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Report on EURAMET Project 1214

Density measurement of viscous oils (using vibrating tube density meters)

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Abstract

A comparison of vibrating tube liquid density meters has been undertaken between six measurement laboratories: NPL, VSL (density), IPQ, VSL (flow), Mettler-Toledo and H&D Fitzgerald. NPL acted as the pilot laboratory and the density standards were provided by VSL (density). The three reference oils were sent to the participants in October 2011 and measurements were made over the period November 2011 to February 2012. Measurements were made over the temperature range 10 °C to 70 °C by most participants. Seven measurements (out of a total of sixty) were not in agreement with the calculated reference values. Two of these can be accounted for by the high viscosity of one of the samples (Vitrea 220 oil at 10 °C), whilst others may be explained by the different approaches to viscosity correction adopted by the participating laboratories.

CONTENTS

1 INTRODUCTION

In 2010 a tri-lateral comparison of vibrating tube liquid density meters was undertaken between VSL (d), IPQ and PTB. Discrepancies were found between the results of the participants for the measurement of the density of viscous oil. A follow-up comparison was agreed to investigate the discrepancy and to provide preparatory information for the EURAMET supplementary density comparison (using the same devices) planned for 2012/3.

The density of three increasingly viscous oils (Vitrea 10, Vitrea 100 and Vitrea 220) was measured at temperatures of 10 °C, 20 °C, 40 °C and 70 °C.

The aims of this project were:

- To establish the level of equivalence with regard to the density correction of viscous oils
- To gain insight into the various methods used for the calibration of vibrating tube density meters
- To link density measurements performed by non-EURAMET accredited laboratories to international measurements in order to support their (accredited) measurement capability declarations
- To provide information to assist the planning of a EURAMET Supplementary Comparison of vibrating tube liquid density meters

Table 1 lists the participating laboratories. VSL (density laboratory) and NPL acted as joint pilots for the comparison with VSL (d) providing the standard liquids and NPL collecting and analysing the results.

Table 1 List of Participating Laboratories

Laboratory		Country
National Physical Laboratory	NPL	United Kingdom
Van Swinden Laboratory (density laboratory)	VSL(d)	Netherlands
Instituto Português da Qualidade	IPQ	Portugal
Van Swinden Laboratory (flow laboratory)	VSL(f)	Netherlands
Mettler-Toledo	M-T	Netherlands
H&D Fitzgerald Ltd.	H&D	United Kingdom

2 DESCRIPTION OF THE TRANSFER STANDARDS

The liquids used for this comparison were three Vitrea oils designated Vitrea 10, Vitrea 100 and Vitrea 220. The properties of the three oils are given in Table 2.

Table 2 Properties of Vitrea oils

Oil designation	Nominal Density (at 20 °C) kg/m^3	Viscosity (70 °C – 10 °C) mPa.s
Vitrea 10	842	3 – 24
Vitrea 100	882	20 – 670
Vitrea 220	887	50 – 1060

Samples of approximately 100 mL of the three liquids were sent to each participating laboratory contained in glass bottles as shown in Figure 1.

Figure 1 Liquid samples as sent to participating laboratories

3 COMPARISON SCHEDULE

Samples of approximately 100 mL of each of the three standard liquids were sent out by VSL (d) to the participants in October 2011. Measurements were made by the participants over the ensuing period with the final set of results being received by NPL in February 2012. Previous measurements, performed at VSL (d), had been made to ensure that the selected transfer standards would be stable over the period of the comparison.

4 PROCEDURES AND EQUIPMENT

The comparison protocol required the participants to make measurements of the three transfer standards over the temperature range 10 °C to 70 °C. One participant (VSL (f)) measured only over the range 10 °C to 40 °C and one (M-T) only performed measurements at 20 °C.

Each participant measured the density of the liquid standards according to their normal calibration procedure using a vibrating tube liquid density meter. Details of the procedures and equipment used by the six participating laboratories are summarised in Table 3 and are described in more detail in Section 7. The table summarises both the measurement method used to determine the density of the transfer standards and the procedure used to characterise the density meter for viscosity dependence.

Table 3 Calibration equipment and procedures used by participating laboratories

Participating laboratory	Density meter	Meter Characterisation	Calibration liquids	Measurement procedure
NPL	Paar DMA5000	Air and water calibration. Temperature checked. Viscosity correction determined using CRMs.	Dodecane, Tetrachloroethylene, Lube oil 8, Base lube oil 30, Base lube oil110, Lube oil A90	Viscosity corrections manually applied to (uncorrected) density reading
VSL (density)	Paar DMA5000	Air and water calibration. Temperature checked. Viscosity correction determined using CRMs.	Lube oil 8, Base lube oil 30, Base lube oil 110, Lube oil A90	Viscosity corrections manually applied to (uncorrected) density reading
IPQ	Paar DMA5000	Air and water calibration. Temperature checked. Viscosity correction determined using CRMs.	Tetrachloroethylene, Dimethyl phatalate, 2,2,4 trimethylpentane, Lube oil 8, Base lube oil 30, Base lube oil 110, Lube oil A90, n-nonane	Viscosity corrections manually applied to (uncorrected) density reading
VSL (flow)	Paar DMA5000	Water and air calibration only		PAAR built in correction for liquids viscosity <700 mPa.s used
Mettler-Toledo	Mettler DM40	Water and air calibration only		Active viscosity correction applied (see Appendix A for details).
H&D Fitzgerald Ltd.	Paar DMA5000	Viscosity correction algorithm based on period & damping of cell determined using CRMs		Viscosity correction applied based on an algorithm

Five of the participants used Paar DMA 5000 density meters and the sixth used a Mettler DM40, which works on a similar principle. The DMA 5000 sensing element consists of a glass U-tube into which the liquid sample to be measured is injected. The resonant frequency of the tube is proportional to the density of the liquid sample being measured. In addition, by measuring the damping of the U-tubes' oscillation, caused by the viscosity of the liquid sample, a correction to the density of the liquid can be made. The meter will, among other parameters, display both corrected and uncorrected density values.

Adjustment of the DMA 5000, as defined by Paar Scientific [1], uses the density values for air and (pure) water as reference points. Adjustment can be performed either at 20 °C or over the temperature range 20 °C to 60 °C. In addition to the adjustment the DMA 5000 can be calibrated using Certified Reference Materials (CRMs) with traceable density reference values (and known viscosities).

Figure 2 Paar DMA 500 density meter

5 RESULTS OF THE COMPARISON

The results as reported by the participants are given in Tables 4 to 6.

Table 4 Participants' reported results for Vitrea 10 oil

Temperature °C	Lab ID	Measured density Uncorrected kg/m^3	Measured density Corrected kg/m^3	Estimated unc. (k=1) kg/m^3
10	NPL	849.566	849.352	0.01
	VSL(d)	849.566 5	849.340	0.02
	IPQ	849.639	849.335	0.03
	VSL(f)	849.45	849.45	0.08
	M-T			
	H&D		849.33	0.08
20	NPL	842.961	842.789	0.01
	VSL(d)	842.964 3	842.780	0.02
	IPQ	843.030	842.788	0.03
	VSL(f)	842.89	842.89	0.08
	M-T	842.9	842.9	0.1
	H&D		842.77	0.08
40	NPL	829.840	829.708	0.01
	VSL(d)	829.834 0	829.710	0.02
	IPQ	829.899	829.713	0.03
	VSL(f)	829.77	829.77	0.08
	M-T			
	H&D		829.70	0.08
70	NPL	810.216	810.105	0.01
	VSL(d)	810.222 0	810.150	0.02
	IPQ	810.285	810.116	0.03
	VSL(f)			
	M-T			
	H&D		810.21	0.08

Table 5 Participants' reported results for Vitrea 100 oil

Temperature °C	Lab ID	Measured density		Estimated unc. (k=1) kg/m³
		Uncorrected kg/m³	Corrected kg/m³	
10	NPL	888.587	887.907	0.01
	VSL(d)	888.547 3	887.920	0.02
	IPQ	888.651	887.854	0.03
	VSL(f)	887.93	887.93	0.08
	M-T			
	H&D		887.89	0.08
20	NPL	882.314	881.692	0.01
	VSL(d)	882.277 4	881.670	0.02
	IPQ	882.377	881.627	0.03
	VSL(f)	881.66	881.66	0.08
	M-T	882.3	881.7	0.1
	H&D		881.68	0.08
40	NPL	869.723	869.279	0.01
	VSL(d)	869.691 7	869.260	0.02
	IPQ	869.781	869.219	0.03
	VSL(f)	869.33	869.33	0.08
	M-T			
	H&D		869.26	0.08
70	NPL	851.042	850.830	0.01
	VSL(d)	851.030 3	850.820	0.02
	IPQ	851.104	850.705	0.03
	VSL(f)			
	M-T			
	H&D		850.76	0.08

Table 6 Participants reported results for Vitrea 220 oil

Temperature °C	Lab ID	Measured density		Estimated unc. (k=1) kg/m^3
		Uncorrected kg/m^3	Corrected kg/m^3	
10	NPL	893.570	892.890	0.01
	VSL(d)	893.538 3	892.880	0.02
	IPQ	893.634	892.871	0.03
	VSL(f)	893.20	893.20	0.08
	M-T			
	H&D		893.12	0.08
20	NPL	887.392	886.712	0.01
	VSL(d)	887.361 2	886.730	0.02
	IPQ	887.454	886.709	0.03
	VSL(f)	886.76	886.76	0.08
	M-T	887.3	886.7	0.1
	H&D		886.73	0.08
40	NPL	875.045	874.471	0.01
	VSL(d)	875.016 7	874.460	0.02
	IPQ	875.103	874.435	0.03
	VSL(f)	874.42	874.42	0.08
	M-T			
	H&D		874.45	0.08
70	NPL	856.529	856.218	0.01
	VSL(d)	856.521 7	856.210	0.02
	IPQ	856.595	856.206	0.03
	VSL(f)			
	M-T			
	H&D		856.13	0.08

6 CALCULATION OF REFERENCE VALUES AND DATA ANALYSIS

Initially reference values were calculated based on all (corrected) measurements reported by the participants for each oil and at each measurement temperature using a least squares analysis of the measurement data [2]. It was assumed that there was no correlation between the results of the participants. The largest consistent subset (LCS) of the data was then identified using the method proposed by Cox [3] and this data used to re-calculate a reference value for each oil, at each measurement temperature.

Reference values were calculated for each oil, at each measurement temperature by least squares analysis of the (consistent) measurement results taking into account the uncertainties of the measured values. Normalised deviations from the reference value (*d*) for each result were calculated from the difference between the measured value and the reference value divided by the standard uncertainty of the difference.

$$d = \frac{(m - m_{ref})}{u(m - m_{ref})} \qquad (2)$$

The normalised deviations were used to identify results which are discrepant compared with the reference values. Results are normally considered discrepant (at a 5 % level of significance) where the normalised deviation is greater than 2. However, due to the limited amount of (consistent) data, results with normalised deviations of 2.1 have been included in the calculation of the reference value.

6.1 VITREA 10

Table 7 gives the results of the least squares analysis calculation of the reference value for the Vitrea 10 oil at the four measurement temperatures. Where the normalised deviations are reported in red they exceed the limit for consistent values and these results have been excluded from the calculation of the reference value. The results of the Vitrea 10 for the four reference temperatures are shown in figures 3a to 3d. All uncertainties shown are standard uncertainties (k=1).

Table 7 Results, reference values and normalised deviations for the Vitrea 10 oil

Temp. °C	Lab ID	Measured (corrected) value		Reference value		Normalised deviation d
		Density kg/m^3	Uncertainty kg/m^3	Density kg/m^3	Uncertainty kg/m^3	
10	NPL	849.352	0.01	849.348 2	0.004 3	1.5
	VSL(d)	849.340	0.02	849.348 2	0.004 3	-0.9
	IPQ	849.335	0.03	849.348 2	0.004 3	-0.9
	VSL(f)	849.45	0.08	849.348 2	0.004 3	2.5
	M-T					
	H&D	849.33	0.08	849.348 2	0.004 3	-0.5
20	NPL	842.789	0.01	842.787 1	0.004 3	0.7
	VSL(d)	842.780	0.02	842.787 1	0.004 3	-0.8
	IPQ	842.788	0.03	842.787 1	0.004 3	0.1
	VSL(f)	842.89	0.08	842.787 1	0.004 3	2.6
	M-T	842.9	0.1	842.787 1	0.004 3	2.3
	H&D	842.77	0.08	842.787 1	0.004 3	-0.4
40	NPL	829.708	0.01	829.709 4	0.004 2	-0.5
	VSL(d)	829.710	0.02	829.709 4	0.004 2	0.1
	IPQ	829.713	0.03	829.709 4	0.004 2	0.3
	VSL(f)	829.77	0.08	829.709 4	0.004 2	1.5
	M-T		0.1			
	H&D	829.70	0.08	829.709 4	0.004 2	-0.2
70	NPL	810.105	0.01	810.142 5	0.008 1	-3.9
	VSL(d)	810.150	0.02	810.142 5	0.008 1	1.3
	IPQ	810.116	0.03	810.142 5	0.008 1	-2.1
	VSL(f)					
	M-T					
	H&D	810.21	0.08	810.142 5	0.008 1	1.7

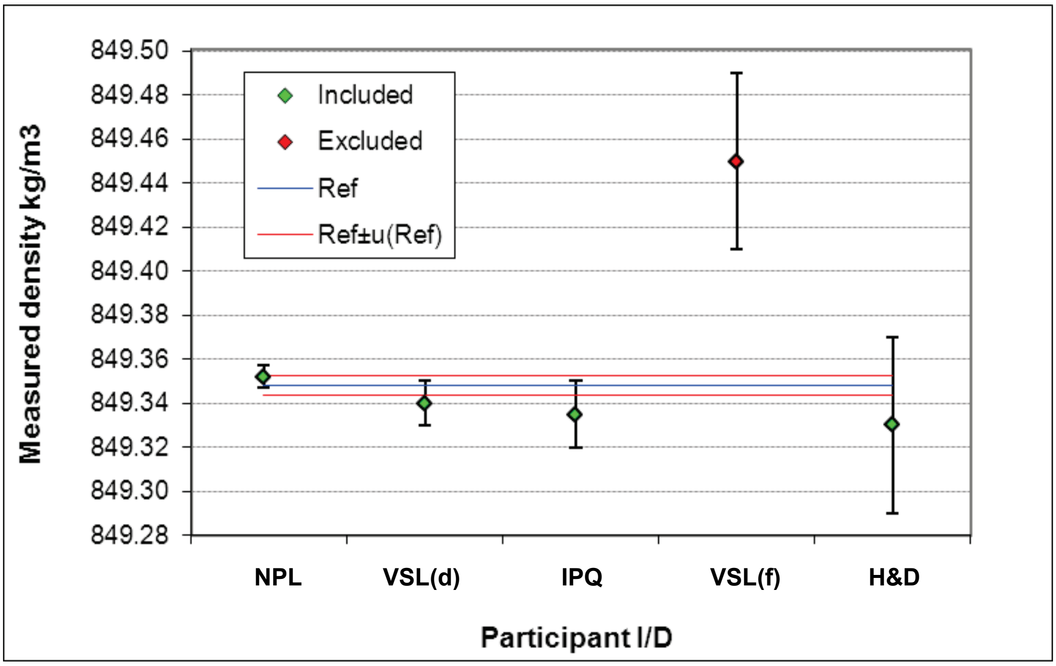

Figure 3a Results of the comparison for the Vitrea 10 oil at 10 °C

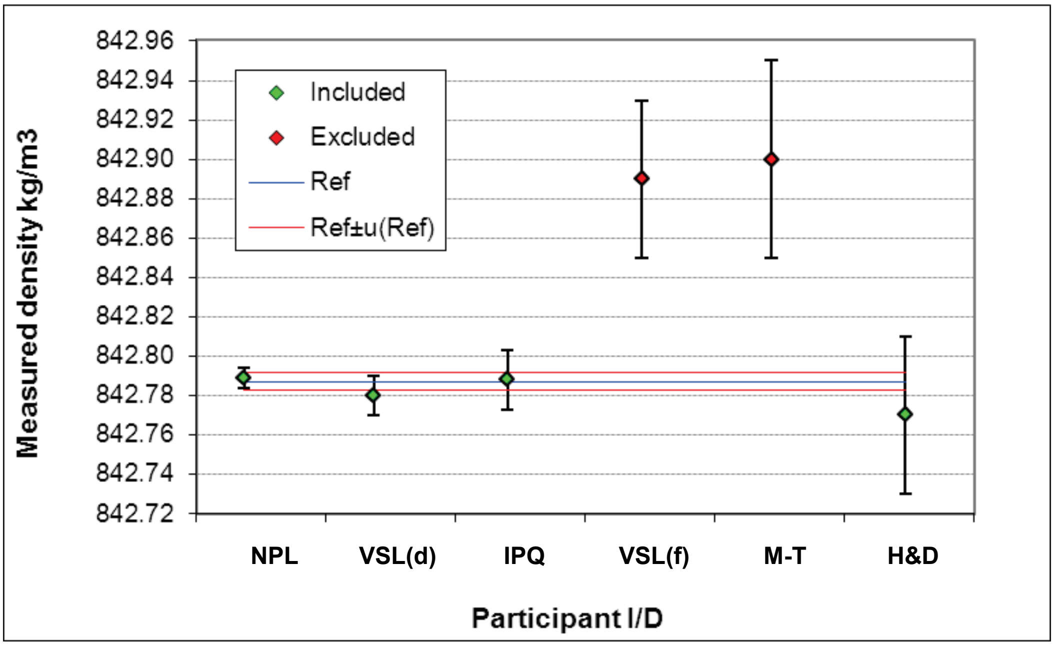

Figure 3b Results of the comparison for the Vitrea 10 oil at 20 °C

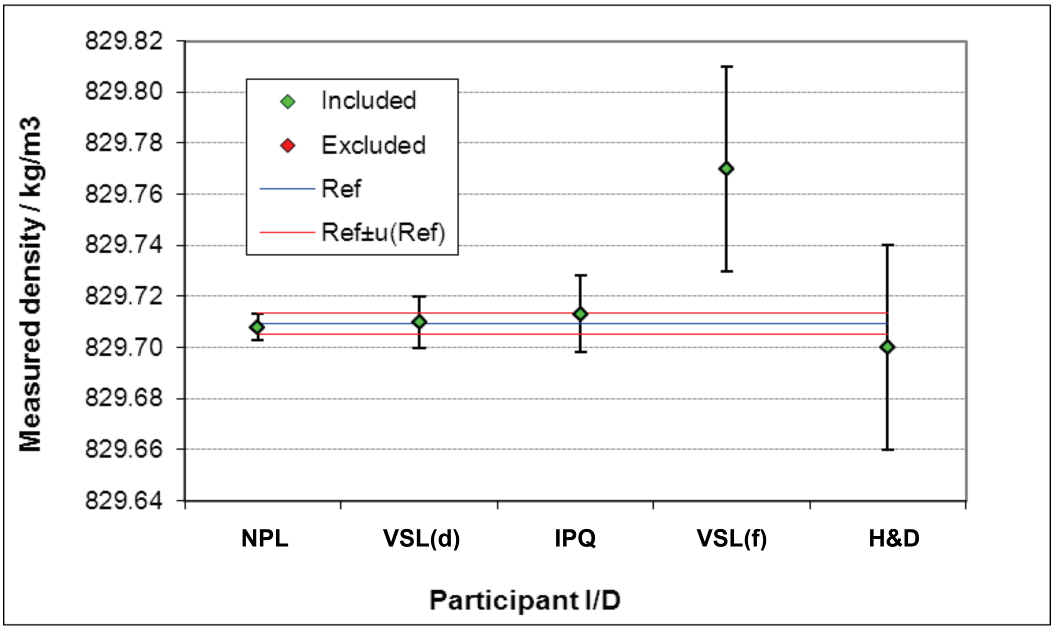

Figure 3c Results of the comparison for the Vitrea 10 oil at 40 °C

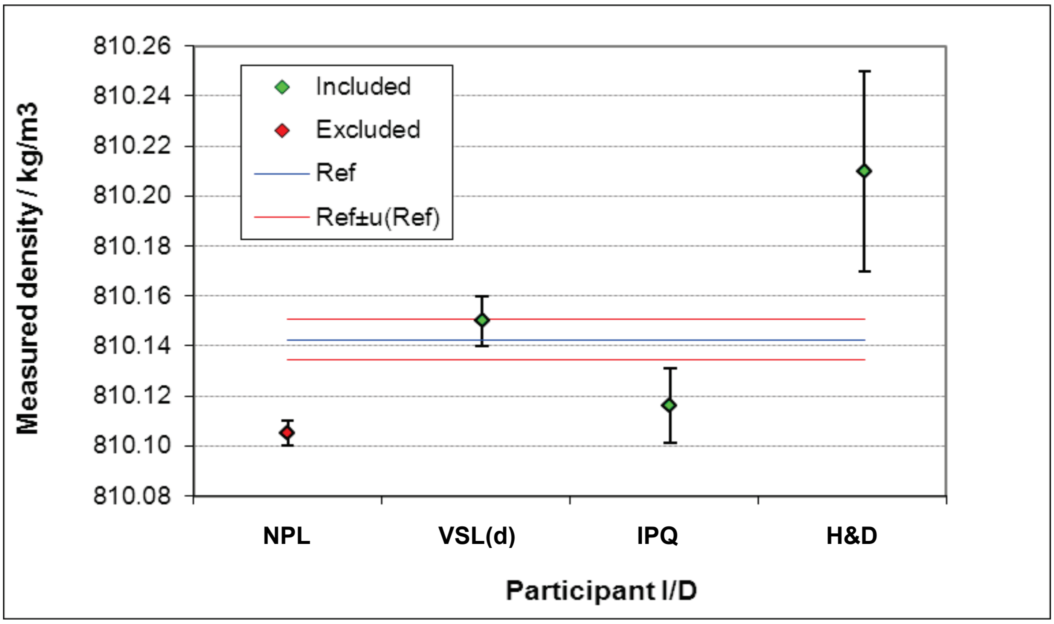

Figure 3d Results of the comparison for the Vitrea 10 oil at 70 °C

6.2 VITREA 100

Table 8 gives the results of the least squares analysis calculation of the reference value for the Vitrea 100 oil at the four measurement temperatures. Where the normalised deviations are reported in red they exceed the limit for consistent values and these results have been excluded from the calculation of the reference value. The results of the Vitrea 100 for the four reference temperatures are shown in figures 4a to 4d. All uncertainties shown are standard uncertainties (k=1).

Table 8 Results, reference values and normalised deviations for the Vitrea 100 oil

Temp. °C	Lab ID	Measured value		Reference value		Normalised deviation
		Density kg/m^3	Uncertainty kg/m^3	Density kg/m^3	Uncertainty kg/m^3	d
10	NPL	887.907	0.01	887.909 6	0.004 4	-1.1
	VSL(d)	887.920	0.02	887.909 6	0.004 4	1.2
	IPQ	887.854	0.03	887.909 6	0.004 4	-3.6
	VSL(f)	887.93	0.08	887.909 6	0.004 4	0.5
	M-T					
	H&D	887.89	0.08	887.909 6	0.004 4	-0.5
20	NPL	881.692	0.01	881.687 3	0.004 4	2.0
	VSL(d)	881.670	0.02	881.687 3	0.004 4	-1.9
	IPQ	881.627	0.03	881.687 3	0.004 4	-3.9
	VSL(f)	881.66	0.08	881.687 3	0.004 4	-0.7
	M-T	881.7	0.1	881.687 3	0.004 4	0.3
	H&D	881.68	0.08	881.687 3	0.004 4	-0.2
40	NPL	869.279	0.01	869.275 7	0.004 4	1.4
	VSL(d)	869.260	0.02	869.275 7	0.004 4	-1.7
	IPQ	869.219	0.03	869.275 7	0.004 4	-3.6
	VSL(f)	869.33	0.08	869.275 7	0.004 4	1.4
	M-T					
	H&D	869.26	0.08	869.275 7	0.004 4	-0.4
70	NPL	850.830	0.01	850.827 2	0.004 4	1.2
	VSL(d)	850.820	0.02	850.827 2	0.004 4	-0.8
	IPQ	850.705	0.03	850.827 2	0.004 4	-7.8
	VSL(f)					
	M-T					
	H&D	850.76	0.08	850.827 2	0.004 4	-1.7

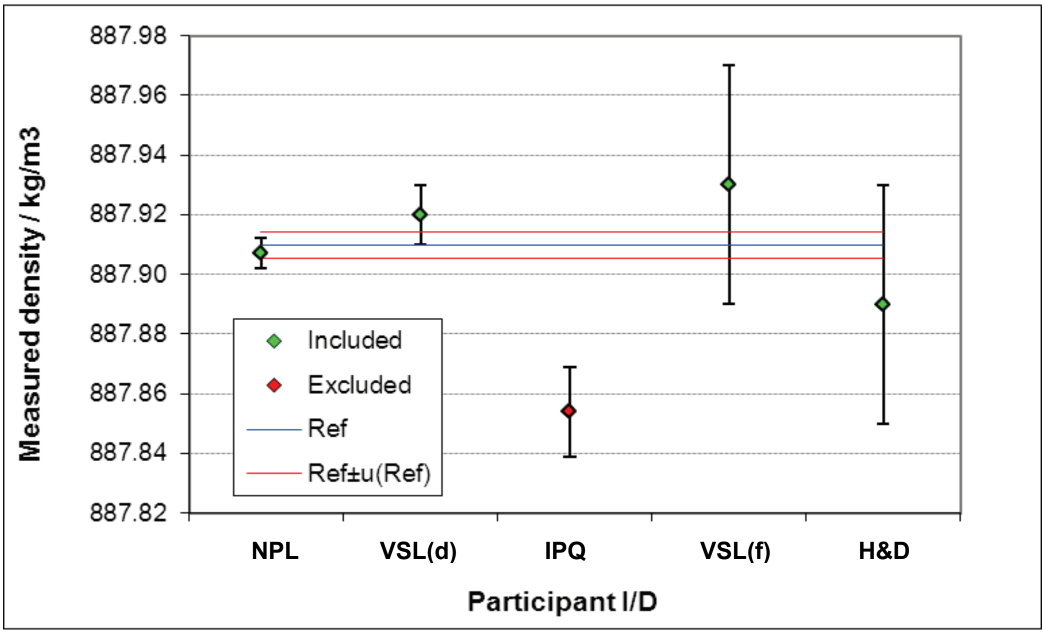

Figure 4a Results of the comparison for the Vitrea 100 oil at 10 °C

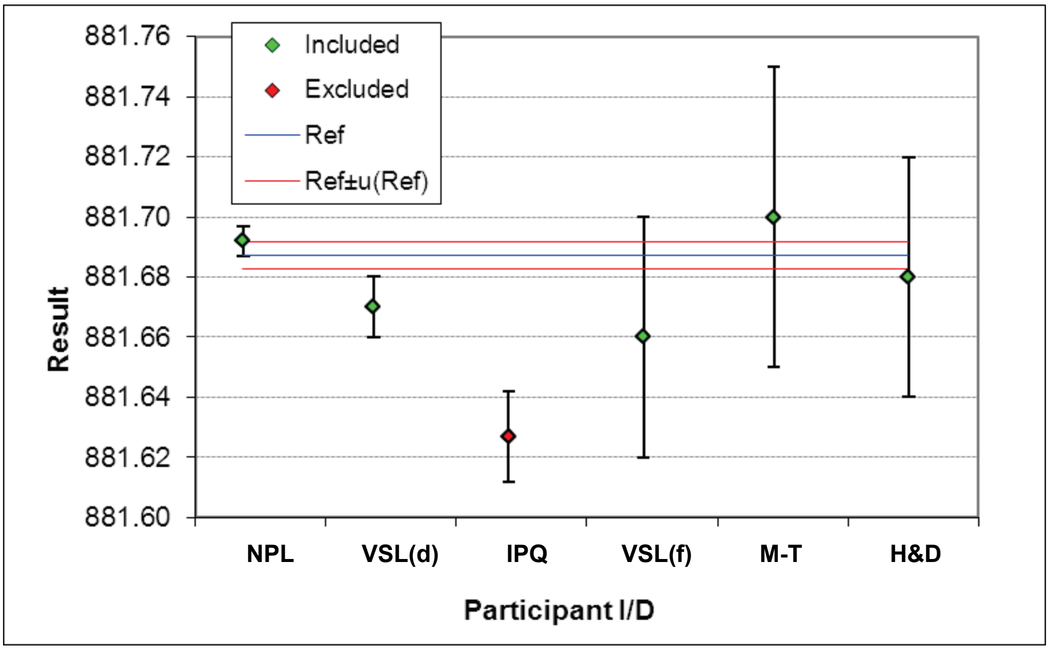

Figure 4b Results of the comparison for the Vitrea 100 oil at 20 °C

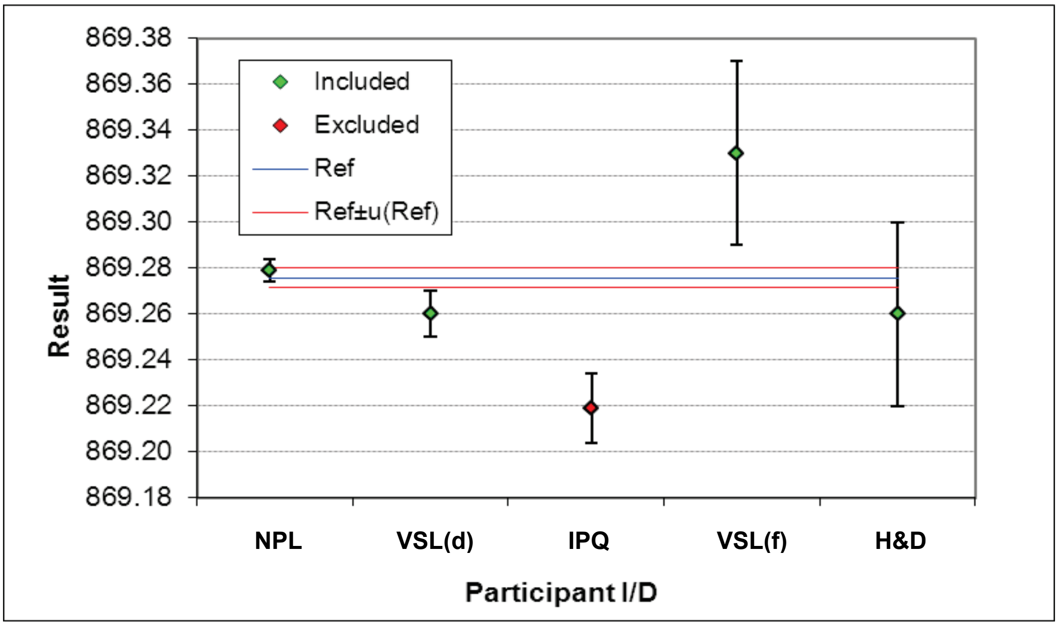

Figure 4c Results of the comparison for the Vitrea 100 oil at 40 °C

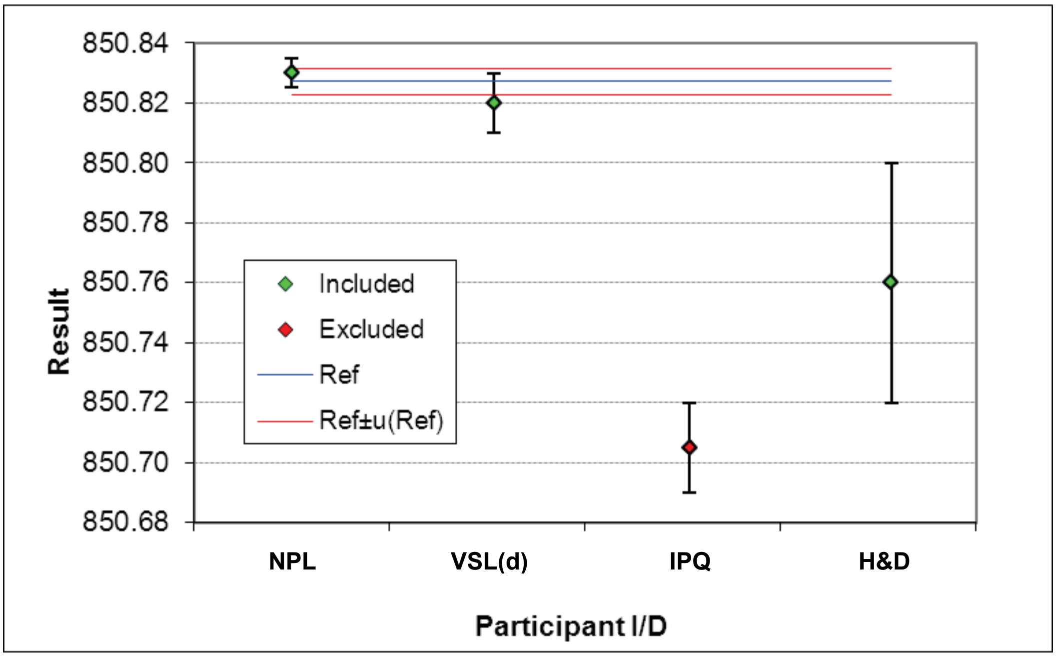

Figure 4d Results of the comparison for the Vitrea 100 oil at 70 °C

6.3 VITREA 220

Table 9 gives the results of the least squares analysis calculation of the reference value for the Vitrea 220 oil at the four measurement temperatures. Where the normalised deviations are reported in red they exceed the limit for consistent values and these results have been excluded from the calculation of the reference value. The results of the Vitrea 220 for the four reference temperatures are shown in figures 5a to 5d. All uncertainties shown are standard uncertainties (*k*=1).

Table 9 Results, reference values and normalised deviations for the Vitrea 220 oil

Temp. °C	Lab ID	Measured value		Reference value		Normalised deviation
		Density kg/m^3	Uncertainty kg/m^3	Density kg/m^3	Uncertainty kg/m^3	*d*
10	NPL	892.890	0.01	892.886 6	0.004 3	1.3
	VSL(d)	892.880	0.02	892.886 6	0.004 3	-0.7
	IPQ	892.871	0.03	892.886 6	0.004 3	-1.1
	VSL(f)	893.20	0.08	892.886 6	0.004 3	7.8
	M-T					
	H&D	893.12	0.08	892.886 6	0.004 3	5.8
20	NPL	886.712	0.01	886.715 6	0.004 2	-1.4
	VSL(d)	886.730	0.02	886.715 6	0.004 2	1.6
	IPQ	886.709	0.03	886.715 6	0.004 2	-0.5
	VSL(f)	886.76	0.08	886.715 6	0.004 2	1.1
	M-T	886.7	0.1	886.715 6	0.004 2	-0.3
	H&D	886.73	0.08	886.715 6	0.004 2	0.4
40	NPL	874.471	0.01	874.465 3	0.004 2	2.1
	VSL(d)	874.460	0.02	874.465 3	0.004 2	-0.6
	IPQ	874.435	0.03	874.465 3	0.004 2	-2.1
	VSL(f)	874.42	0.08	874.465 3	0.004 2	-1.1
	M-T					
	H&D	874.45	0.08	874.465 3	0.004 2	-0.4
70	NPL	856.218	0.01	856.214 6	0.004 3	1.3
	VSL(d)	856.210	0.02	856.214 6	0.004 3	-0.5
	IPQ	856.206	0.03	856.214 6	0.004 3	-0.6
	VSL(f)					
	M-T					
	H&D	856.13	0.08	856.214 6	0.004 3	-2.1

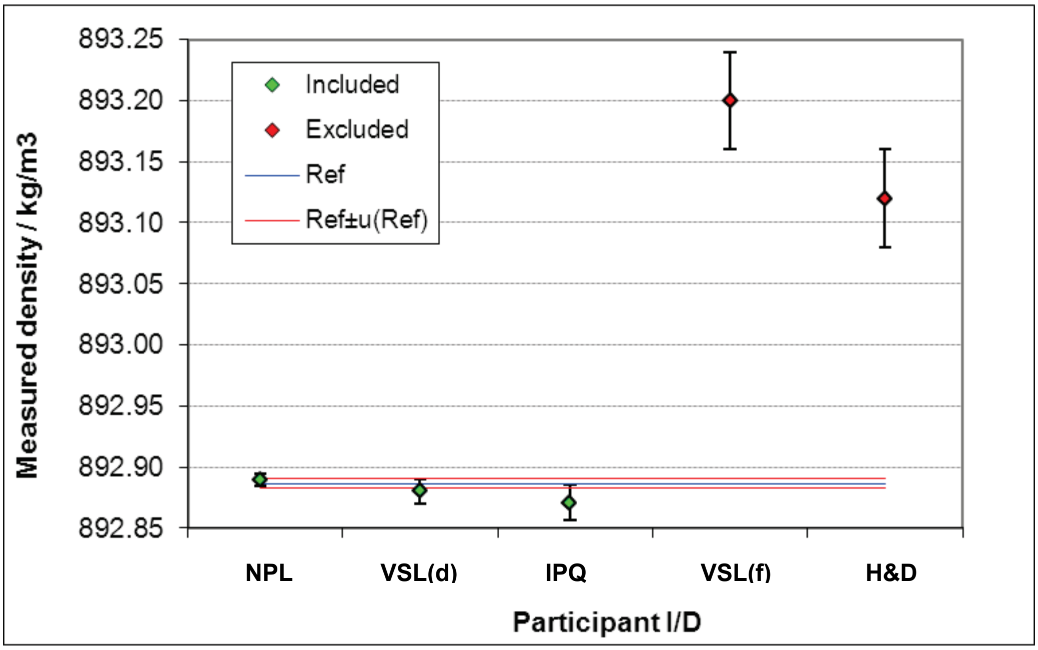

Figure 5a Results of the comparison for the Vitrea 220 oil at 10 °C

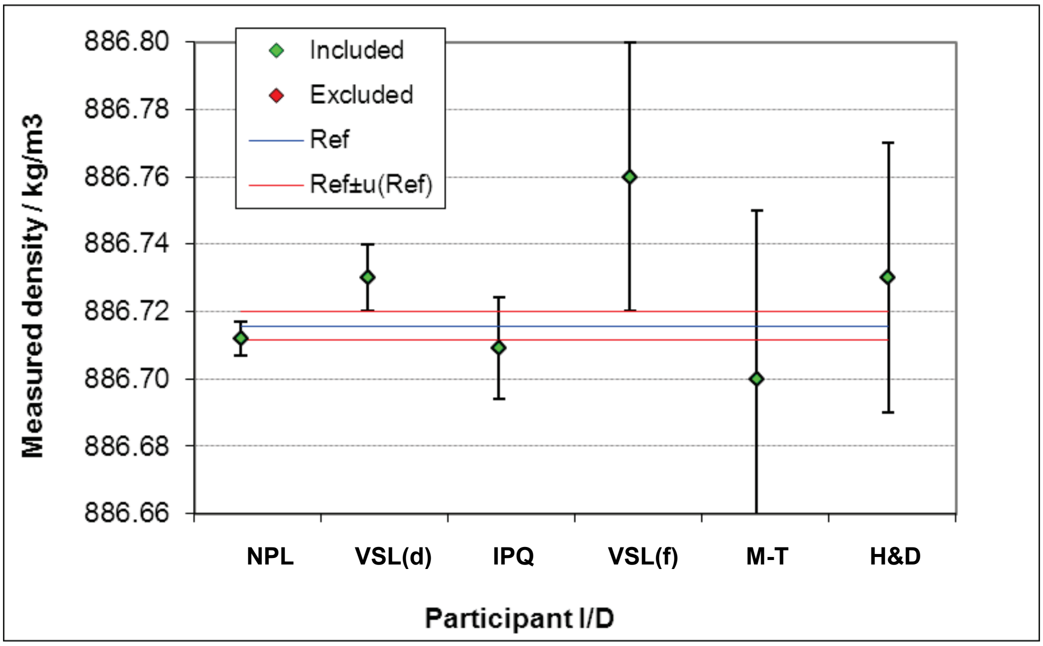

Figure 5b Results of the comparison for the Vitrea 220 oil at 20 °C

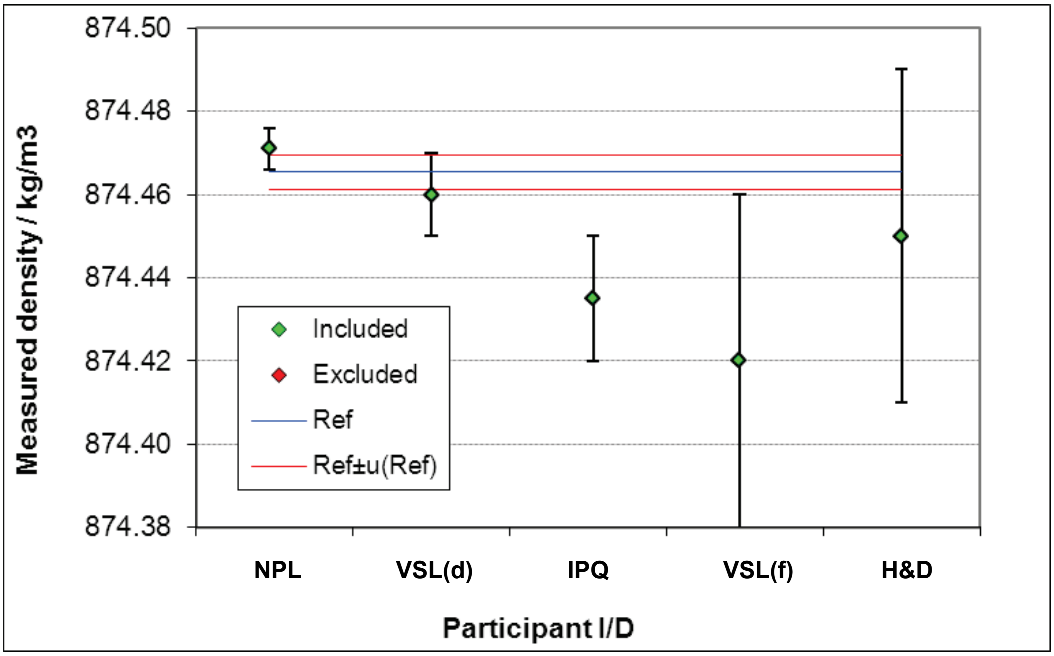

Figure 5c Results of the comparison for the Vitrea 220 oil at 40 °C

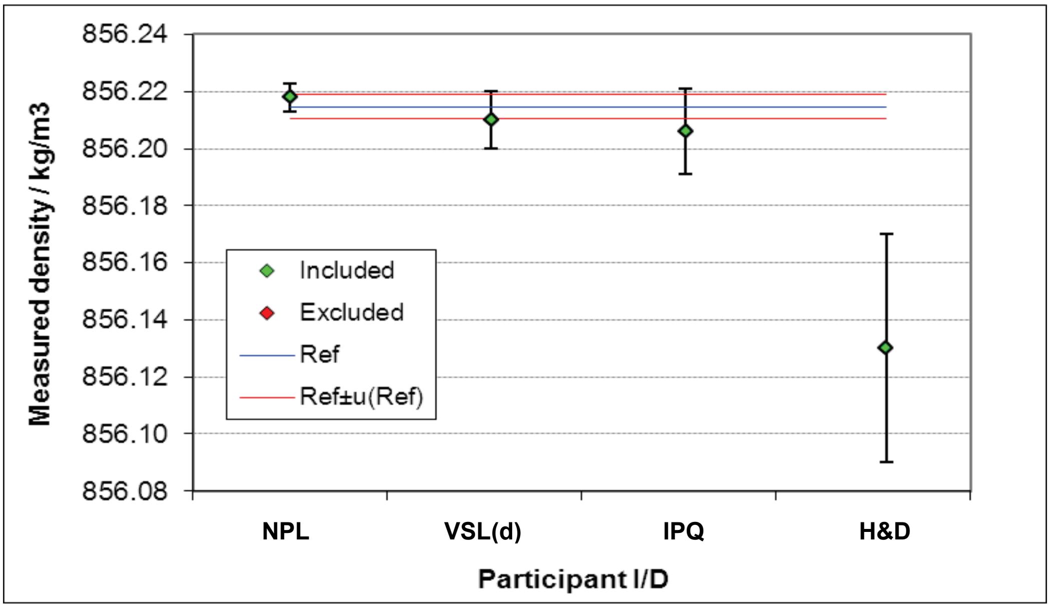

Figure 5d Results of the comparison for the Vitrea 220 oil at 70 °C

6.4 AMENDMENT TO IPQ RESULTS

Following the initial reporting of data, calculation of reference values and circulation of the results a discrepancy in the results of IPQ for the Vitrea 100 oil (when compared with the reference value) was noted. IPQ repeated the calibration of their DMA 5000 meter (using a new sample of the CRM Lube oil 110 oil) and corrected the values obtained in the comparison for the Vitrea 100 oil. Using these corrected values new values for the reference values were calculated by the pilot laboratory. The corrected values of IPQ for Vitrea 100 and the recalculated reference values are given in table 10. The results of the recalculated Vitrea 100 measurements for the four reference temperatures are shown in figures 6a to 6d. All uncertainties shown are standard uncertainties (k=1).

Table 10 Results, recalculated reference values and normalised deviations for the Vitrea 100 oil (based on amended IPQ results)

Temp. °C	Lab ID	Measured value		Reference value		Normalised deviation *d*
		Density kg/m^3	Uncertainty kg/m^3	Density kg/m^3	Uncertainty kg/m^3	
10	NPL	887.907	0.01	887.910 8	0.004 2	-1.4
	VSL(d)	887.920	0.02	887.910 8	0.004 2	1.0
	IPQ	887.925	0.03	887.910 8	0.004 2	1.0
	VSL(f)	887.93	0.08	887.910 9	0.004 2	0.5
	M-T					
	H&D	887.89	0.08	887.910 8	0.004 2	-0.5
20	NPL	881.692	0.01	881.686 9	0.004 2	1.9
	VSL(d)	881.670	0.02	881.686 9	0.004 2	-1.9
	IPQ	881.683	0.03	881.686 9	0.004 2	-0.3
	VSL(f)	881.66	0.08	881.686 9	0.004 2	-0.7
	M-T	881.7	0.1	881.686 9	0.004 2	0.3
	H&D	881.68	0.08	881.686 9	0.004 2	-0.2
40	NPL	869.279	0.01	869.273 6	0.004 2	2.0
	VSL(d)	869.260	0.02	869.273 6	0.004 2	-1.5
	IPQ	869.250	0.03	869.273 6	0.004 2	-1.6
	VSL(f)	869.33	0.08	869.273 6	0.004 2	1.4
	M-T					
	H&D	869.26	0.08	869.273 6	0.004 2	-0.3
70	NPL	850.830	0.01	850.827 2	0.004 4	1.2
	VSL(d)	850.820	0.02	850.827 2	0.004 4	-0.8
	IPQ	850.757	0.03	850.827 2	0.004 4	-4.5
	VSL(f)					
	M-T					
	H&D	850.76	0.08	850.827 2	0.004 4	-1.7

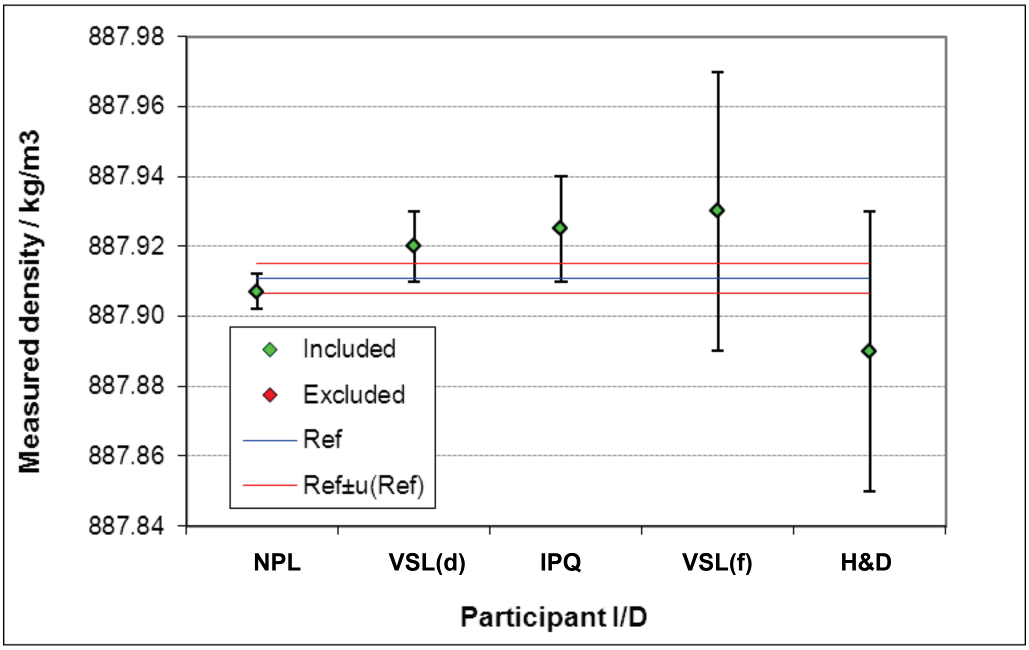

Figure 6a Amended results of the comparison for the Vitrea 100 oil at 10 °C.

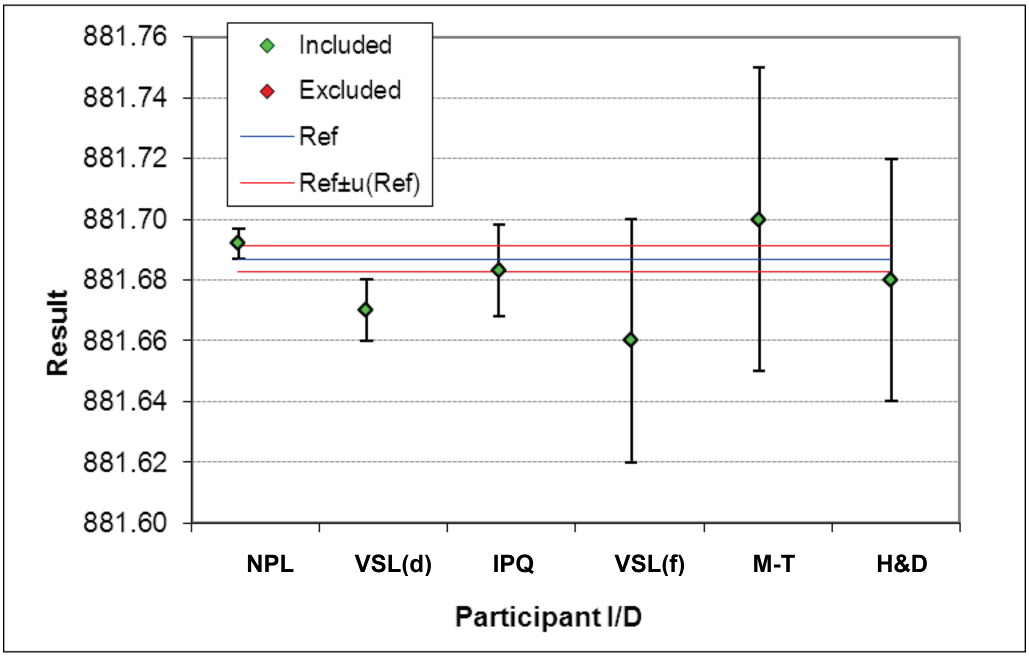

Figure 6b Amended results of the comparison for the Vitrea 100 oil at 20 °C.

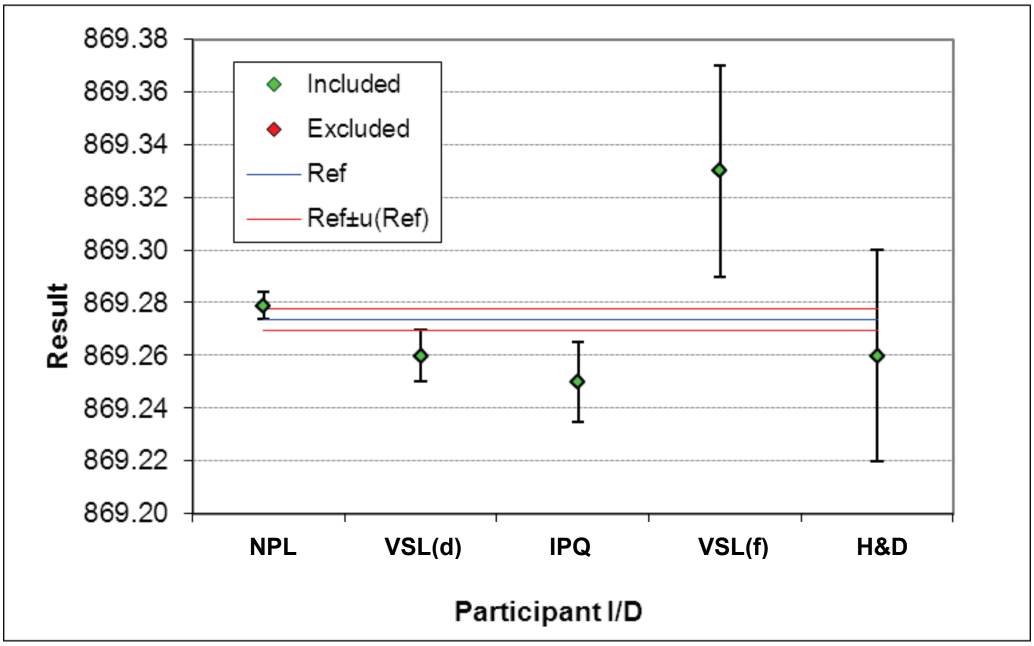

Figure 6c Amended results of the comparison for the Vitrea 100 oil at 40 °C.

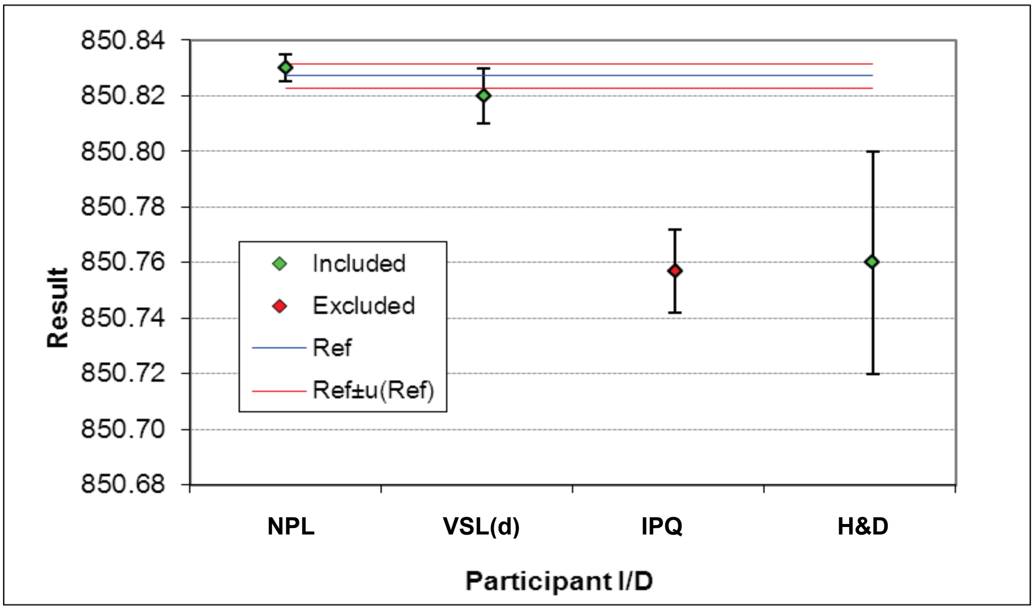

Figure 6d Amended results of the comparison for the Vitrea 100 oil at 70 °C.

7 INTERPRETATION OF THE RESULTS

Taking into account the corrected results for the Vitrea 100 oil, there are seven measurements (out of a total of sixty) that are not in agreement with the calculated reference values. Two of these can be accounted for by the high viscosity of the Vitrea 220 oil at 10 °C (outside the range of CRMs used by most of the participants to characterise their density meters). Other discrepant values show no correlation with the properties of the transfer standard and should be individually checked by the participating laboratories. Note that for the measurements at 70 °C the limited amount of data (4 measurements) mean that identification of the LCS and calculation of the reference value could be open to alternative interpretation (see Cox [3]).

The nominal viscosities of the Vitrea oils are shown in table 11. Not all viscosity values were measured but have been interpolated or extrapolated from manufacturers values and thus are subject to large uncertainties. With the exception of the Vitrea 220 oil at 10 °C all viscosities are in the range over which the density meters had been characterised by those participants who performed such an analysis. Corrections were applied by interpolation (and extrapolation) of the values measured when characterising the density meters with CRMs. Some participants also measured (and corrected for) deviations in the temperatures displayed by their density meters compared with the true temperature of the liquid under test. In all cases the corrections were less than 20 mK.

Figure 7a and 7b shows the correlation between the deviations in the measured densities (from the reference values) for all participants and the viscosity (7a) and measurement temperature (7b) of the transfer standards.

Table 11 Nominal viscosities of Vitrea oils

Oil	Temperature °C	Nominal viscosity mPa.s
Vitrea 10	10	23.8
	20	15.2
	40	7.1
	70	3.2
Vitrea 100	10	672.2
	20	295.7
	40	87.7
	70	23.4
Vitrea 220	10	1057.0
	20	731.0
	40	190.1
	70	46.4

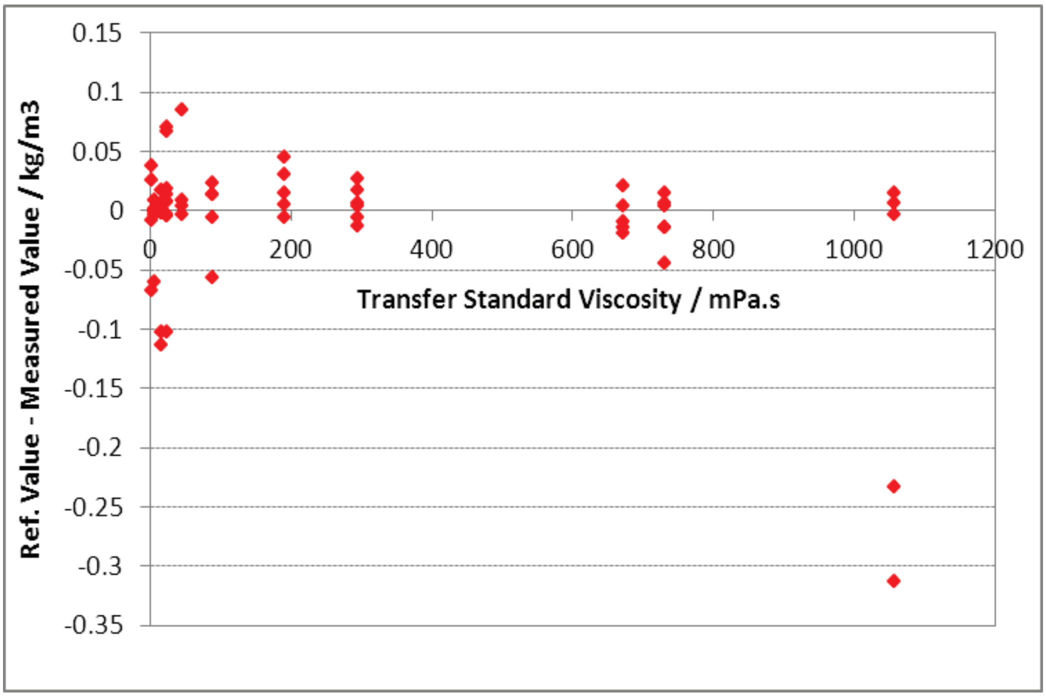

Figure 7a Correlation of deviations from reference values as a function of viscosity.

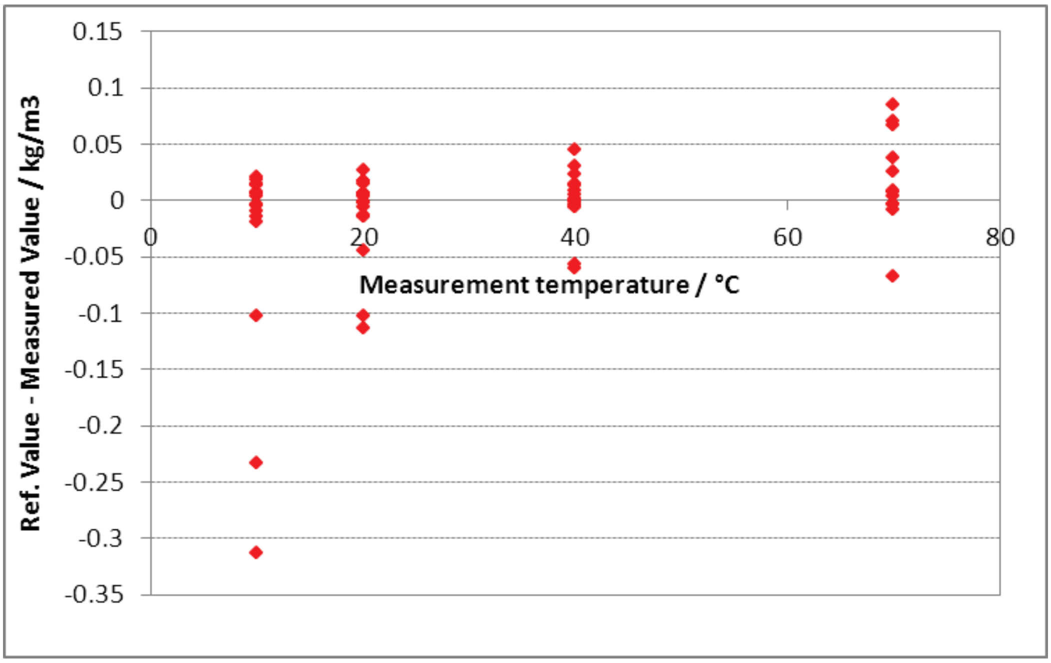

Figure 7b Correlation of deviations from reference values as a function of measurement temperature.

As expected the two major deviations from the reference values occur at the highest viscosity value. Interesting there is also a relatively high spread in the data at low viscosities (<50 mPa.s). With the exception of the two large deviations mentioned there appears to be no correlation between temperature and deviation from the reference value of the results.

The results of the participants have been assumed to have no correlation. This does not take into account the fact that five of the laboratories use the same measurement device and, more significantly, that three laboratories (NPL, VSL(d) and IPQ) use the same approach to the characterisation of the density meter and application of viscosity dependant corrections to the measured density values. The viscosity corrections applied by the participants are shown in figure 8. The corrections applied by NPL, VSL density laboratory and IPQ, based on characterisation of their density meters using CRMs, are very similar. Mettler Toledo applied a correction of -0.6 kg/m^3 to the Vitrea 100 and Vitrea 220 oils (at 20 °C). VSL flow laboratory applied no corrections. H&D Fitzgerald did not supply uncorrected density results and calculated the true density values (corrected for viscosity) calculated from measurements of the period and damping of the DMA 5000 cell and based on an algorithm derived from previous measurements using CRMs. Full details of the participants' density meter characterisation and applied viscosity corrections are given in Appendix A.

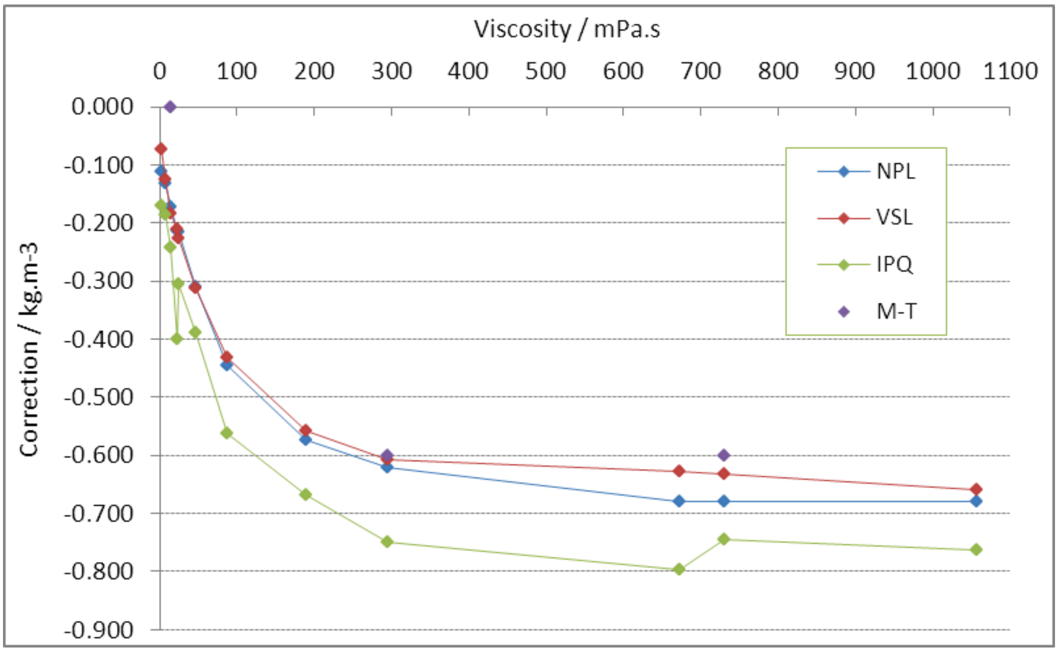

Figure 8 Viscosity corrections applied by participants.

7 CONCLUSIONS

The results of the comparison show a reasonable level of equivalence between the participants and the results will allow the participants to investigate individual discrepancies in the results (as has already been done by IPQ).

The results of the participants have been assumed to be uncorrelated. However, some correlation may be expected because;

- The same model of density meter has been used by five of the six participants
- The same method has been used to characterise the meter and apply viscosity dependant correction by four of the participants.
- There is some common traceability for CRMs between four of the six participants

Of these the similarity in the characterisation methods is likely to be most significant, particularly where limited measurement data is available (e.g. for measurements made at 70 °C) and the possibility of systematic bias in the calculated reference values therefore exists.

8 ISSUES FOR FUTURE COMPARISONS

When planning future comparisons of (vibrating tube) liquid density meters, assignment of the reference values to the transfer standard densities needs to be carefully considered. Ideally the transfer standard liquids should be characterised using a fundamental density determination technique (e.g. hydrostatic weighing) to avoid correlation effects between participants' measurements influencing the calculated reference value.

9 REFERENCES

[1] DMA4500/5000 Density/Specific Gravity/Concentration meter – Instruction Handbook, Anton Paar GmbH, 2000).
[2] Nielsen,, L. Evaluation of measurement intercomparisons by the method of least squares, *DFM-99-R39,* 2000.
[3] Cox, M. G. The evaluation of key comparison data: determining the largest consistent subset, *Metrologia,* **44,** 2007, 187–200.

APPENDIX A: Characterisation and measurement procedures of participants.

Appendix A outlines the procedures which were used by the participants to characterise their density meters and to make the measurements performed as part of this comparison. The procedures are given as reported by the individual participants.

A1. NPL

Characterisation

The Paar DMA 5000 is regularly checked for drift using the densities of air and pure water as references. If the readings depart significantly from those expected (*i.e.* >0.005 kg/m^3) the meter is recalibrated (using air and pure water as recommended by Paar Scientific).

Every 18 months the DMA 5000 is characterised for accuracy, viscosity dependence, repeatability and temperature accuracy and distribution. Temperature is measured inside the cell using an Isotech microK resistance thermometer, checking the accuracy of the displayed temperature and the temperature distribution within the measurement cell.

Accuracy, viscosity dependence and repeatability of the DMA 5000 are checked using water and a range of certified reference density samples (normally supplied by H&D Fitzgerald Ltd.) as well as samples measured at NPL by hydrostatic weighing. At the last characterisation (Nov 2011) the following liquids were used:

- Dodecane
- Tetrachloroethylene
- Lube oil 8
- Base lube oil 30
- Base lube 110
- Lube oil A90

A spline fit (using three second order polynomials) was used to characterise the viscosity dependence up to about 1200 mPa.s.

Measurements

Five separate injections were made into the measurement cell using two samples of the transfer standards. The samples were injected manually using a glass syringe. No preconditioning of the samples was undertaken.

Viscosity corrections were made based on the previous characterisation of the DMA 5000. Uncertainties were calculated based on the repeatability of the measurement, the temperature uncertainty of the cell and the uncertainty in the viscosity correction algorithm.

A2. VSL (density laboratory)

Procedure

A plastic syringe is used to inject the samples and when drift is visible at 20 °C the sample is pre-heated to 50 °C to remove any remaining air bubbles.
Before and after each filling the DMA was checked with air and doubly distilled water.
The not corrected density is the average of 2-3 sample fillings of the DMA.
DMA measured density during a temperature scan (from 10-70 °C, by step 5-10 °C).
Before and after each scan the density at 20 °C was measured as an extra check.
At 20° C both single measurements and the density during temperature scan are used to calculate the average.

Corrections

The deviation in temperature (from -0,015 to 0,002 °C) is determined using the CKT100. The temperature is checked every 1-2 years (depending on previous drift)

The measured (not corrected) density is corrected for the deviation in temperature.
The correction due to viscosity is determined using CRMs supplied by H&D.
Used are :

- Lube oil 8
- Base lube oil 30
- Base lube oil 110
- Lube oil A90

The correction due to dynamic viscosity is modelled as a 1-4 degree polynomial, depending on the dynamic viscosity range.
The dynamic viscosity is taken from the values provided by H&D, checked against values found in literature and a large uncertainty is applied.
The estimated dynamic viscosity presented in the above list, is based on measurements done by VSL and extrapolations based on tables provided by the manufacturer of vitrea.

A3. IPQ

Protocol

Density measurement with oscillation-type density meter Anton Paar DMA 5000 of three samples, vitrea 10, vitrea 100 and vitrea 220, at four different temperatures (10 ºC, 20 ºC, 40 ºC and 70 ºC). Samples were manually injected with a glass syringe with no pre-conditioning.

The measurements of each sample were done through three temperature scans (one upward and two downwards) with 1 ºC steps.

Results

The results presented consist on the uncorrected results (density nc), on the result with the density correction (density) and on final result with the corrections of the DMA calibration with reference certified materials of H&D Fitzgerald, Ltd. The correction due to viscosity was determined using the following CRMs supplied by H&D Fitzgerald Ltd.:

- Lube oil 8
- Base lube oil 30
- Base lube oil 110
- Lube oil A90

The calibration of the internal temperature sensor of DMA 5000 was performed by comparison with the indication of the platinum resistance thermometer Anton Paar CKT 100 calibrated by Laboratory of Temperature of IPQ and with the reference supra-pure water from PTB.

A4. VSL (flow laboratory)

Measurements

All Measurements based on 4 repeats and corrected to 1013 hPa.
The AP has been corrected for temperature and error reading in comparison with double distilled water.
Checks have been made with reference oils and they measured within 0,01 %.
70 °C is not possible at our facility due to all kind of reasons.
No correction for viscosity has been made.

Extra info VSL Liquid Flow & Volume Metrology

Anton Paar CMC for liquid oil density with a viscosity <500 mPa.s = 0,02 %. Calibration range 600-1000 kg/m3. For lower uncertainties we use pycnometers. The basis for our hydrocarbon flow lab. CMC for water density = 0,005 %. The basis for our water flow lab and Volume lab. Our work range during normal operation is between 15 - 25 °C (for flow calibration loops)

A5. Mettler-Toledo

Viscosity correction

Density measurements of viscous samples without viscosity correction result in slightly higher results on the DE density meter. The reason for this is that the oscillation of the U-shaped tube is attenuated by shear forces which appear in viscous samples. The measured oscillation frequency is too low for such samples, and the displayed density, therefore, is too high. Example: for pure glycerine (viscosity 1490 mPa.s at 20 °C), the DE density meter would display a density that was at least 0.0007 g/cm3 too high without viscosity correction.

To avoid false measurements, density measurements of samples with a viscosity > 7 mPa.s have to be performed with activated viscosity correction. Measurements with viscosity correction take longer. The instrument performs three measurements under different conditions, analyses the occurring harmonic oscillations and, from that, determines the attenuation constant dependent on the sample's viscosity. Using the attenuation constant, the instrument then calculates the viscosity of the sample ascertains the measuring error due to viscosity and directly displays the corrected value for density.

The viscosity correction is automatic for samples with a viscosity < 2 000 to 5 000 mPa.s, *i.e.*, the measuring error caused by the samples viscosity is properly corrected by the DE density meter without the user having to enter the viscosity of the sample.

For samples with a very high viscosity > 5'000 mPa.s (in general even honey has a viscosity <5 000 mPa.s), the setting > 2 000 mPa.s must be selected for the viscosity correction in order to get correct results.

If you are not sure whether a correction for viscosity is necessary for your samples, you should perform a measurement with activated correction for viscosity, and d and dRaw as results. The printout will then contain both values calculated with and without correction for viscosity. Comparison of the two results will help you in assessing the significance of the measuring error that was caused by the viscosity of the sample.

How to make the right selection for the viscosity correction in the measuring or test method, i.e.
< 2000 mPa.s or > 2000 mPa.s?

- Set the viscosity correction to < 2000 mPa.s, and measure the sample. This setting will give the correct viscosity corrected density for most of your samples.
- Only if you see that your sample is very viscous (like liquid honey or more), and the measurement above yields a viscosity correction of Zero, *i.e.* d is the same value as dRaw, then the sample has to be measured with the setting > 2000 mPa.s.
- Please note that the setting > 2000 mPa.s will always apply a maximum viscosity correction, regardless of the sample viscosity! So a maximum correction will be applied even if the sample is water with this setting!

To perform measurements with viscosity correction, the density meter must have been adjusted with activated viscosity correction. If you attempt to perform a measurement with viscosity correction without having adjusted the instrument with activated viscosity correction, this will trigger an error message at the beginning of a measurement, and no measurement will be made!

Viscosity correction in an adjustment

A viscosity corrected adjustment is only possible for the standard adjustment set Air & Water, because the viscosity properties of these standards are perfectly known and stored in the instrument. Therefore the appropriate setting < 2000 mPa.s is shown for information only in the parameters of the adjustment method, it cannot be selected.

In the adjustment the instrument will determine the cell-specific viscosity properties of the measuring cell for these known standards air and water, and store them together with the adjustment data. These data will be used later-on for performing the viscosity correction in the measurements.

Measurements

Samples were injected in the measuring cell by means of a syringe.
For each sample a new syringe was used.
Between the samples the measuring cell was thoroughly rinsed with iso-propanol, dry-purged, and the dry-cell (air) value was checked.

A6. H&D Fitzgerald

Measurements (and characterisation)

All data was gathered over a four day period on a Paar 5000 which was not adjusted prior to use. All injections were made with a glass syringe, and there were normally two injections of each liquid.

Water and 2,2,4 trimethylpentane (iso-octane) were injected at room temperature; all other CRMs and samples were transferred to sealed glass syringes, stood vertically in an oven at about 60°C for an hour to encourage micro-bubbles to the surface; allowed to cool until handleable – 45 °C? – and injected.

At 20°C, six CRMs were used, and a linear regression of certified density against Q^2, Q^4 [$(Q^2)^2$] and damping used to derive the relationship of density to these terms. The standard error of estimate was 0.0070 kg/m^3.

Previous experience had shown that the Paar 5000 cells do vary slightly in linearity with density, and that this is a meter which warrants having a $(Q^2)^2$ term.

At 40°C, the lube 30 CRM was omitted from the regression, since it showed an unusually large residual of about 50 ppm, compared with the others of typically 1 ppm to 10 ppm. The standard error of estimate was 0.0073 kg/m^3.

Our hydrostatic weighing facility has a temperature limit of 55 °C, and we have no CRMs available above 50 °C. At 70 °C, we used the same method as before, but the iso-octane was omitted due to its vapour pressure at this temperature. The densities used were extrapolated from the hydrostatic weighing data, and are therefore not certificate densities.

Again, for consistency, the predicted density was regressed against Q^2, (Q^4) and damping; though, not surprisingly, in view of the standard error of 0.06 kg/m^3, the Q^4 term is not significant.

At 10 °C, the water and iso-octane CRM densities had to be extrapolated, since neither of these are routinely hydrostatic weighed at 10°C. It is known from previous experience that the integral damping function does not work correctly for a damping value exceeding 10. The lube A90 CRM was therefore not included in the regression. The standard error of estimate was 0.0088 kg/m^3.

Luckily, the most viscous oil (Vitrea 220) exhibited Q and damping values very similar to the lube A90 CRM; and since the A90 displayed a corrected density 150ppm below its certified value, the density as reported for Vitrea 220 was the displayed corrected density increased by 0.15 kg/m^3.