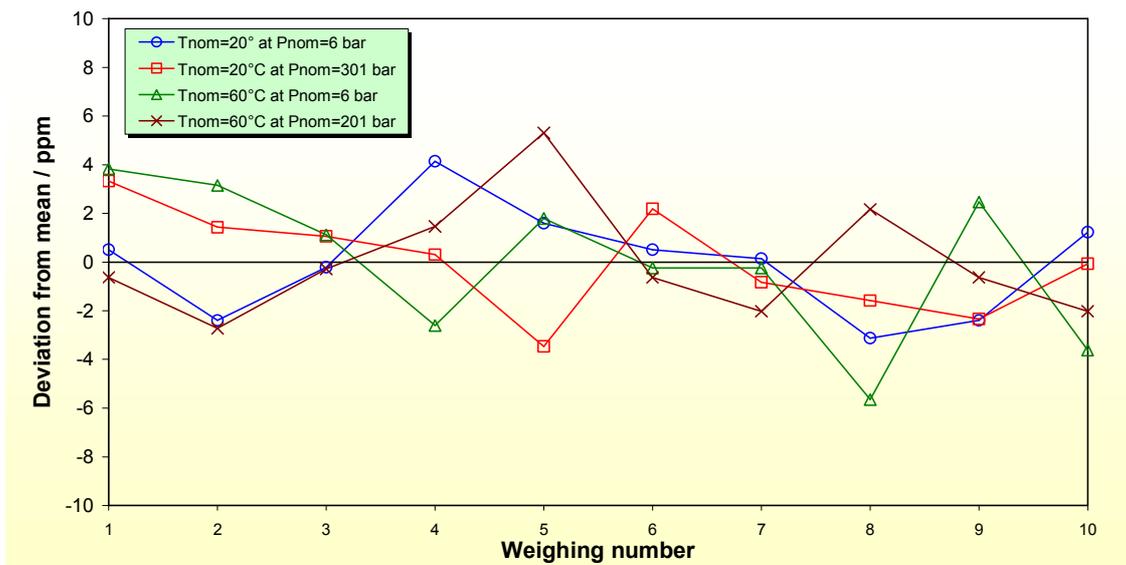


Figure 4 Example of weighing stability, toluene sample, 2007

These data confirm that the magnetic suspension coupling and weighing system is operating as expected and is capable of determining the weight of the sinker in the fluid to within a few parts per million.

The data from the measurements made in 1999 were fitted to an equation of the form

$$\rho_{t,p} = 1000 \sum_{i=1}^{13} a(i) \theta^{m(i)} \pi^{n(i)} \quad (14)$$

where θ is the reduced temperature, $\theta = t / 100$ for t in degrees Celsius 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.

Equation 14 represents the 1999 TUV NEL data set to within minimum and maximum deviations of -8 and +10 parts per million respectively. The total uncertainty in the measured values of density was assessed as 0.01 % at a 95 % confidence level, leading to the values calculated from equation 14 having an uncertainty not exceeding 0.012% across the temperature range from 0 to 80°C at pressures up to 30MPa.

Table 1 shows the data obtained for toluene from the current measurement programme up to 80°C and values at corresponding temperatures and pressures calculated from equation 14. Whilst the agreement between the two data sets is within their combined uncertainty, it is clear from Figure 5 that there is both an absolute difference and a temperature dependence to the difference. The origins of these effects are still being investigated.

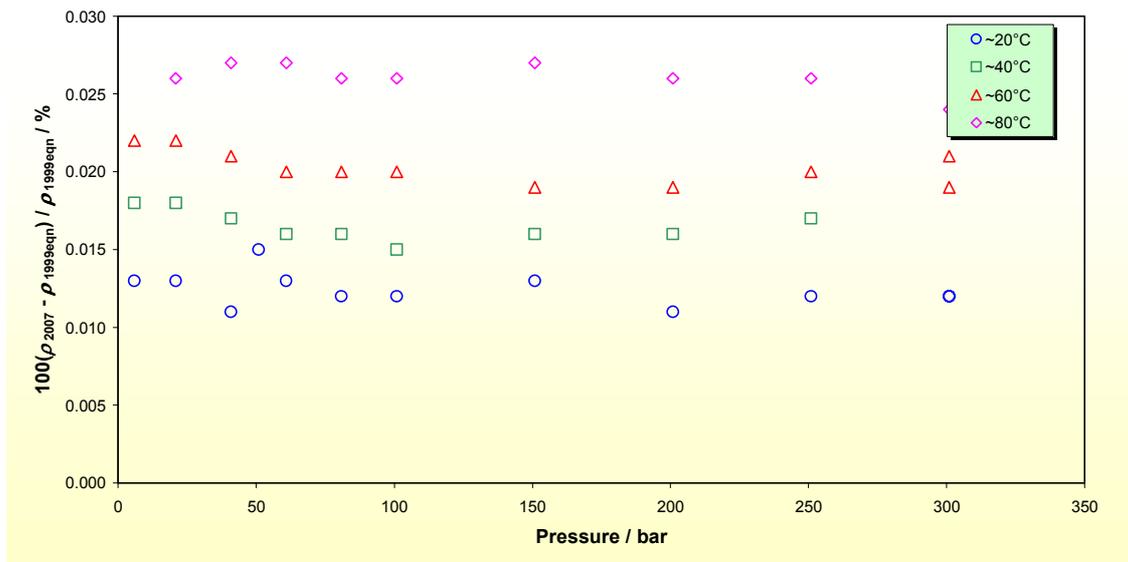


Figure 5 Comparison of 1999 and 2007 toluene density measurements

Table 1
Comparison of 1999 and 2007 toluene density measurements

t °C	p MPa	ρ_{2007} kgm ⁻³	ρ_{1999} kgm ⁻³	$100(\rho_{2007}-\rho_{1999})/\rho_{1999}$ %
19.993	0.5821	867.302	867.189	0.013
19.994	2.0821	868.438	868.327	0.013
29.991	5.0897	861.628	861.496	0.015
19.996	4.0815	869.920	869.820	0.011
19.992	6.0817	871.409	871.295	0.013
19.994	8.0823	872.844	872.741	0.012
19.991	10.0842	874.272	874.170	0.012
20.005	15.0859	877.744	877.629	0.013
19.993	20.0873	881.087	880.986	0.011
19.994	25.0892	884.328	884.221	0.012
19.994	30.0909	887.462	887.358	0.012
19.992	30.0930	887.469	887.361	0.012
19.992	30.0929	887.471	887.361	0.012
19.995	30.0926	887.469	887.358	0.012
39.990	0.5880	848.731	848.576	0.018
39.990	2.0884	850.016	849.864	0.018
39.990	4.0893	851.698	851.553	0.017
39.989	6.0880	853.351	853.210	0.016
39.990	8.0892	854.977	854.837	0.016
39.990	10.0895	856.566	856.433	0.015
39.990	15.0909	860.444	860.306	0.016
39.991	20.0919	864.156	864.019	0.016
39.990	25.0935	867.738	867.593	0.017
59.990	0.5889	829.858	829.676	0.022
59.990	2.0885	831.321	831.140	0.022
59.990	4.0889	833.232	833.055	0.021
59.990	6.0888	835.098	834.928	0.020
59.990	8.0889	836.927	836.763	0.020
59.990	10.0891	838.725	838.559	0.020
59.991	15.0898	843.060	842.895	0.019
59.988	20.0905	847.195	847.032	0.019
59.992	25.0916	851.150	850.984	0.020
59.991	30.0924	854.964	854.785	0.021
59.992	30.0927	854.949	854.785	0.019

Table 1 (continued)

t °C	p MPa	ρ_{2007} kgm ⁻³	ρ_{1999} kgm ⁻³	$100(\rho_{2007}-\rho_{1999})/\rho_{1999}$ %
79.994	2.0879	812.259	812.046	0.026
79.994	4.0875	814.439	814.222	0.027
79.993	6.0878	816.571	816.349	0.027
79.995	8.0877	818.633	818.422	0.026
79.991	10.0875	820.662	820.453	0.026
79.995	15.0878	825.542	825.322	0.027
79.997	20.0891	830.155	829.938	0.026
79.998	25.0892	834.544	834.326	0.026
79.996	30.0898	838.721	838.520	0.024

4.2 The TUV NEL Industrial Densitometer Calibration Facility

The TUV NEL Industrial Densitometer Calibration Facility consists of a thermostated enclosure capable of containing a densitometer, as shown in Figure 6. In conjunction with a pressurising system, this enables the temperature and pressure of the fluid in the densitometer to be set and maintained at any set-point across the range from 10 to 110°C at pressures between 0.1 and 20 MPa and the period output signal from the densitometer to be measured.

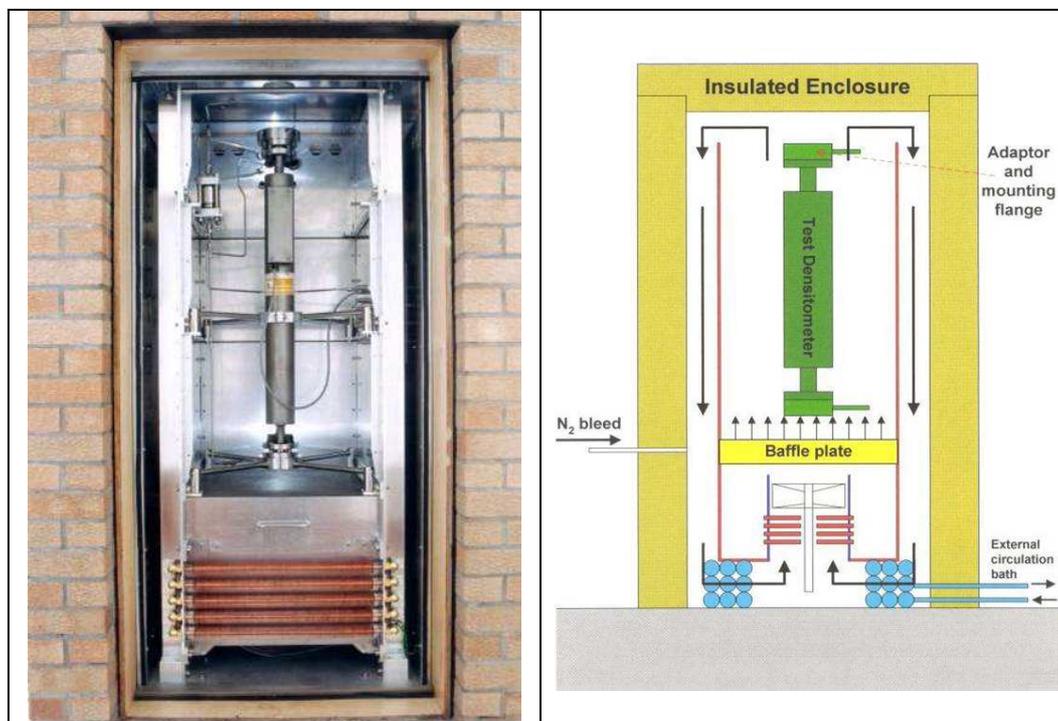


Figure 6 The TUV NEL Industrial Densitometer Calibration Facility

4.2.1 Temperature and Pressure Control

Temperature control is provided by an insulated enclosure plus heating and cooling circuits. A series of coils in the base of the enclosure are connected to an external circulation bath capable of maintaining the temperature of the coils between -80 and 20°C. This provides a constant background temperature against which the heating circuit operates. The control temperature of the enclosure is monitored by a 25 ohm standard platinum-resistance thermometer positioned close to the mid-point of the enclosure. The thermometer is monitored by a control computer similar to that used in the Primary Liquid Standard Densitometer and the power inputs to the heating/cooling circuits are adjusted using PID control software. The temperature of the densitometer under test is measured using two 25 ohm standard platinum-resistance thermometers attached to the body of the densitometer.

The temperature stability of the enclosure is within ± 5 mK over its entire operating range and the absolute temperature can be set by the computer to within a few millikelvins of the desired conditions. The total uncertainty in the temperature of the working fluid in the densitometers is estimated to be 4 mK.

An external pressurising circuit generates and controls the pressure of the fluid in the densitometer under test. A computer-controlled pump supplies hydraulic fluid to a piston in cylinder interface to the test fluid. The feedback signal for the control system is provided by a Quartzdyne pressure transducer on the test fluid side of the piston in cylinder interface.

A gas-operated pressure balance of the highest metrology class, located in the Primary Standards Densitometer Laboratory, is used to provide reference gauge pressures accurate to within 5 parts in 10^5 . Atmospheric pressure is measured by means of the calibrated digital barometer used for the Primary Liquid Standard Densitometer, providing values accurate to within 20 Pa.

The pressure of the test fluid in the densitometer under test is obtained with reference to the pressure of nitrogen in the gas-operated balance through a Yokogawa differential pressure transducer. The transducer was calibrated across a range of differential pressures from -5000 to 5000 Pa at static pressures from 2.5 to 15 MPa and a function derived to calculate differential pressure from the output voltage. The uncertainty in the measurement of differential pressure is within 50 Pa.

As shown in Figure 7 and equations 15 to 18, the absolute pressure of the test fluid in the densitometer is obtained from the atmospheric pressure, gas-operated pressure balance and Yokogawa differential pressure transducer, corrected for temperature effects and pressure heads in the connecting lines as necessary. The uncertainty in the calculated total pressure is assessed as $7 \cdot 10^{-5} p \pm 100$ Pa.

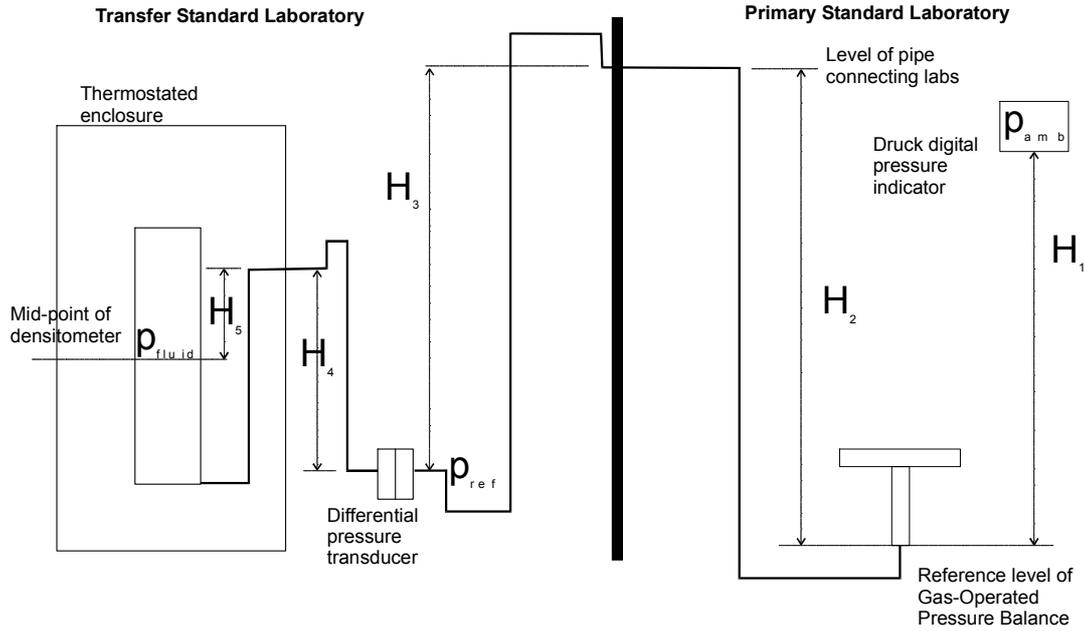


Figure 7 Schematic of pressure circuit for industrial densitometer calibration facility

$$\begin{aligned}
 p_{ref} = & \{ p_{amb,pri} + g \cdot \rho_{air}(p_{amb,pri}, t_{amb,pri}) \cdot H_1 \} \\
 & + \{ p_{stand} + g \cdot \rho_{N_2}(p_{stand}, t_{amb,pri}) \cdot H_2 \} \\
 & + \{ g \cdot \rho_{N_2}(p_{stand}, t_{amb,sec}) \cdot H_3 \}
 \end{aligned} \quad (15)$$

$$\begin{aligned}
 p_{fluid} = & p_{ref} + dp_{sep} + \{ g \cdot \rho_{fluid}(p_{ref}, t_{amb,sec}) \cdot H_4 \\
 & + g \cdot \rho_{fluid}(p_{ref}, t_{dens}) \cdot H_5 \}
 \end{aligned} \quad (16)$$

$$dp_{sep} = \{ a_0 + a_1 \cdot v_{Yok} \} + \{ b_1 \cdot p_{ref} + b_2 \cdot p_{ref}^2 + b_3 \cdot p_{ref}^3 \} \quad (17)$$

4.2.2 Calibration Facility Performance

Once the system has stabilised at a set temperature and pressure, the temperature of the densitometer, the pressure of the fluid within the densitometer and the period output signal from the densitometer are measured. The time take to complete one measurement cycle is of the order of one minute. A minimum of two measurement cycles are made at each set point. Table 2 provides an indication of the stability and repeatability of the temperature and pressure control achieved at the densitometer within the thermostated enclosure. These results relate to a new densitometer (Solartron 7835) supplied by the manufacturer (Emerson Process Management) and filled with a sample of the same toluene used in the Primary Standard Liquid Densitometer.

Table 2
Temperature and pressure stability in Industrial Densitometer Calibration Facility

Date	$t_{den,NEL}$ °C	p_{fluid} bar	ρ_{nel} kgm ⁻³	τ_{den} µs	ρ_{den} kgm ⁻³
27/10/2006 15:20	19.792	41.028	869.79	1358.974	870.59
27/10/2006 16:18	19.793	41.026	869.79	1358.977	870.60
19/01/2007 15:00	19.778	40.978	869.76	1358.942	870.49
19/01/2007 15:06	19.778	40.978	869.76	1358.940	870.48
13/11/2006 14:44	59.480	81.053	836.87	1352.288	838.19
13/11/2006 14:50	59.484	81.053	836.87	1352.289	838.19
26/01/2007 11:55	59.492	81.053	836.86	1352.279	838.15
26/01/2007 12:04	59.490	81.052	836.86	1352.279	838.15

4.3 Transfer Standard Fluids

As noted previously, to be considered for use as true transfer standard fluids, fluids must either be single components or stable mixtures of known composition. Furthermore, for this application, they must also cover the range of other fluid properties that will influence the operation of an oscillatory densitometer across its full operational range. For an oscillatory device, the most important secondary property will be fluid viscosity. A survey was therefore undertaken of the project's industrial sponsors to determine the temperature, pressure, density and viscosity ranges over which their densitometers operate. The results are summarised in Table 3.

Table 3 Densitometer operating conditions		
Parameter	Full range	Most common range
Temperature / °C	8 - 105	20 - 80
Pressure / MPa	0.5 - 14.0	0.5 - 5.0
Density / kgm ⁻³	530 - 1180	700 - 850
Viscosity / mPa s	0.3 - 40	2 - 8

Whilst it would be ideal to cover the full operational range, in practice it would be very difficult to find suitable fluids. By agreement with the project sponsors, it was therefore decided to concentrate on the most common range, allowing the use of four fluids, as shown in Figure 8. In addition to providing coverage of the key parameters, the fluids must be readily available in sufficiently high purity at reasonable cost. Iso-octane (2,2,4-trimethylpentane), toluene, and di-(2-ethylhexyl) sebacate meet these criteria, covering the low density / low viscosity, high density / low viscosity and high density / high viscosity conditions respectively. However, to a first approximation, fluid density and viscosity are correlated, making it difficult to find a low density / high viscosity

fluid. Although 9-n-octylheptadecane would cover a significant part of the range (particularly at elevated temperatures), it is not readily available in sufficient purity at reasonable cost and so an alternative fluid is being sought.

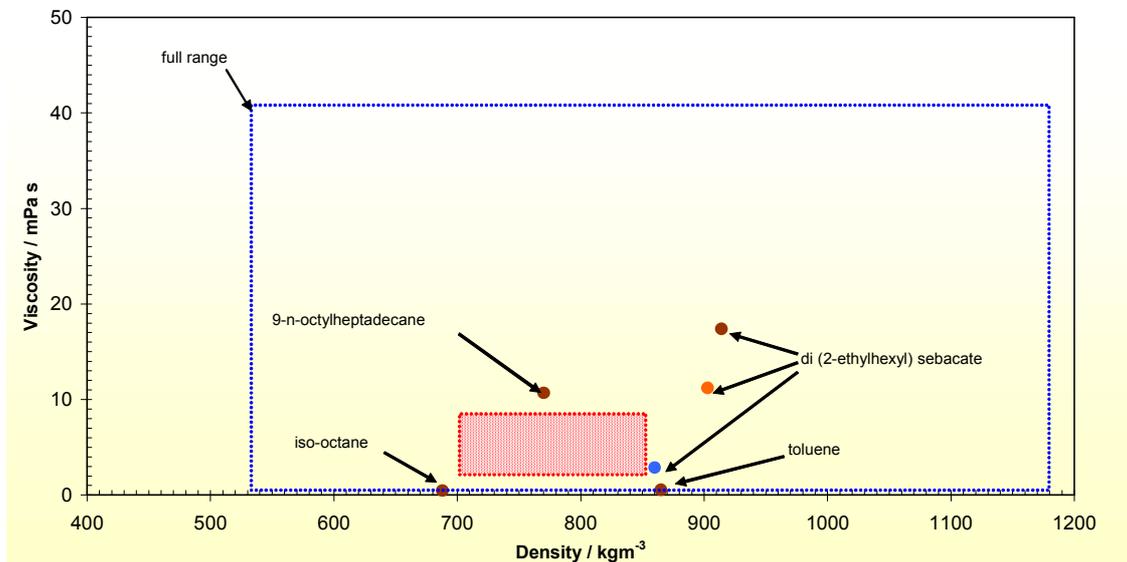


Figure 8 Transfer standard fluids

5 RESULTS

Measurements on the first transfer standard fluid, toluene, have been completed in the Primary Standard Liquid Densitometer and the results are summarised in Table 1. The fluid sample measured, CHROMASOLV® Plus, for HPLC, was obtained from Sigma-Aldrich and used as received. The stated minimum purity of the sample (by gas liquid chromatography) was 99.90%, with a maximum water content of 0.02% (by titration). The measurements cover the temperature range from 20 to 100°C at pressures from 0.1 to 30 MPa.

Measurements with the three transfer standard fluids already identified have been completed with the Emerson Process Management-supplied Solartron 7835 densitometer in the Industrial Densitometer Calibration Facility across the temperature range from 20 to 100°C at pressures from 0.1 to 100 MPa. In addition to toluene, the other two fluids were Sigma-Aldrich anhydrous 2,2,4-trimethylpentane (stated minimum purity 99.75% by gas liquid chromatography, maximum water content 0.003% by titration) and Sigma-Aldrich Fluka Bis(2-ethylhexyl) sebacate (stated minimum purity 97.0% by gas liquid chromatography).

6 DISCUSSION

The initial results obtained for the density of a sample of toluene measured in the Primary Standard Liquid Densitometer agree within the combined uncertainty with data obtained previously for a sample of toluene of similar purity.

The measurement principle used in the Primary Standard Liquid Densitometer, Archimedes' Principle, is as close to a primary method as can be obtained for density, a derived unit. All the measurements required to determine the density are fully traceable to primary standard measurements and the quoted uncertainty of 0.015% is derived from the component uncertainties in each of those measurements, thus providing traceability to National Standards.

As noted in Section 4.1.4, Whilst the agreement between the two data sets is within their combined uncertainty, it is clear from Figure 5 that there is both an absolute difference and a temperature dependence to the difference. The origins of these effects are still being investigated.

Initial results for the Emerson Process Management-supplied Solartron 7835 densitometer in the Industrial Densitometer Calibration Facility appeared to show systematic deviations between the values calculated from the measured period outputs and values calculated at corresponding conditions for the transfer standard fluids.

The coefficients used for the densitometer (the K_a to K_f in equations 5 and 6) were those originally supplied by the manufacturer. In work undertaken by them on pressure effects, entirely independently of but in parallel with this project, they have now issued a revised calculation procedure and new pressure coefficients. Whilst this brings the results from the industrial densitometer in to line with the values calculated for toluene, no further conclusions can be drawn until the measurement programme is complete for all the transfer standard fluids.

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