An assessment of laboratory density meters

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Many thousands of liquid density determinations are made worldwide every day and substantial sums of money depend upon the outcome. Although at one time, a wide variety of methods were employed, most laboratories now use either hydrometers or density meters.

Hydrometry has been used for many years and the uncertainties associated with it are reasonably well understood, if often appreciably underestimated. Laboratory density meters have been developed from the work of Stabinger et al [1967] and use a miniature U shaped tube of glass as a measurement cell. The oscillating period of the cell is a function of the density of the liquid injected into it. About 20,000 bench top and 10,000 portable instruments are installed worldwide and since the majority of these are manufactured by Anton Paar K.G. of Austria, it is their machines which have been assessed.

Several papers have already been published on the effect of viscosity on the Paar instruments but unfortunately, most used aqueous sugar or glycerol solutions, giving a very tight correlation of density to viscosity, and as far as is known, few if any had access to a hydrostatic weighing system, and so needed to determine the density of viscous liquids by pyknometry, no easy task. No previous publications have been identified covering cell linearity or calibration.

H & D Fitzgerald Ltd developed a hydrostatic weighing system with an uncertainty of ± 0.01 kg m^{-3}, at the 95 percent confidence level for which they hold NAMAS accreditation from NPL. Liquids calibrated by this system were used to assess three of the most popular instruments in the current Paar range, the DMA 48 which indicates density to 0.1 kg m^{-3}, the DMA 58 (0.01 kg m^{-3}), and the portable DMA 35 (1 kg m^{-3}). In addition, a DMA 55 (0.01 kg m^{-3}), a type no longer manufactured, was tested since its cell temperature is controlled by use of an external water bath, and it uses the same cell design as the instruments used by National Bureau of Standards (now NIST) Whetstone et al [1978] to gather the experimental data upon which the current Petroleum Measurement Tables are based.

All viscosities were measured by SGS Redwood Ltd, a NAMAS accredited testing laboratory, using IP 71 with an uncertainty of ± 0.4 percent of quoted viscosity at the 95 percent level.

Cell temperature

Table 1 shows $\delta\rho/\delta t$, the change in density per degree at 20°C, and $\delta t/\delta\rho$, the temperature change causing a density shift of 0·1 kg m^{-3} for a number of liquids. If density is to be determined with an uncertainty of ± 0.1 kg m^{-3}, cell temperature must be known with an uncertainty no greater than about half the $\delta t/\delta\rho$ figure, to allow for a contribution from cell calibration errors. For a typical oil or product this equates to about ± 70 mK.

In all the bench top instruments, the oscillating tube is inside a low pressure hydrogen jacket. In most early models, including the DMA 55, cell temperature was maintained by surrounding this with an outer jacket through which water could be pumped, in newer instruments such as the DMA 48 and 58, the hydrogen jacket is surrounded by a metal block equipped with an internal Peltier temperature control system. The oscillator feeds 50 to 100 mW continuously into the cell, most of which appears as heat in the cell walls and the 0.7 ml of sample. The hydrogen therefore also serves to maintain sample temperature in equilibrium with the water jacket or Peltier block.

The classic method of measuring cell temperature is to insert a thermometer into the cell thermowell. The difference between the average of the inlet and outlet water temperatures in a DMA 55 and that indicated by a miniature 25Ω platinum resistance thermometer in the thermowell is shown in **Table 2**.

When a four-wire miniature platinum resistance thermometer was

	A $\delta\rho/\delta\tau$ kg $m^{-3}K^{-1}$	B $\delta\tau/\delta\rho$ K (0.1 kg m^{-3})$^{-1}$
Water	0.21	0.48
2,2,4 trimethylpentane	0.82	0.12
Petrol	0.92	0.11
Kerosine	0.74	0.14
Crude oil (840 kg/m^3)	0.73	0.14
Lube oil (110 cSt @40°C)	0.62	0.16
40% aqueous ethanol	0.70	0.14
Trichlorotrifluoroethane	2.33	0.04

Table 1: Typical coefficients of thermal expansion

Average water temperature °C	*Thermowell temperature* °C	*Best fit temp using liquids* °C	*Liquids s.d. of residuals* kg m^{-3}
14.95	14.95	14.95	0.002
14.97	14.96	14.97	0.009
20.03	20.02	20.00	0.003
50.29	50.00	50.27	0.009

Table 2: DMA 55 cell temperatures

inserted into the cell bore using a light oil to provide thermal continuity with the cell wall, indicated temperature was somewhat lower when the oil in the cell was pumped by syringe very slowly past the probe and out of the cell, and it therefore seemed possible that indicated temperature was being influenced by heat transfer along the probe leads from outside the instrument. Smaller changes were seen when the test was repeated using a two wire thermistor sensor coupled to a Paar DT 100 thermometer and since the four leads on the platinum resistance thermometer had a much greater cross section area than the two on the thermistor probe, this appeared a reasonable supposition. As a further check, the end of the cell was insulated and the probe cable heated; indicated cell temperature rose appreciably within a short time. Tests using a very small thermistor probe suggested that temperature gradients normally exist in the cell both from front to back and from the open end to the closed end.

Since knowledge of the liquid temperature is all important when measuring density, a technique was therefore developed in which a variety of liquids for which the density/temperature relationship had already been determined by hydrostatic weighing, were injected into the instrument and cell oscillation period, τ, noted, along with average water temperature. In theory, density is proportional to τ^2, and a computer routine was developed to determine at what temperature τ^2 best represented the hydrostatic weighing densities. This method appears to work well, and has an estimated 95 percent uncertainty of ± 10 mK.

Table 2 shows the results for a DMA 55; **Table 3** for a DMA 58, and **Table 4** for a DMA 48.

The DMA 58 displays cell temperature with a readability of 10 mK, using a thermistor probe in a cell thermowell. The probe can be removed for calibration and the one checked in this exercise was found to have a maximum error between 10 and 70°C of only 10 mK, with an average error of about 5 mK. Although the probe is not used to control cell temperature, it suggests that the quality of the control system is good, since the maximum observed differential between set point and indicated temperature was no greater than 10 mK over the range of 10 to 50°C.

Although cell block temperature is displayed on the front panel of the DMA 48, the design unfortunately makes no provision for its direct measurement. A resistance thermometer inserted into the cell bore of a DMA 48 indicated that when the cell light was on, cell temperature increased by about 50 mK. Although the instrument manual stresses that the light should be off before the density is read, the 48 and 58 have a relatively narrow angle for viewing the cell, and it is therefore felt desirable that the design be modified so that, as in the older 55, the displayed density flashes if the light has been inadvertently left on.

The repeatability and stability of cell temperature in two DMA 48s at a set point of 20°C was examined. The cell was filled with trichlorotrifluoroethane (Freon TF), and after the period had stabilised the set point was briefly changed to mimic the injection of a hot or cold sample and then reset to 20°C. The period was noted once it had restabilised and cell temperature changes calculated from changes in the indicated density of the Freon. Over three to four hours variations of about ± 25 mK were seen for one machine and ± 35 mK for the other. Over several days, the variations were ± 65 mK for the latter instrument. Freon was used since it has an exceptionally high value for $\delta\rho/\delta t$ at 2.34 kg m^{-3} K^{-1}.

A DMA 58 was found to take several days to temperature stabilise after first being switched on; it is recommended that if possible instruments are left running continuously. Glass cells take some time to settle after the set temperature has been changed. Once the instrument is indicating that the cell is at its new set-point, a DMA 48 takes a minimum of two minutes per degree of change, before the cell is properly equilibrated at the new temperature, and a DMA 58 fifteen minutes per degree.

The DMA 35 has a built-in thermometer displaying to ± 100 mK. Several of these were tested, by passing water of a known temperature through the cell and noting the displayed temperature. In the range from 10 to 35°C the maximum error in indicated temperature was 0·2°C, although this increased to 0.3°C if the instrument was held in the hand for an extended period. Since the density is only displayed to the nearest 1 kg m^{-3}, this error is insignificant.

The assessment was carried out in an air conditioned laboratory held at 20°C ± 0·6°. The miniature resistance thermometers used were calibrated against a 25≃ platinum resistance thermometer which had previously been certified by NPL. Once errors due to self-heating had been accounted for, they had an estimated uncertainty of ± 4mK (0.004°C).

Linearity

As mentioned above, a technique was developed to determine cell temperature using liquids which had been calibrated in the hydrostatic weighing system and then determining mathematically the temperature at which the calibrated densities gave the best fit to τ^2. Five liquids were normally used, 2,2,4-trimethylpentane 692 kg m^{-3}, cyclohexane 780 kg m^{-3}, water, dichloromethane 1323 kg m^{-3} and Freon TF 1575 kg m^{-3}. These liquids were chosen since they covered the density range of interest to most

laboratories, were of low viscosity and had a wide range of thermal expansion coefficients from 0·22 kg $m^{-3}K^{-1}$ for water to 2.3 kg $m^{-3}K^{-1}$ for Freon.

Tables 2 to 4 show that once viscosity corrections had been applied, the standard deviation of the residuals after fitting to τ^2 was typically <0.01 kg m^{-3}, even for a DMA 48. For none of the instruments tested was advantage normally found in fitting to any function other than τ^2, and the residual standard deviations for the shorter density range of cyclohexane to dichloromethane were normally no improvement over those for the full range. Fitting τ^2 to the densities at the nominal cell temperature gave worse residual standard deviations than at the best fit temperature, without apparently introducing any pattern into the residuals. This is taken to indicate that τ^2 is a linear function of density over the range 690 to 1575 kg m^{-3} and that the cell is almost certainly operating at the best fit rather than the nominal temperature. It also suggests that it should be possible reliably to establish both the cell constants and the cell temperature by use of water and a minimum of two calibration liquids, preferably of densities about 1000 kg m^{-3} apart.

Viscosity effects

Almost every vibrating tube density meter is sensitive to sample viscosity to some extent and the Paar range are no exception. In the earlier instruments such as the DMA 55, the viscosity dependent error is a relatively simple function of sample viscosity (see **Figure 1**), while in the later DMA 48 and 58, a facility exists to switch *viscosity compensation* on or off. When this is turned off, the error curve is similar in form to that of the DMA 55, with it on however, the curve becomes more complex. **Figure 2** shows both curves for a DMA 48. We understand from the manufacturer that the intention was to modify the cell response so that the viscosity error for liquids of less than 100 mPa-s was no greater than the specified precision of the cell when used with low viscosity liquids. The price to be paid, would be a steeper error curve above 100 mPa-s. In practice, possibly due to incorrect adjustment, most of the instruments studied had a minimum in the correction curve at about 15 mPa-s which could be down to -0.3 kg m^{-3} in a DMA 48 and $-0{\cdot}12$ kg m^{-3} in a DMA 58.

Irrespective of whether viscosity compensation was switched on or off, or of instrument model, the error for liquids between 800 and 4000 mPa-s appears to change little with viscosity.

Machine id #	*Indicated temperature °C*	*Best fit temp using liquids °C*	*Liquids s.d. of residuals kg m^{-3}*
18	15.00	14.98	0.007
18	20.00	20.01	0.003
12	15.00	15.02	0.002
12	20.00	20.01	0.003
14	15.00	15.02	0.006
14	20.00	20.02	0.0003
16	15.00	15.02	0.003
16	20.00	20.04	0.003

Table 3: DMA 58 cell temperatures

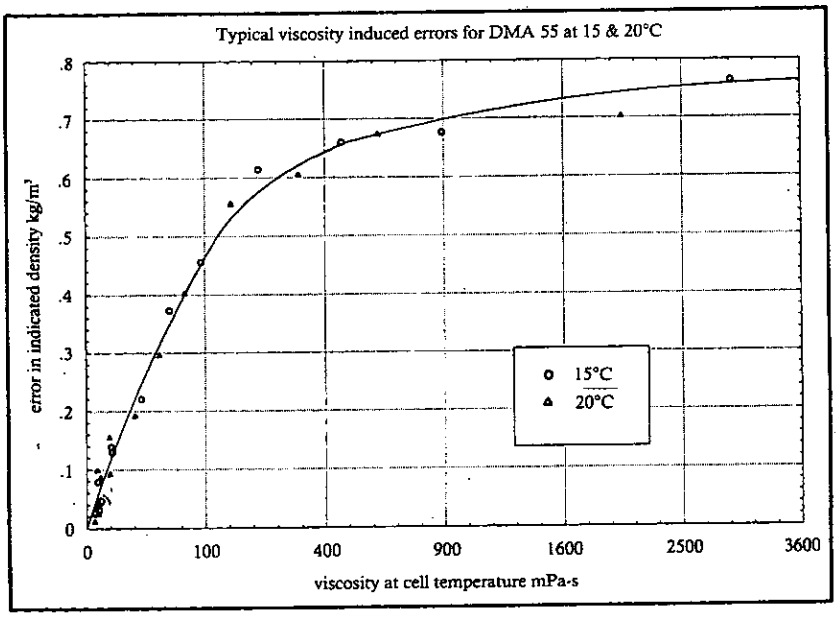

Figure 1

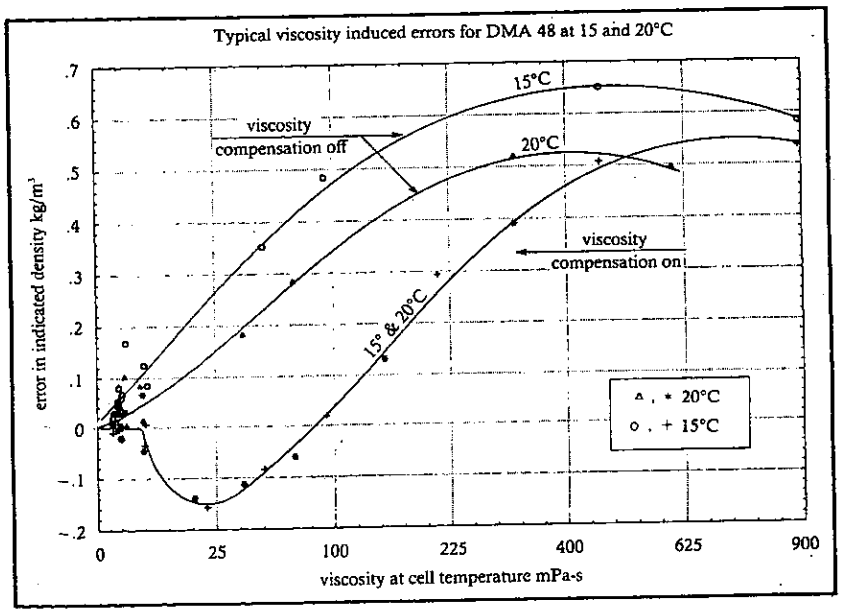

Figure 2

Machine id ♯	*Indicated temperature °C*	*Best fit temp using liquids °C*	*Liquids s.d. of residuals kg m^{-3}*
3	15.00	14.99	0.017
3	20.00	19.95	0.011
3	20.20	20.14	0.002
9	15.00	15.34	0.0004
9	20.00	20.33	0.002

Table 4: DMA 48 cell temperatures

Some of the experimental data suggested that viscosity dependent errors for certain low viscosity liquids might not lie quite on the normal error/viscosity curve, but there is at present insufficient data to assert this with any confidence.

Dr H Stabinger, one of the original patent holders for this type of cell, has suggested in discussion that over the normal working temperature range, the viscosity effects should depend purely on the sample viscosity at cell temperature. Although this appears to be the case for the DMA 55 and 58, it is probably not quite so for the DMA 48, where for several instruments the errors for a given viscosity are smaller at 20°C than at 15°C. The reason for this is not clear, but may be due to the characteristics of the glass cell wall changing with temperature.

Figure 3 shows the combined 15°C and 20°C curves for a DMA 58 for both viscosity compensation on and off.

Table 5 shows the viscosity correction terms for the instruments tested, where $\delta\rho$ is the error in kg m^{-3} by which a meter will overestimate density due to sample viscosity. It should therefore be subtracted from the indicated density to find the true density. The corrections for different instruments of the same model were effectively identical and appeared to be independent of cell ageing. Provided that the corrections given in **Table 5** are applied, it is estimated that the residual viscosity induced error in the corrected reading is unlikely to be more than twice the standard deviation quoted in the table.

In all models which have it, the viscosity compensation facility is switched on before the instrument leaves the factory and can only be altered as the machine is reset. Unfortunately, only the very latest instruments have a (undocumented) software facility to establish the current setting through keyboard interrogation, and this is felt to be unacceptable in a machine used for

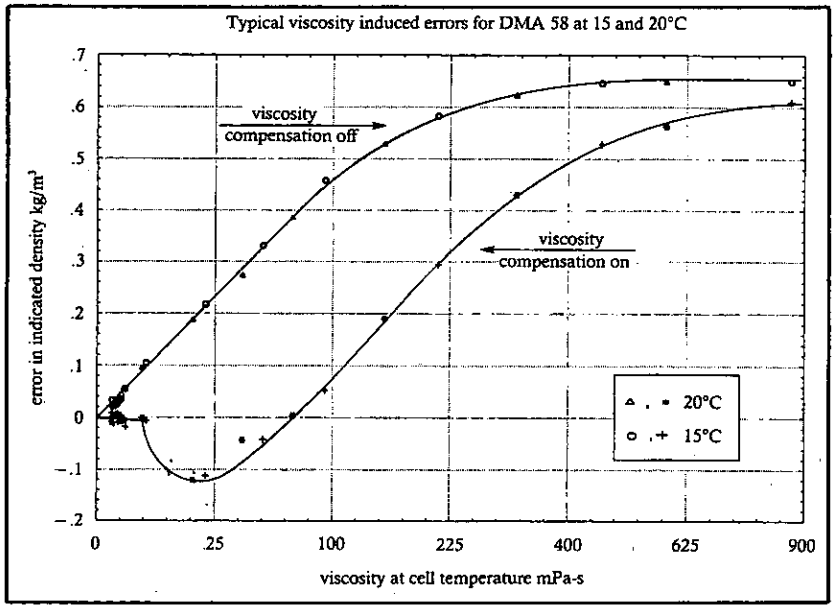

Figure 3

$\delta\rho$ is the amount in kg m^{-3} by which a meter will overestimate density due to sample viscosity. It should therefore be subtracted from the indicated density to find the true liquid density.

DMA 58 at 15 and 20°C,		
$0 > \eta < 100$ mPa-s	$\delta\rho = -0.007 + 0.048\sqrt{\eta}$	residual s.d. 0.010 kg m^{-3}
$0 > \eta < 1000$ mPa-s	$\delta\rho = -0.018 + 0.058\sqrt{\eta} - 0.001\,24\eta$	residual s.d. 0.014 kg m^{-3}
DMA 48 at 15°C,		
$0 > \eta < 100$ mPa-s	$\delta\rho = -0.003 + 0.05\sqrt{\eta}$	residual s.d. 0.01 kg m^{-3}
$0 > \eta < 1000$ mPa-s	$\delta\rho = -0.01 + 0.063\sqrt{\eta} - 0.001\,43\eta$	residual s.d. 0.01 kg m^{-3}
DMA 48 at 20°C,		
$0 > \eta < 100$ mPa-s	$\delta\rho = -0.01 + 0.033\sqrt{\eta}$	residual s.d. 0.02 kg m^{-3}
$0 > \eta < 1000$ mPa-s	$\delta\rho = -0.02 + 0.044\sqrt{\eta} - 0.000\,92\eta$	residual s.d. 0.03 kg m^{-3}
DMA 55 at 15 and 20°C,		
$0 > \eta < 100$ mPa-s	$\delta\rho = -0.008 + 0.050\sqrt{\eta}$	residual s.d. 0.014 kg m^{-3}
$0 > \eta < 1000$ mPa-s	$\delta\rho = -0.016 + 0.060\sqrt{\eta} - 0.001\,26\eta$	residual s.d. 0.020 kg m^{-3}

Table 5: Viscosity correction terms

fiscal puposes. Twice during these trials, being unaware of the interrogation facility, it only became obvious that the correction facility in a DMA 58 had not switched correctly when the data from a series of standards was plotted.

Calibration

Although all models other than the DMA 35 have a facility to allow them to be calibrated with two liquids, the manufacturer recommends that the instruments be calibrated with air and water, the resultant errors in displayed density are shown in **Table 6**. The only comparable value identified in the literature can be calculated from data given in Whetstone et al. [1978] in an early Paar, where using air and water calibration the error shown for xylene $\rho \approx 867$ kg m^{-3} would have been +0.05 kg m^{-3}.

The errors appear to be independent of temperature for the DMA 48 and 58, at normal working temperatures but not for the DMA 55. They also appear to be characteristic of the machine type, varying little between different instruments of the same model.

In addition to the errors shown above, calibrating with air and water places great reliance on the water figure, and little on the air, whilst calibrating with two liquids, one of which would presumably be water, spreads the weighting more or less evenly between the two. It is also possible, by calibrating with two liquids of similar viscosity to the samples normally tested, to cancel out the viscosity dependent errors in the instrument during the calibration.

In view of the uncertainties introduced by using only air and water, it is very doubtful that a machine so calibrated could be regarded as traceably calibrated for fiscal purposes.

The DMA 35 which can only be calibrated by the user with one liquid, normally water, displayed the correct density ±1 kg m^{-3} over the entire density range. With sample viscosities below ≈350 mPa-s, no viscosity dependent errors were seen, above that, the maximum error appeared to be 1 kg m^{-3}.

Additional tests

The density calculation algorithms in the DMA 48 and DMA 58 appear to be correct, as do the internal tables of air and water density.

Reducing the supply voltage by 6 percent appeared to have no effect on machine performance.

model	*at 650 kg m^{-3}*	*at 1600 kg m^{-3}*
DMA 48	−0.1 kg m^{-3}	+0.2 kg m^{-3}
DMA 58	+0.05 kg m^{-3}	−0.08 kg m^{-3}
DMA 55 @ 15°C	+0.08 kg m^{+3}	−0.14 kg m^{-3}
DMA 55 @ 20°C	−0.11 kg m^{-3}	+0.11 kg m^{-3}

Table 6: Errors due to calibrating with air and water

If a DMA 48 or 58 is tilted, the displayed period starts to change at 3° and the density at 4.5°. It is therefore important that a densitometer installed in a mobile laboratory be calibrated immediately prior to use.

In a DMA 48, variation in atmospheric pressure between 920 and 1050 mbar caused no change in displayed period when the cell was full of air, beyond that commensurate with changes in the density of air.

Although no tests aimed specifically at looking for surface tension effects were carried out, no errors attributable to this were observed.

The manuals supplied with the machines probably contain all the necessary data likely to be needed by the operator but the layout, illustrations, and indexing are felt to be poor and the manuals should be rewritten.

Uncertainties in use

In the light of this assessment, what uncertainty should be attached to densities determined at a nominal 15 or 20°C by a laboratory following good practice?

The repeatability of the instruments is normally excellent, although duplicate injections should always be made to check for inconsistency due to the presence of bubbles in the cell.

Assuming that:—

a The cell is clean and cleanliness is monitored by checking the air period.
b Syringes, autosampler lines and other sample handling equipment are clean.
c Cell temperature is stable.
d The cell has been traceably calibrated using two liquids with densities known to 0.01 kg m^{-3}, which bracket the sample density. Calibrations should be carried out:—
   After disturbing the cell by maintenance,
   After disturbing the cell by inserting or removing a thermometer in the thermowell,
   After resiting a machine if there is any possibility of it being at a different angle to the horizontal,
   If calibration has not been carried out at this temperature within the last month,
   After changing cell temperature (0.01 kg m^{-3} instruments)
e Sample viscosity is below 1000 mPa-s and is known to ±25% for a 0.1 kg m^{-3} instrument or ±10% for a 0.01 kg m^{-3} instrument.

The density determined by a DMA 48 after applying the viscosity correction given in **Table 5** will probably be within ±0.25 kg m^{-3} of the true value and by a DMA 58 within ±0.05 kg m^{-3}. These figures can both be substantially improved upon if sample viscosities are known with greater precision, actual cell temperature has been determined using calibration liquids and the viscosity error curve has been determined for that particular instrument.

For comparison, if the IP 160 hydrometer method is followed using a traceably calibrated L50, and no losses of light components occur from the sample:—

a Hydrometer calibration 0.15 kg m^{-3}
b Surface tension known to ±5 mN m^{-1} 0.15 kg m^{-3}
c Temperature known to ±250 mK (0.25°C) 0.20 kg m^{-3}
d Repeatability of reading the hydrometer 0.15 kg m^{-3}

The total uncertainty in hydrometer density will be about ±0.6 kg m^{-3}. When handling volatile samples such as road fuels or crude oils, an uncertainty of ±1.1 kg m^{-3} is probably the best which can be achieved using this type of hydrometer.

Conclusions

It is suggested that the DMA 48 is operated with viscosity compensation switched on and a correction applied for samples of more than 100 mPa-s. The operator of the DMA 58, who is presumed to use it because of the need for higher precision densities, has a more difficult choice to make, since small viscosity changes can lead to relatively substantial errors. Even a low viscosity sample such as Derv of 4 mPa-s has an error of 0.09 kg m^{-3}. The difference in displayed densities with viscosity compensation on and off

will actually be slightly larger, since when it is on, the error in displayed density will be negative at this viscosity.

If a DMA 58 is to be used for fiscal or high precision purposes, it is recommended that the compensation be turned off and a standard correction applied to the displayed density using one of the terms in **Table 5**. For all fiscal work or measurement requiring proven traceability, four and five place machines should be calibrated using two liquids rather than with one liquid and air, and, if the internal cell temperature indicator is being relied upon, it should be independently checked annually. The air period should be monitored regularly and used as an indicator of cell cleanliness. ■

References

Ashcroft SJ, DR Brooker and JCR Turner, 1990. J Chem. Soc. Faraday Trans, **86**(1), 145–149.

Bernhardt J, H Pauly, 1977. J Phys Chem, **81**, 1290.

Bernhardt J, H Pauly, 1980. J Phys Chem, **84**, 158.

Stabinger H, O Kratky and H Leopold, 1967. Monatsh Chem, **98**, 436.

Wagenbreth H, 1987. *Lecture to the 17th Sudzucker-Frankenzucher-Symposium, 11 Nov 1986,* reported in Confructa Studion.

Whetstone JR, et al, 1978, *Density and Thermal Expansion Coefficients of Petroleums,* N.B.S. Washington.

Acknowledgements

The authors would like to thank Dr H Stabinger, Paar Scientific Ltd, Mrs S Lewis, Dr K Sommer and Mr J R Whetstone for their help. The work was financially assisted in part by a grant from the Institute of Petroleum.