Technical Assessment of the Anton Paar DMA5000 density meter
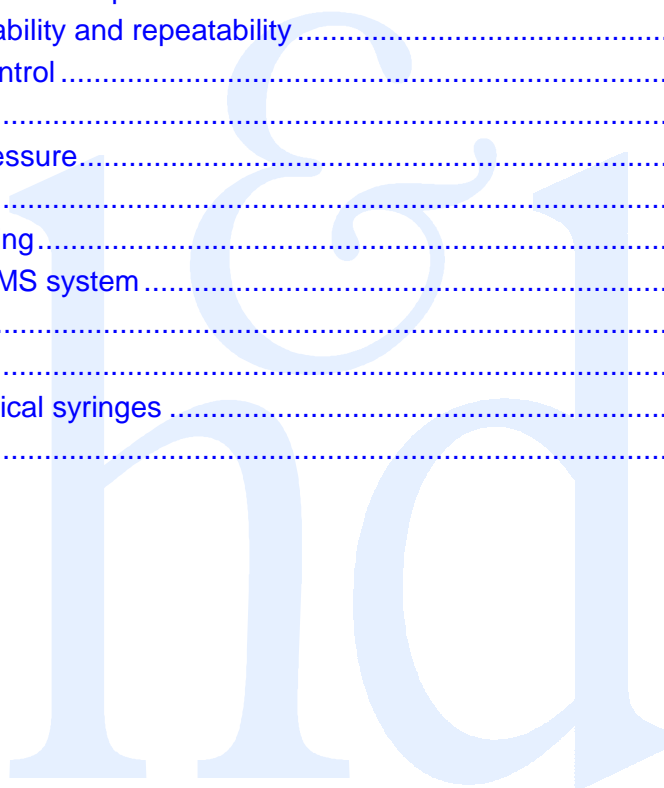
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Summary

The DMA 5000 density meter appears to be an excellent instrument.

Once correctly calibrated, it is capable of measuring the density of almost any liquids between 650 to 1650 kgm^{-3}, 0 to 600 mPa·s with a maximum error of $\pm$ 0.03 kgm^{-3}.

Over a narrower viscosity range, <30 mPa·s, the maximum error is of the order of $\pm$ 0.015 kgm^{-3}.

Temperature control, with the exception of one odd quirk, is excellent.

Although the computer interface works adequately, it has several unusual features which can catch out an unwary operator.

Background

Some years ago Fitzgerald et al [1992] published an assessment of the Paar DMA 48 and DMA 58 density meters, probably the most commonly used laboratory meters at that time. This showed that both machines were subject to viscosity-induced errors for most samples, which could be up to 0.7 kgm^{-3} on an instrument reading to 0.01 kgm^{-3}.

At about the same time, Dr. Hans Stabinger, the inventor of oscillating tube density meters, started work on a new design of measurement cell, with the aim of overcoming these and other problems. The instrument he developed eventually entered the market in early 1998 as the Paar DMA 5000.

This paper covers an assessment of this model of density meter carried out over the last two years.

Introduction

Five DMA 5000s were used during this assessment. Although most of the figures given here are derived from one particular machine, they are typical of all those seen to date.

Except where stated otherwise, all samples used in this work were liquid density Certified Reference Materials (CRMs) with valid UKAS certificates. These have a density uncertainty of ± 0.007 kgm^{-3} at $k = 2$ (95%). They are produced in our laboratories by hydrostatic weighing.

The methodologies laid down in ISO 15212-1:1998 were used wherever appropriate.

Air densities were calculated using the formula given by Davis R.S. [1992]

Water densities were calculated using the formula given by Patterson J.B. and Morris E.C. [1994]

Corrections for the deviation of water samples from V-SMOW due to isotopic variability was calculated using the formulae given by Girard, G. and Menarche M. [1971].

Water densities above 40°C, and corrections for water density changes due to atmospheric pressure were derived from Kell, G.S. [1975].

Principle of operation

Almost all laboratory density meters, both the Paar range and the instruments derived from them by the Japanese company, Kyoto, have a measurement cell comprising a borosilicate glass U tube inside a thermostated jacket. This typically holds about 0.7 ml of sample.

The U tube is oscillated at its fundamental frequency, which is a function of the system mass. If we assume that the sample volume trapped between the oscillation nodes is constant, it can be seen that the oscillation frequency is therefore a function of sample density.

$$\tau = 2\pi\sqrt{\frac{\rho v + m}{c}}$$

where τ = oscillation period

ρ = sample density

v = cell volume

m = cell mass

c = spring constant

Taking the square of this expression, and substituting $G = \dfrac{4\pi^2 v}{c}$ $\qquad H = \dfrac{4\pi^2 m}{c}$

we obtain $\quad \rho = (\tau^2 - H)/G$

As the U tube is oscillating, the sample will have the effect of damping the oscillation. This damping will be a function of the sample viscosity.

The sample viscosity will also have the effect of apparently moving the oscillation nodes slightly, thus increasing the apparent volume of the cell. When these two effects are combined, the error is of the order of

$$k \approx 0.05\sqrt{\eta}$$

where $\quad k$ = error in kgm^{-3}

η = viscosity in $\text{mPa} \cdot \text{s}$

The measurement cell in the DMA 5000 oscillates at several frequencies and in two modes. This allows the damping due to the sample to be measured and corrected for.

If the instrument has been correctly calibrated, density is now a function of the oscillation period τ and the damping. This gives an instrument with a markedly better precision than any others so far produced.

Calibration

The internal software of the meter includes the assumption that

$$\rho = A \cdot \tau^2 \cdot (1 + D \cdot damping + E \cdot damping^2) - B + C \cdot \tau^4 \tag{1}$$

Analysis of a number of different instruments using a range of density CRMs and water suggests that this equation with its interaction term between period and damping is unnecessarily complex. We have found that, for samples between 690 and 1620 kgm^{-3} and viscosities up to 600 mPa·s an equation of the form

$$\rho = A + B \cdot \tau^2 + C \cdot damping \tag{2}$$

is to be preferred. For liquids of the same density range, but viscosities below 30 mPa·s,

$$\rho = A + B \cdot \tau^2 + C / damping \tag{3}$$

describes cell behaviour better.

The table below shows the results obtained from injecting two separate samples of a range of CRMs and water. The optimum function to fit all the data is,

$$\rho = (204.15371 \cdot \tau^2) - (0.0938 \cdot damping) - 1007.255 \qquad (4)$$

Considering only those samples having viscosities below 30 mPa·s.

$$\rho = (204.1540 \cdot \tau^2) + (1.50778 / damping) - 1008.026 \qquad (5)$$

sample	viscosity at 20°C mPa·s	indicated cell temp °C	hydrostatic weighing density kgm^{-3}	density predicted from (4) kgm^{-3}	$\delta\rho$ hw – pred density kgm^{-3}	density predicted from (5) kgm^{-3}	$\delta\rho$ hw – pred density kgm^{-3}
iso octane	0.5	20.000	691.884	691.866	0.019	691.877	0.007
iso octane	0.5	20.000	691.884	691.866	0.018	691.879	0.005
dodecane	1.5	19.999	749.490	749.505	-0.016	749.500	-0.011
dodecane	1.5	19.998	749.490	749.505	-0.015	749.501	-0.011
cyclohexane	0.9	20.001	778.541	778.524	0.018	778.526	0.016
cyclohexane	0.9	20.001	778.541	778.522	0.019	778.525	0.017
lubricating oil 8	16.6	20.002	867.509	867.509	0.000	867.510	-0.001
lubricating oil 8	16.6	20.001	867.509	867.508	0.001	867.509	0.000
lubricating oil 30	68.4	20.001	870.903	870.932	-0.029		
lubricating oil 30	68.4	20.001	870.903	870.933	-0.030		
lubricating oil 110	317	20.000	881.651	881.660	-0.009		
lubricating oil 110	317	19.999	881.652	881.661	-0.009		
lubricating oil A90	583	19.999	886.537	886.513	0.023		
lubricating oil A90	583	19.998	886.537	886.517	0.020		
41% ethanol	2.9	20.000	947.124	947.137	-0.013	947.124	0.000
41% ethanol	2.9	20.000	947.124	947.137	-0.013	947.124	0.000
11% ethanol	1.6	20.000	983.665	983.672	-0.007	983.666	-0.001
11% ethanol	1.6	20.000	983.665	983.674	-0.009	983.668	-0.003
water	1.0	20.000	998.202	998.201	0.001	998.199	0.003
water	1.0	19.999	998.202	998.201	0.002	998.199	0.003
dimethylphthalate	17.4	20.001	1191.230	1191.216	0.014	1191.229	0.001
dimethylphthalate	17.4	19.999	1191.232	1191.216	0.016	1191.229	0.003
tetrachloroethylene	0.9	20.001	1621.086	1621.085	0.001	1621.084	0.002
tetrachloroethylene	0.9	20.000	1621.088	1621.089	-0.001	1621.089	-0.001
standard deviations					**0.015**		**0.007**

Linearity

The linearity of five meters was checked using CRMs with a density range from 690 to 1620 kgm^{-3}. For only one meter was an additional term of τ^4 significant, and even here, the effect of ignoring the term was an additional error of only 0.0013 kgm^{-3}. All the cells tested to date could be regarded as acceptably linear.

Parasitic resonance

One density meter was checked at 90 points over the range 800 to 2200 kgm^{-3} using gravimetric mixes of tetrachloroethylene and either iso-octane or dibromomethane. No unexpected density deviations were found, which is taken to indicate that that the instrument is free of any problems due to parasitic resonance.

Temporal stability

The measurement cell appears to have consistent characteristics, even in one of our instruments which is temperature cycled from 5 to 50°C several times a day.

A meter in heavy use was checked daily but not adjusted. Over a two month period it gave a reasonably consistent (±0.005 kgm^{-3}) density for water. There was then a sudden step change in indicated density of 0.04 kgm^{-3}, after which the variation was no more than ±0.002 kgm^{-3} for a further month.

No corresponding step change in oscillation period was seen when the cell contained dry air. It has however been noticed on many occasions that compared to previous density meters from Paar, the cell of the DMA 5000 can be more difficult to clean. It should also be remembered that cleanliness becomes much more important with such a high precision instrument.

Repeatability

A repeatability test using 11 independent manual injections of a light lubricating oil CRM over a period of an hour gave a standard deviation of 0.0013 kgm^{-3}. However, it is thought that some amount of this variability maybe due to fractional changes in liquid density caused by the injection technique, as all liquids dissolve a certain amount of air.

Cell temperature

Measurement cell temperature is a very important aspect of a high precision density meter. If testing a sample of, for example, gasoline where $\beta \approx 1$ kgm^{-3}K^{-1}, a 10 mK temperature error gives a density error of 0.01 kgm^{-3}.

The DMA 5000 cell is surrounded by a metal block, the temperature of which is maintained by Peltier units. Unfortunately, it is impossible to withdraw the measurement thermometer for external calibration, and some way must therefore be found to calibrate the sensor in situ.

Once a liquid sample has been in the cell for several minutes, a thermodynamic equilibrium is probably achieved, with at least the following sources:

a)   Heat generated as the cell wall is forced to oscillate.

b)   Energy transfer along the liquid paths into and out of the cell.

c)   Heat generated within the sample due to work done on it by the oscillator.

It seems likely that sample temperature will vary slightly, since although a) probably has a consistent value for a given cell, b) & c) are dependent on the sample's thermodynamic properties.

Two independent methods have been used to determine cell temperature, a resistance thermometer and calculation from density CRMs.

Direct thermometry

A Paar CKT 100 resistance thermometer was calibrated using certified water triple point and gallium melting point cells (both are fixed points on the ITS90 temperature scale). Probe linearity between these two temperatures was checked by comparison with a Tinsley 5187SA class I probe, which had itself been calibrated by NPL.

The density meter cell was filled with light spindle oil, and the thermometer probe inserted as far as reasonably possible. This was done several times over a period of six months. At a cell temperature of 20°C, a maximum error of 2 mK was found.

It is essential to remember when using a thermometer that the temperature being measured is that of the probe. Experience has shown that there can be problems using certain types of 4 wire probes in density meter cells, due to energy transfer along the wires. Laboratory ambient temperature is maintained at 18.5°C so a slight underestimation of cell temperature was possible.

Indirect thermometry

We suggested in a previous paper (Fitzgerald et al 1992) that it should be possible to deduce cell temperature by injecting density CRMs and water into the cell and then finding the temperature at which the optimum fit of certificate density to τ^2 occurs.

When this was done for the 11 CRMs and water in the table above, the optimum fit was found at 14 mK above the indicated temperature, with a residual standard deviation of 0.0150 kgm^{-3}.

When the data set was restricted to those samples having viscosities below 30 mPa·s, the optimum fit was found 1 mK above the indicated temperature, with a residual standard deviation of 0.0066 kgm^{-3}.

Speed of temperature equilibrium

ISO 15212-1:1998 section 6.1.3 lays down a simple test to ensure that a density meter does not display a density as "valid" before the sample has thermally equilibrated at cell temperature.

A sample of isooctane was heated to 30°C and immediately injected into a density cell which was at 20°C. The first density shown as "valid" was 693.435 kgm^{-3} at an indicated cell temperature of 20.002°C.

After waiting the 10 minutes required by the ISO, the displayed density was 693.438 kgm^{-3} at an indicated 20.001°C.

Iso octane has an expansivity of 0.821 kgm^{-3}K^{-1} at 20°C. If it is assumed that the final displayed cell temperature of 20.001°C accurately reflected sample temperature, then, at the time the meter first showed the "valid" flag, sample temperature was probably about 3 mK above the indicated cell temperature.

Temperature stability and repeatability

The measurement cell was filled with tetrachloroethylene, a liquid chosen for its high expansivity of 1.66 kgm^{-3}K^{-1} (crude oil $\approx$ 0.7 kgm^{-3}K^{-1}, motor gasoline $\approx$ 0.9 kgm^{-3}K^{-1}, spirits $\approx$ 0.7 kgm^{-3}K^{-1}, beer $\approx$ 0.2 kgm^{-3}K^{-1}).

The density meter was joined to a PC and indicated cell temperature and oscillation period collected at 20 second intervals, together with atmospheric pressure. Three different measurement methods were set up in the meter, differing only in the set temperatures: 15, 20 and 25°C. The PC was programmed to change method periodically, and data gathered for about three and a half days. This gave over 16,000 density measurements covering 71 changes of temperature.

The density of the tetrachloroethylene in the cell was calculated from the τ values using typical cell constants for the three temperatures. A multiple regression of calculated density against indicated temperature and atmospheric pressure gave a residual standard deviation of 0.0019 kgm^{-3}.

Since the liquid has an expansivity of 1.66 kgm^{-3}K^{-1}, this equates to 1.18 mK.

This implies that the cell temperature indicated by the instrument reflects true changes in cell temperature to 2 mK.

This procedure was carried out several times over a year, and the values quoted are typical of all the data gathered.

Temperature control

There is a minor problem with the temperature control algorithm in certain circumstances.

If the cell temperature is forced to change for some time, as might happen if an air line is attached to the cell to dry it, and then forgotten, the instrument will stabilise at a cell temperature about 100 mK away from the set point. It appears that the only way to overcome this problem is to leave the instrument totally untouched for about 7 to 9 minutes, after which the control algorithm will reset itself.

Other tests

Atmospheric pressure

Variation in atmospheric pressure between 940 and 1040 mbar gave no change in displayed cell period beyond that commensurate with changes in air density.

Surface tension

No errors due to surface tension effects were noted at any time during the evaluation of the machines.

Unstable benching

When the DMA 5000 was tilted either longitudinally or laterally, no significant changes in displayed period were seen at an angle of 4°.

Interfacing with LIMS system

Several DMA 5000s have been operated using PCs for data capture. Although the interface worked well and was reliable, a number of quirks were noted:

1. The RS232 cable requires several non-standard connections to be made to the handshaking lines.
2. Although the mechanism for making data available at the RS232 interface is consistent with that for choosing which data items are to be displayed within a method, it is felt that both could be more intuitive.
3. Cell temperature cannot be controlled directly by the PC, instead a series of methods must be set up in the density meter at different temperatures. The PC can then switch the meter from one method, and hence cell temperature, to another. Since few laboratories measure densities at more than one temperature, this would affect very few users.
4. The data items are only available to the PC from an output buffer holding up to 100 historical data sets. A 'clear buffer' command is available as one of the sub-menu choices, the theory being that once the buffer has been cleared, only current data is available to the PC. This requires the PC to request data at a rate faster that the density meter has been instructed to generate it.
   It appears that on some occasions the clear buffer command leaves old data in the buffer which is then available to the PC.
   It is therefore important that if a laboratory is going to change the test method frequently, the PC must check the time of the data set, to ensure that the data received is that required.

In summary, data can be passed reliably to a PC, but the system is not intuitive, and would benefit from some redesign.

Handbook

The instruction manual is comprehensive, and appears to cover all aspects of operating the instrument.

Precision

Considering liquids between 650 and 1800 kgm^{-3}, and viscosities <600 mPa·s.

Assuming that

- The cell is clean and is monitored daily using air and water periods.
- The sample introduction system, be it syringe, autosampler etc. is clean (see below for note on use of disposable medical syringes).
- Cell indicated temperature is periodically checked.

A DMA 5000 'calibrated' using air and water will have an uncertainty at best of ±0.15 kgm^{-3}. If, on the other hand, it is correctly calibrated so that the cell constants and damping function have been determined for the particular cell, rather than using the default "typical" values, an uncertainty of ± 0.03 kgm^{-3} can be expected.

If testing is restricted to samples having a viscosity of less than 30 mPa·s, and the instrument is calibrated using the equation $\rho = A + B \cdot \tau^2 + C / damping$, an uncertainty of ±0.015 kgm^{-3} is attainable. However, at this level of precision, great care must be taken in sample handling, and for certain samples, atmospheric pressure corrections might need to be applied.

Disposable medical syringes

Many laboratories use plastic disposable medical syringes to inject samples into the instrument. On several occasions, inconsistent results have been tracked down to the use of these syringes. Medical syringes are specified in ISO 7886-1 1993, which allows up to 0.6% by mass of the barrel to be lubricant. Discussions with several manufacturers have revealed that a wide range of chemicals are acceptable as lubricants. In some cases, lubricants were dissolving in samples as they were injected into the density meter. Use of these syringes should not therefore be encouraged for high precision work, unless it is known that the lubricant will not contaminate the sample.

References

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