**Density determination of 300cSt fuel oil**

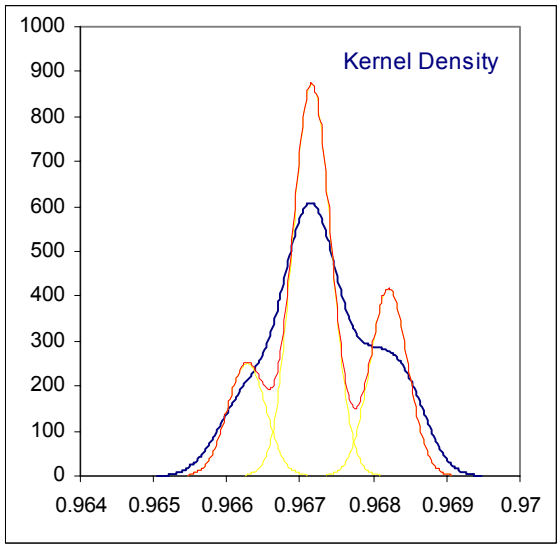
The determination of density in high viscosity fuel oil has been problematic during the iis round robins of November 2006 and February 2007, see the reports iis06F02 and iis07F01.
The reproducibity requirement of the hydrometer method ASTM D1298, being 0.0015 kg/L, was not met in these last round robins and very large spreads were observed (see below table).

| | R (all=n results) | R (x hydrometer results) | R (y U-tube results) | Kin. Viscosity @50°C in cSt |
|---|---|---|---|---|
| Feb. 2007 | 0.00188 (119) | 0.00177 (67) | 0.00195 (49) | 232 |
| Nov. 2006 | 0.00252 (26) | 0.00214 (10) | 0.00268 (14) | n/a |
| Feb. 2006 | 0.00155 (108) | 0.00166 (53) | 0.00107 (49) | 357 |
| Feb. 2005 | 0.00144 (102) | 0.00160 (54) | 0.00117 (45) | 333 |
| Feb. 2004 | 0.00158 (89) | 0.00173 (45) | 0.00134 (39) | 316 |
| Feb. 2003 | 0.0022 (83) | 0.0025 (35) | 0.0016 (44) | 345 |
| Feb. 2002 | 0.0019 (79) | 0.0028 (28) | 0.0012 (34) | 291 |
| Oct. 2000 | 0.0023 (71) | 0.0024 (35) | 0.0020 (22) | 341 |
| Jan. 2000 | 0.0023 (72) | 0.0026 (36) | 0.0011 (23) | 340 |
| Jan. 1999 | 0.0024 (67) | 0.0025 (31) | 0.0014 (23) | 369 |
| Feb. 1998 | 0.0034 (67) | 0.0036 (20) | 0.0014 (25) | 55.7 |
| Feb. 1997 | 0.0021 (58) | 0.0031 (19) | 0.0016 (26) | 378 |
| Apr. 1996 | 0.0020 (46) | 0.0021 (26) | 0.0014 (17) | 351 |

table: Evolution of reproducibilities (Density @15°C) of round robin samples

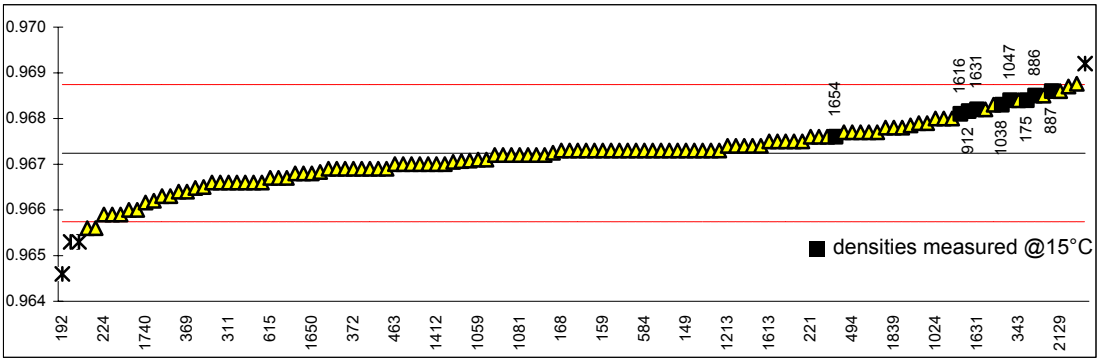
From the above summary of observed reproducibilities several things are striking. The observed reproducibility of the D1298 results is decreasing during the years and consequently the performance of these laboratories is increasing. However, during the same period, the performance of the laboratories using the oscillating U-tube methods ASTM D4052 and ISO12185 is decreasing, sometimes leading to very high reproducibilities. In the last two rounds, the spread of the oscillating U-tube results was even larger than the spread of hydrometer results!

In April 2007, the results of the oscillating U-tube methods ASTM D4052, ISO12185 and IP365 showed a trimodal distribution (see figure 1) with maxima at 0.9663, 0.9672 and 0.9682 kg/L.
This phenomenae may explain for the extremely large reproducibility found in this round robin. The average of the majority of the oscillating U-tube results (57%) was 0.9672, which is in good agreement with the average of the hydrometer results (0.9672).




Therefore an investigation was started to find the cause of the deviating oscillating U-tube measurements. An inquiry was sent to a number of participants.
The items asked were:
1 - What was the original density measured?
2 - At which temperature was the original density measured?
3 - How was the original density converted to the density @15°C
4 - Was the glass expansion factor (HYC) factor used in this conversion? If yes, how was it used?
5 - Was a correction for viscosity used in this conversion? If yes, please explain how it was used.
From the laboratory responses it became clear that several laboratories did measure the sample at 15°C. And these results appeared all to be extremely high, ranging from 0.9676 to 0.9686! There may be two reasons for this deviation. First it is not clear whether this 230cSt (at 50 °C) Fuel Oil will be a true liquid at 15°C. In the case some solid is present during the measurement an aberrant density may be observed.

Secondly, many laboratories erratically were of the opinion that no corrections should be applied on the density as measured at 15°C. However, in reality the viscosity correction should be applied in this case, resulting in much lower densities than the uncorrected ones. In below graph (figure 2) the nine densities measured at 15°C are marked as black boxes:




When the nine densities measured at 15°C are rejected, the reproducibility of the 40 remaining results of the oscillating U-tube methods is decreased from 0.00195 to 0.00159 kg/L.

Another observation that was made from the laboratory responses was that several laboratories could not tell whether the viscosity correction was applied or not. Obviously the apparatus manuals and the newer types of apparatus often are hard to understand.
When the measured densities were converted and corrected manually to densities at 15°C, the group of highest densities results (see figure 1) is reduced to only one result and the reproducibility of the oscillating U-tube methods of these 40 results decreases further to 0.00131 kg/L, which is in good agreement with the reproducibility requireement of ISO12185 (IP365) of 0.0015 kg/L.

Conclusion: With a correct use of the oscillating U-tube methods, the results are well in line with the respective Standard Methods and also with the results found using the hydrometer methods.

Lessons to learn: When reading the various apparatus manuals of the various types of instruments and the Standard Methods, it is very well understandable that laboratories may have problems understanding the necessary corrections.
In ASTM D4052-96 no correction for viscosity is mentioned but the scope of this method is "petroleum distillates and viscous oils that can be handled in a normal fashion as liquids at test temperatures between 15 and 35°C". Also the following restriction is mentioned in D4052: "This test method should not be applied to samples so dark in color that the absence of air bubbles in the sample cell cannot be established with certainty".
In ISO12185:96 (identical to IP365-97) more explicite guidelines are given in paragraph 5.1: "Research has shown that the density meter may show a bias up to 1 kg/m3 due to viscosity effects. Users should ascertain whether a viscosity correction is required….". Especially with high viscosity Fuel Oils (180 cSt and higher at 50 °C, which is 700 cSt and higher at 15 °C) the viscosity correction has a substantial effect on the observed density.

In practice the various generations of density meters are also very different. To give some examples on some commonly used density meters:
On a DMA 48 all corrections have to be applied manually, which makes it quite easy to be aware of the actual settings. The built-in table 53B is not corrected for the HYC factor.
This is much harder on the next generation of density meters, e.g. the DMA 58. Corrections like the viscosity correction may be set on or off, but the actual setting is hard to find and definitely not seen in one glance.
The newest generation of density meters, e.g. D4500, is programmed to perform all necessary corrections as default settings. Most important settings are visible on the display. But as most settings may be changed, also the display settings may be changed and the easy visibility of the actual settings may be changed negatively.
The user of the equipment must ensure himself of the proper settings and get in touch with their service supplier in case of any doubt or unclarity.