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# OSCILLATION-TYPE DENSITY METER CALIBRATION IN VISCOSITY BY ICUMSA SUCROSE SOLUTIONS

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***Abstract*** – This communication evidences the applicability of the use of sucrose solutions, of whom density and viscosity were obtained via ICUMSA tables by means of refractive index measurements, to deduce calibrations curves for viscosity damping of a density meter in viscosity range from 20 mPa·s to 55 mPa·s, at 20 ºC, with an expanded uncertainty of 0,030 kg·m$^{-3}$. An interesting relationship between the difference of density indication without viscosity correction and density indication with viscosity correction was observed for DMA 5 000 density meter, allowing, without knowing the viscosity of the sample, to predict the correction to apply. The maximum deviations obtained in this work are much larger than the one earlier described.

***Keywords***: oscillation-type densimetry; viscosity; refractometry; metrological compatibility; ICUMSA tables.

## 1. INTRODUCTION

Density, $\rho$, is defined as the mass per unit volume of a fluid or a solid [1] and, in general, it depends on both temperature and pressure. It is a property of extreme importance, as it is routinely applied in the control of industrial processes, but it is also used in fields such as biomedical diagnostics, fiscal control and basic research. The uncertainty requirement in a density measurement depends on its specific application and it can vary from better than 0,1 % to 1 % [2].

The density of a fluid can be determined using several measuring instruments. Recently the oscillation-type density meters have shown great versatility and they are being used in various branches of industry. The advantages of using these measuring instruments are their response time, their use simplicity and the small volume of the needed sample [3].

The working principle of an oscillation-type density meter is based on the law of harmonic oscillation, in which a U-shaped tube, i.e. the measuring cell, is completely filled with the sample to be analysed and is subjected to an electromagnetic force. The measurement of the frequency and duration of vibration of the tube filled with the sample allows the determination of the density value of the sample. This measuring principle is based on the Mass-Spring Model [4].

During the oscillation of the U tube, the sample shows the effect of damping of the oscillation. This damping is a function of the viscosity sample. The sample viscosity will have also the effect of apparently slightly move the oscillation nodes, thus increasing the apparent volume of the cell. The measurement cell oscillates at several frequencies in two modes. This allows the damping in the sample to be measured and properly corrected. When the standard is calibrated, the density is a function of the oscillation period, $\tau$ , and of the damping.

The internal software of the measuring instrument establish an algorithm with coefficients that are determined during the measuring instrument adjustment, using two substances of known densities, typically air and water.

In earlier studies [5] made in several instruments of the same type, using a wide range of Certified Reference Materials (CRM) and water, suggested that the equation proposed by the manufacturer, with the interaction between the period and damping, was unnecessarily complex [1]. The author [5] describes that once correctly calibrated, the DMA 5 000 density meter from Anton Paar, is capable of measuring the density of almost any liquid between 650 to 1 650 kg·m$^{-3}$, 0 to 600 mPa·s with a maximum error of ± 0,030 kg·m$^{-3}$, and over a narrower viscosity range, $< 30$ mPa·s, being the maximum error the order of ± 0,015 kg·m$^{-3}$.

Like all measuring instruments, the measurement results obtained by an oscillation-type density meter may vary with time. Measurement errors may be caused by: instrumental changes due to physical changes in the U-tube (mass, volume or elasticity coefficient); changes in the electronic operation of the measuring instrument; damage due to mishandling; instrument movement during measurement, especially if at a different angle to the horizontal; effects of liquid on the surface of the tube, such as deposition of material or erosion by the sample or by the cleaning method. Therefore the calibration is an essential key to understand and take into account the measuring behaviour of the measuring instruments [6].

The refractive index, $n$, of a medium is defined by the ratio of the velocity of an electromagnetic radiation at a given frequency in vacuum to the phase velocity of the radiation in the considered medium [7]. Thanks to the miniaturizing of electronic devices, high quality refractometers are nowadays available to measure refractive index of solutions with good performance, for instance with $2\cdot10^{-5}$ expanded uncertainty within a [1,33299; 1,52000] interval. Comparatively to densimetry and viscosimetry, refractometry is far easier to use.

At the National Metrology Institute (NMI) of Portuguese Institute for Quality (IPQ), , the mass fraction ($X_m$) of sugar aqueous solutions can be determined by the Laboratory of Refractometry (LFR) and by the Laboratory of Properties of Liquids (LPL), from refractive index and density or dynamic viscosity measurements, respectively. More specifically, the LPL performs density measurements of liquid samples with an oscillation-type density meter. In its turn, the LFR performs refractive index measurements of liquids not only with an Abbe refractometer but also and mainly with a digital refractometer with an expanded uncertainty of 0,02 cg/g up to 70 cg/g, for aqueous sugar solutions.

Like for density measurements, the refractive index measurements allows to deduce the mass fraction values from the correspondence tables between the measured quantity and the measurand, published by the ICUMSA (International Commission for Uniform Methods of Sugar Analysis) [8, 9].

In a previous communication [10] it was displayed that the linear interpolation in the interval of two successive referenced data was equivalent albeit with lower uncertainty value than the linear least square regression upon considering at least 30 values. Therefore, the linear interpolation strategy in the two successive points interval is followed in the present work for mass fraction measurement from density and refractive index measurements.

Metrological compatibility of mass fraction measurement results [12], by densimetry and refractometry, of glucose solutions, within the interval of 3 to 40 cg/g, was already demonstrated in previous work [13]. There is some interest of studying aqueous solutions of sugars, as glucose and sucrose as they are used as reference materials for calibration and for metrological control of refractometers. Indeed, the refractive index values with respect to the sugar concentrations of these solutions are well documented [14, 15].

Some test and industrial laboratory, which perform density measurements with oscillation-type density meters, works with very viscous samples, and therefore their density meter, must be calibrated with viscous reference liquid as well. Sometimes, there are no CRMs available for the range of interest, or even for the similar matrix that the one of the liquids measured. The costs of such CRMs can be also an additional difficulty that may lead to obtaining an inadequate or insufficient calibration.

In this work, the suitability of the use of sucrose solutions, which density and viscosity was determinate via ICUMSA tables by means of refractive index measurements, to obtain calibrations curves for viscosity damping of a density meter in viscosity range from 20 to 55 mPa·s, at 20 ºC, it will be evaluated.

## 2. EXPERIMENTAL PROCEDURE

### *2.1. Density meter calibration for viscosity damping*

An oscillation-type density meter DMA 5 000 (Anton Paar), with a $10^{-3}$ kg·m$^{-3}$ density resolution and a temperature resolution of 0,001 ºC, was calibrated, at 20 ºC, with 8 reference liquids with viscosity from 1 mPa·s to 583 mPa·s: three liquids from EURAMET Comparison Project 1240 “Comparison of density determinations of liquid samples by density meters” (deutered water, pentadecane and viscosity oil) and four Certified Reference Liquids (CRMs) from H&D Fitzgerald (lube oil largo 3 and 32, lube oil 110 and A90 and dimethyl phthalate). The density reference values of these liquids were measured by hydrostatic weighing. The deviation from density reference value of measuring results were analysed for both DMA 5 000 indication of density with internal algorithm of correction of viscosity damping, $\delta\rho$, and for indication without internal corrections algorithm of correction, $\delta\rho_{\mathrm{nc}}$. The difference between these two indications was also analyzed, $\rho_{\mathrm{nc}}-\rho$.

The temperature measurements are traceable to the IPQ primary Laboratory of Temperature.

The uncertainty budget was performed according to GUM methodology [11] and as previously established [3].

### *2.2. Determination of refractive index and density of sucrose solutions*

Five D(+)-sucrose (extra pure, Scharlau) aqueous solutions, with mass fractions from 20 cg/g to 55 cg/g, were prepared gravimetrically with ultra-pure water (grade I) [16], produced by a MilliQ Advantage (Millipore), followed with a 2 hours stirring at room temperature.

The sucrose solutions refractive index, at 20 ºC, was measured with a digital refractometer RE 50 from Mettler Toledo, with a $10^{-5}$ resolution and a 0,01 ºC resolution thermostat. These measurements are traceable to SI through the use of CRMs from the NMI of the USA, the NIST and from the NMI of Poland, the GUM.

The density of sucrose solutions was measured with the same DMA 5 000 from Anton Paar.

The values of refractive index and density of different sucrose solutions were measured five times, from five different aliquots of the same sample, at 20 ºC, using internal procedures based on the OIML R 124 [15] and according to ISO 15 212 [17], respectively.

### *2.3. Determination of the density of sucrose solutions through ICUMSA tables*

The mass fraction and the viscosity of each sucrose solution, through the refractive index mean values, were determinate by use of ICUMSA SPS-3 and SPS-5 [9, 18], respectively. The mass fraction obtained was then converted in density by mean of ICUMSA SPS-4 [8]. These density values were considered as reference values for the comparison with the density values obtained with the density meter.

## 3. RESULTS

### 3.1. Density meter calibration for viscosity damping

The DMA 5 000 calibration results for viscosity damping are presented in Table 1.

Table 1. Calibration results of DMA 5000 calibration for viscosity.

| Reference liquid | $\eta$ | $\rho_{\text{ref.}}$ | $\delta\rho$ | $\delta\rho_{\text{nc}}$ | $\rho_{\text{nc}}$-$\rho$ |
|---|---|---|---|---|---|
| | (mPa·s) | (kg m$^{-3}$) | | | |
| Deuterated water[1] | 1,00 | 998,471 | 0,015 | 0,015 | 0,000 |
| Pentadecane[1] | 2,85 | 768,810 | 0,015 | 0,030 | 0,015 |
| Lube oil Largo 8[2] | 16,60 | 823,934 | 0,058 | 0,118 | 0,060 |
| Dimethyl phthalate[2] | 24,16 | 1191,261 | 0,059 | 0,171 | 0,112 |
| Lube oil Largo 32[2] | 76,27 | 866,689 | 0,071 | 0,365 | 0,294 |
| Viscosity oil[1] | 144,24 | 831,943 | 0,027 | 0,492 | 0,465 |
| Lube oil 110[2] | 317,0 | 881,783 | 0,025 | 0,643 | 0,618 |
| Lube oil A90[2] | 583,00 | 886,653 | 0,058 | 0,679 | 0,621 |

Legend: 1 - Liquids from EURAMET Comparison Project 1240 “Comparison of density determinations of liquid samples by density meters”; 2 – certified reference oils from H&D Fitzgerald; $\rho_{\text{ref.}}$ - the density reference values were determinate by hydrostatic weighing; $\delta\rho$, $\delta\rho_{\text{nc}}$ - deviation from density reference value of DMA 5 000 indication of density with correction of viscosity, and the indication without corrections; The expanded measurement uncertainty for the density values presented, *U,* for a coverage factor, *k, of* 2,00, at a 95 % level of confidence, is 0,030 kg·m$^{-3}$.

The obtained results display that DMA 5 000 density indication with viscosity correction, $\rho$, evidences a maximum deviation from the reference density value of 0,071 kg·m$^{-3}$ and no dependence was observed with viscosity. On other hand, DMA 5 000 density indication without viscosity correction, $\rho_{\text{nc}}$, increases with viscosity and evidences a similar behaviour to $\rho_{\text{nc}}$-$\rho$ , as can be seen on Fig. 1.

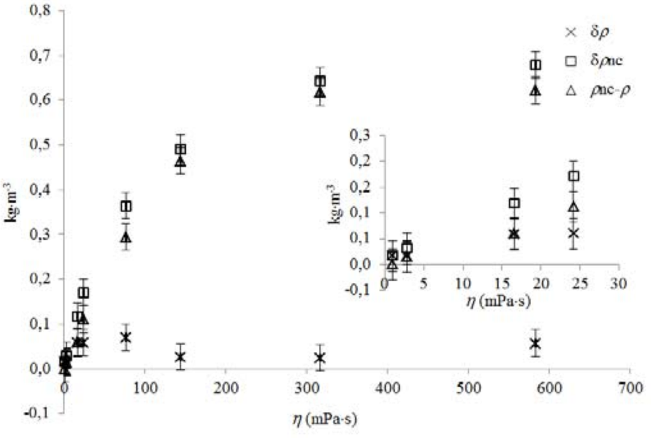

Fig. 1. Density deviation, $\delta\rho$, $\delta\rho_{\text{nc}}$, and difference between DMA 5 000 density indication without viscosity correction and with viscosity correction, $\rho_{\text{nc}}$-$\rho$, as a function of viscosity, at 20 ºC.

A linear relation can be observed between the density deviation of DMA 5 000 density indication without viscosity correction, $\delta\rho_{\text{nc}}$, and the difference between the indication without and with viscosity correction, $\rho_{\text{nc}}$-$\rho$ (Fig. 2). The maximum deviation of the linear curve presented in Fig.2 is within the order of magnitude of the expanded uncertainty of the density measurements, i.e. 0,030 kg·m$^{-3}$.

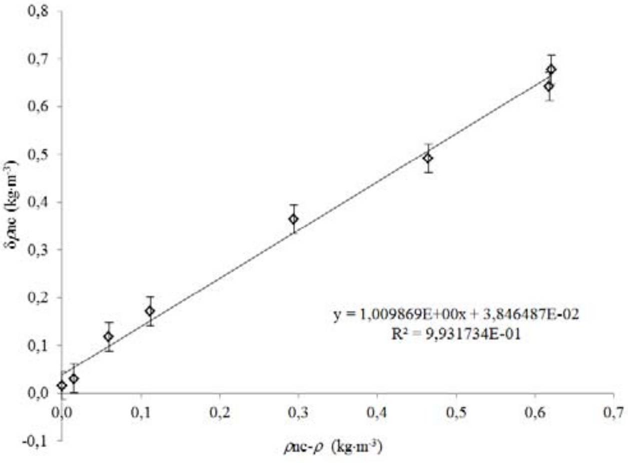

Fig. 2. Relation between the deviation of DMA 5 000 density indication without viscosity correction, $\delta\rho_{\text{nc}}$, and the difference between the indication without and with viscosity correction, $\rho_{\text{nc}}$-$\rho$, at 20 ºC

### 3.2. Validation of damping curve with sucrose solutions

Through the ICUMSA tables [5] and from a refractive index with an expanded uncertainty of $2\cdot10^{-5}$, it was possible to deduce the density of the sucrose solutions with a maximum expanded uncertainty of 0,030 kg·m$^{-3}$.

The results presented in Table 2 show that the difference between the experimental values, $\delta\rho_{\text{nc}}$, and the values obtained by the curve of $\delta\rho_{\text{nc}}$ *vs* $\rho_{\text{nc}}$-$\rho$ displayed in Fig. 2, $\delta\rho_{\text{nc'}}$, for the deviation of DMA 5 000 density indication without viscosity correction is smaller than the expanded uncertainty of the density measurements, i.e. < 0,030 kg·m$^{-3}$.

Table 2. Validation of damping curve with sucrose solutions

| Sucrose $X_m$ | $\eta$ | $\rho_{\text{ref.}}$ | $\delta\rho_{\text{nc}}$ | $\rho_{\text{nc}}$-$\rho$ | $\delta\rho_{\text{nc'}}$ | $\delta\rho_{\text{nc}}$ – $\delta\rho_{\text{nc'}}$ |
|---|---|---|---|---|---|---|
| (cg·g$^{-1}$) | (mPa·s) | (kg.m$^{-3}$) | | | | |
| 20,014 | 1,95 | 1081,038 | 0,040 | 0,005 | 0,044 | 0,003 |
| 30,007 | 3,19 | 1127,064 | 0,037 | 0,014 | 0,052 | 0,015 |
| 39,982 | 6,60 | 1176,426 | 0,107 | 0,046 | 0,085 | -0,023 |
| 49,991 | 15,42 | 1229,607 | 0,134 | 0,100 | 0,139 | 0,005 |
| 54,994 | 28,05 | 1257,615 | 0,242 | 0,179 | 0,220 | -0,022 |

Legend: $\delta\rho_{\text{nc'}}$- deviation from density reference value of DMA 5 000 indication without internal corrections for viscosity obtained by the curve of $\delta\rho_{\text{nc}}$ *vs* $\rho_{\text{nc}}$-$\rho$ obtained in Fig. 2.

## 4. CONCLUSIONS

An interesting relation between the difference of density indication without viscosity correction and density indication with viscosity correction was observed considering DMA 5 000, allowing to predict the correction to apply without knowing the viscosity of the sample.

The maximum deviations obtained in this work are much larger than the one described by [5]. For samples with viscosity < 30 mPa·s the maximum measurement error was 0,059 kg·m$^{-3}$ for $\rho$ and 0,171 kg·m$^{-3}$ for $\rho$nc. For viscosity within the ]30; 600] mPa·s interval, the maximum measurement error was 0,071 kg·m$^{-3}$ for $\rho$ and 0,679 kg·m$^{-3}$ for $\rho$nc.

With the use of sucrose solutions, the density values of whom were achieved by ICUMSA conversion tables [5] through refractive index measurements, allowed to validate the use of the linear relation between the deviation of DMA 5 000 density indication without viscosity correction, $\delta\rho_{\mathrm{nc}}$, and the difference between the indication without and with viscosity correction, $\rho_{\mathrm{nc}}$-$\rho$, in the viscosity values range from 20 mPa·s to 55 mPa·s, at 20 ºC, with an expanded uncertainty of 0,030 kg·m$^{-3}$.

Sucrose is a cheap and a green reagent and the sucrose solutions are easy to prepare. For a test or industrial laboratory using a standard refractometer, it is possible to obtain a calibration curve for viscosity damping of a density meter.

Of course, the deviations and relations obtained in the present work, despite of having been deduced with a DMA 5 000 with factory default, must be validated for each density meter. Indeed, the relationships could depend on other parameters than the sample viscosity.

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