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Density measurements of viscoelastic samples with oscillation-type density meters

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Abstract. The oscillation frequencies produced by oscillation-type density meters during the density measurements suffer damping due to the viscosity of newtonian liquids. The effect of viscoelastic behaviour of non-newtonian liquids in the damping of these oscillations is still not known. So, 5 viscoelastic liquids were rheologically characterized, resorting to a rotational rheometer, and their density measured in order to provide a deeper insight into the damping effects produced by these types of fluids. To do so, oscillatory data was related with the obtained density deviations. The results of this study are one of the first insights for the knowledge of the measuring behaviour of these density meters when measuring viscoelastic fluids, one of the scopes of the EMPIR Project 17RPT02-*rhoLiq*.

1. Introduction

1.1. The metrology of liquids density

Density, ρ , is one of the major driving elements in economic transactions with important goods, ranging from fuels to liquid food products. The actual consumption of high-value liquids, such as wine, olive oil and fuel, can be considered of major importance to the European economy [1-3]. Liquids' physical properties such as: density, surface tension, viscosity and elasticity (i.e. non-Newtonian behaviour due to dissolved gases like carbon dioxide in beverages, suspended particles like in the pulp in a natural juice, etc.), among others, cover a wide spectrum of variation. Additionally, these liquids are handled in a wide range of temperature and pressure. So, the existent methods for density measurement are influenced by one or more of these physical properties as well as by temperature and pressure, meaning that their robustness need to be study. However, currently there are no EURAMET guides on liquid density measurements and the existing international standards [4, 5] and the reference documents used in Legal Metrology [6, 7] are either outdated or incomplete. Improvements in the quality of liquid density measurements will have a direct impact at industrial sites, leading to more competitive national industries and it will allow a free circulation within the EU market.



1.2. 17RPT02-*rho*Liq: a new EMPIR Joint Research Project

In order to bridge this gap in the scientific knowledge of liquid density metrology a 3 years EMPIR project, the 17RPT02-*rho*Liq, counting with a Consortium of 11 National Metrology Institutes (NMI) (IPQ – Portugal, BEV-PTP - Austria; BRML- Romania, CMI – Czech Republic, DMDM – Serbia, GUM – Poland, IMBiH – Bosnia and Herzegovina, JV – Norway, PTB – Germany, TUBITAK – Turkey, INM - Moldova) and one density meters manufacturer (Anton Paar – Austria) has started last May 2019 [8]. One of the main focus of this project is to develop high-level measurements and calibration services, and to produce density reference materials for national stakeholders, e.g. food, chemical, pharmaceutical and petroleum industries. The international recognition of these NMI in this metrological field will indirectly lead to the reinforcement of mutual confidence and cooperation at regional and international levels. This project will facilitate compliance with economically relevant EU Directives, e.g. Directive 2007/45/EC [9], and it will further reinforce the competitiveness of production industries. These NMI will be able to develop strategies for accurately measuring the density of liquids with non-classical physical properties, i.e. with physical properties that differ from water or hydrocarbons which are normally used as standard liquids. This will include robustness studies using liquids with high viscosity, with viscoelastic behavior, and with dissolved gases or suspended particles. These kinds of liquids are the most commonly measured by the end-users (food, chemical, pharmaceutical, petroleum, biofuels, etc.), therefore, the knowledge gained about possible interferences and corrections, will be crucial to obtain accurate and traceable density measurement results. These kinds of measurements can be performed under limited conditions and will often result in larger uncertainties. This knowledge will also be disseminated in international guides and standards for scientific, applied (via 3 new EURAMET guides and the revision of existing ISO standards [4, 5]) and legal (via revision of existing OIML [6] and WELMEC [7] documents) metrology and this will address the lack of documentation on this issue.

1.3. Damping effect on oscillation-type density meters

The working principle of an oscillation-type density meter is based on the law of harmonic oscillation. In this kind of measuring instrument, a U-shaped tube is filled with the sample. This measuring cell containing the sample will act like a flexural oscillator; the density of the liquid is determined by measuring the period of oscillation. It is well known that the viscous component of a liquid during the oscillation leads to a damping and by this to a lower resonance frequency of the measuring system and, thus, to an incorrect density indication. Damping detection is performed by analyzing the frequency of harmonics of the oscillation. From these data, the density meter determines the non-viscosity-corrected density value, ρ_{nc} , and a viscosity-corrected density value, ρ_c [10]. However, the effect of viscoelastic behaviour of non-Newtonian liquids in the damping of these oscillations is still not known. So, the rheological behaviour, in oscillation mode, of 5 viscoelastic liquids was studied and the results correlated with the obtained density deviations, in order to provide a deeper insight into the damping effects produced by these types of liquids. The results of this study are one of the first insights to the knowledge of the measuring behavior of these density meters when measuring viscoelastic liquids, one of the scopes of the EMPIR Project 17RPT02-*rho*Liq.

2. Method and Materials

2.1. Test samples

To carry out the study of the influence of the viscoelasticity of the samples on the result of the measurement of the density by oscillation-type density meters, 3 aqueous solutions of different polymers (Carbopol 940 (Fagron) at 0,15 cg·g⁻¹; polyvinyl alcohol (PVA, Sigma-Aldrich) and sodium borate (Borax, Dimor), both at 0.04 g·ml⁻¹; hydroxymethylcellulose (Sigma-Aldrich) at 0.01 g·ml⁻¹; all in ultrapure water) and 2 food liquids (mayonnaise and ketchup, both commercial formulations) were chosen.

2.2. Density measurements

The oscillation-type density meter used in this study was a DMA 5000 from Anton Paar (figure 1). The density indication errors were obtained by calibration of this density meter with newtonian certified reference liquids (CRM) (from H&D Fitzgerald) within the dynamic viscosity, η , interval from 1 to 795 mPa·s. The reference density values of these liquids were determined by hydrostatic weighing. The density indication errors of the density meter were calculated by the difference between the density measured value and the reference density value [11].

The density of the 5 viscoelastic samples was measured by gravimetric method with a 50 mL Gay-Lussac pycnometer (figure 1), according to ISO 2811-1 [12]. The filling of the pycnometer with these samples was performed with a peristaltic pump (ICC, ISMATEC) in order to avoid the formation of air bubbles. The density of these 5 samples was also measured using the oscillation-type density meter at the same temperature of the pycnometer test, for comparison of results.

Additionally, the density values of the 5 viscoelastic samples obtained by the oscillation-type density meter (i.e., ρ_{nc} - non-viscosity-corrected density value, ρ_c - viscosity-corrected density value and ρ'_c - density value corrected with the calibration curve obtained with the newtonian liquids) were compared against the density results obtained by gravimetric method using a Gay-Lussac pycnometer (ρ_{pic}).

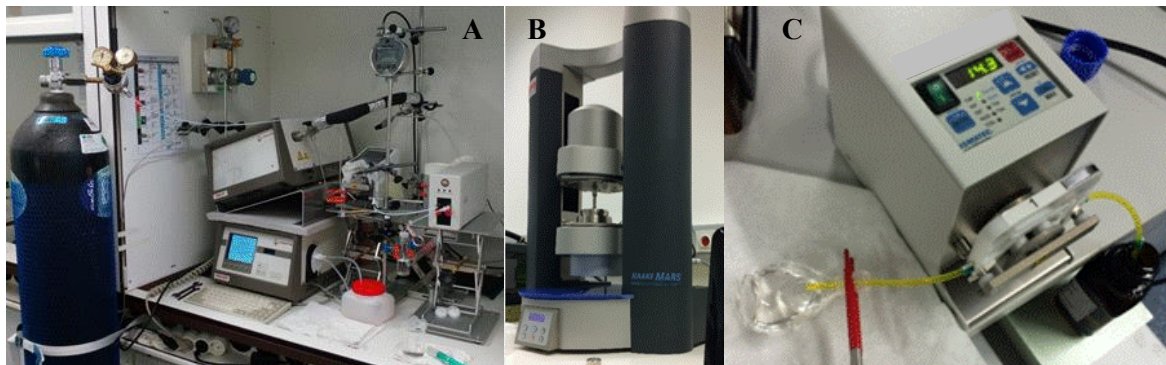


Figure 1. Photos of the measuring apparatus used. **A:** Oscillation-type density meter (DMA 5000, Anton Paar); **B:** Rheometer (Mars III, HAAKE ThermoScientific); **C:** Filling procedure of Gay-Lussac pycnometer with a peristaltic pump (ISMATEC).

2.2.1. Uncertainty budget. The uncertainty of density values obtained in both measuring methods, i.e. with the oscillation-type density meter (1) and with the pycnometer (2), was obtained according to GUM methodology [13], having into account the following major contributions for the uncertainty budget: (1) density meter (resolution, drift and calibration including CRM used), measurements repeatability; (2) calibration of pycnometer volume, balance (resolution, drift and calibration), air buoyancy (and instruments used to measure air temperature, relative humidity and pressure), mass standards used, measurements repeatability, temperature, temperature coefficient of the liquid. In this paper the reported expanded uncertainty, U , is stated as the standard measurement uncertainty multiplied by the coverage factor $k=2$, which for a t-distribution corresponds to a coverage probability of approximately 95 %.

2.3. Rheological determinations

Dynamic viscosity, η' , storage modulus, G' , and loss modulus, G'' , dependence on shear strain and on frequency, of the non-newtonian samples tested were determined by oscillation tests in a rotational rheometer (Mars III, HAAKE ThermoScientific) (Figure 1) using a plate-plate (PP35 TiL) measuring geometry. Two different oscillation mode tests were performed for each sample: (1) amplitude sweep

at a constant angular frequency, ω , of 10 rad/s in the interval of shear strain, γ , from 0.01 to 100 % (log. ramp) for the determination of the linear viscoelastic regime (LVR) and (2) a frequency sweep at a constant shear strain, γ , of 0.1 to 1 % inside the LVR, for an angular frequency interval, ω , of 100 to 1 rad/s (from 0.016 to 16 Hz) (log. ramp). From the amplitude sweep tests it was possible to identify the prevalent behaviour of the sample (viscous or elastic) regarding the shear strain applied and also to check for yield stress value, τ_y , and for the flow stress value, τ_f . The data from frequency sweeps ran for a non-destructive deformation range, will give information regarding the dependence of the dynamic viscosity, η' , with the oscillation frequency, f , up to 16 Hz, the upper limit of the PP35 measuring geometry.

3. Results and Discussion

3.1. Comparison of density results

Because it is a static method of measuring the density of liquids, pycnometry has been chosen to be used in comparison with vibrating tube densimetry. As a static method it is expected that the viscoelastic properties of the samples would not influence the measurement result, as in oscillation-type density meters. However, phenomena related to these properties were observed during the filling of the pycnometer which may have influenced the measurement results, and which cannot be easily accounted for. Table 1 summarizes the deviations of the bulk density results of the test liquids obtained by oscillation-type density meter compared to the results obtained by gravimetric method using the Gay-Lussac pycnometer. A maximum expanded uncertainty of $5.4 \cdot 10^{-5} \text{ g}\cdot\text{cm}^{-3}$ was obtained for the ρ_{nc} , ρ_c and ρ'_c values, with exception of the liquid foods (mayonnaise and ketchup) with a maximum uncertainty value of $3.3 \cdot 10^{-4} \text{ g}\cdot\text{cm}^{-3}$, possible related to the heterogeneity of this kind of samples, leading to a consequent low repeatability of the density measurements. On the other hand, the uncertainty obtained for the pycnometric method was $5.0 \cdot 10^{-3} \text{ g}\cdot\text{cm}^{-3}$. Given this, and considering the results from Table 1, the only significant deviations are those obtained for the mayonnaise sample, with a positive deviation of $1.4 \cdot 10^{-2} \text{ g}\cdot\text{cm}^{-3}$. All the other deviations are lower than the $U\rho_{pic}$ values, therefore are not considered significant.

Table 1. Summary of the density deviations, $\delta\rho$, of the results obtained by the oscillation-type density meter (ρ_{nc} , ρ_c and ρ'_c) and the results obtained by gravimetric method using a Gay-Lussac pycnometer (ρ_{pic}) of the 5 viscoelastic samples.

Samples	$\delta\rho$ ($\text{g}\cdot\text{cm}^{-3}$)		
	$\rho_{nc} - \rho_{pic}$	$\rho_c - \rho_{pic}$	$\rho'_c - \rho_{pic}$
Carbopol	$3.7 \cdot 10^{-3}$	$3.7 \cdot 10^{-3}$	$3.7 \cdot 10^{-3}$
PVA and Borax	$2.1 \cdot 10^{-5}$	$-1.8 \cdot 10^{-5}$	$-5.4 \cdot 10^{-5}$
Hydroxymethylcellulose	$-6.9 \cdot 10^{-4}$	$-8.6 \cdot 10^{-4}$	$-1.3 \cdot 10^{-3}$
Mayonnaise	$1.5 \cdot 10^{-2*}$	$1.4 \cdot 10^{-2*}$	$1.4 \cdot 10^{-2*}$
Ketchup	$-8.1 \cdot 10^{-4*}$	$-1.6 \cdot 10^{-3*}$	$-1.4 \cdot 10^{-3*}$

Notes: ρ_{nc} - non-viscosity-corrected density value, ρ_c - viscosity-corrected density value and ρ'_c - density value corrected with the calibration curve obtained with the newtonian liquids; U - expanded uncertainty stated as the standard measurement uncertainty multiplied by the coverage factor $k=2$, which for a t -distribution corresponds to a coverage probability of approximately 95 %, obtained according to GUM methodology [13]; U for ρ_{nc} , ρ_c and ρ'_c values: $5.4 \cdot 10^{-5} \text{ g}\cdot\text{cm}^{-3}$ and $*3.3 \cdot 10^{-4} \text{ g}\cdot\text{cm}^{-3}$; U for ρ_{pic} values: $5.0 \cdot 10^{-3} \text{ g}\cdot\text{cm}^{-3}$.

3.2. Rheological determinations

The extrapolated value of the dynamic viscosity, $\eta'_{\text{ext.}}$, of each viscoelastic sample at the same oscillation frequency, f_ρ , produced in the oscillation-type density meter during the density measurement, was obtained by extrapolating the experimental lines obtained from the linear regression of $\log(\eta') = a \log(f) + b$ for the interval of frequencies, f , analysed in the rheometer (Table 2). The viscosity values estimated by the results of the oscillation-type density meter (DMA 5000, Anton Paar), $\eta_{\text{est. } \rho}$, are also given in Table 2, together with the description of the viscoelastic character predicted for each sample for f_ρ and the damping factor, $\tan \delta$, for the maximum frequency tested.

The hydroxymethylcellulose sample presented a predominant viscous behavior, $G'' > G'$, in the entire range of frequencies tested. PVA/Borax and mayonnaise samples showed a predominant elastic behavior, with $G' > G''$, for frequencies higher than their crossover frequency, i.e. for $f > 1.5$ Hz, and for $f > 2.3$ Hz, correspondently. Ketchup sample showed a predominant elastic behavior, with $G' > G''$, in the entire range of frequencies tested. At last Carbopol sample showed a $G' \cong G''$.

Earlier studies [10] showed a way of estimate the dynamic viscosity, $\eta_{\text{est. } \rho}$, of newtonian fluids by using the density results given by an oscillation-type density meter, with an uncertainty of 18 %. The same approach was now applied to estimate $\eta_{\text{est. } \rho}$ for each non-newtonian fluid tested. The $\eta_{\text{est. } \rho}$ were compared with the dynamic viscosity values extrapolated $\eta'_{\text{ext.}}$ from the curve $\log(\eta') = a \log(f) + b$, with an uncertainty of 10 %, and the relative deviation of the $\eta_{\text{est. } \rho}$ in relation to $\eta'_{\text{ext.}}$, $\delta\eta_\rho$ calculated (Table 2). Despite Carbopol and PVA/Borax samples presented $\delta\eta_\rho$ values below the $U\eta_{\text{est.}}$, the $\delta\eta_\rho$ results for the other samples showed that this approach seems not to be suitable to be use for non-newtonian fluids (Table 2).

Table 2. Summary of viscosity values estimated by the results of the oscillation-type density meter (DMA 5000, Anton Paar), $\eta_{\text{est. } \rho}$, and the dynamic viscosity values, $\eta'_{\text{ext.}}$, estimated by extrapolation of the $\log(\eta')$ curves as a function of $\log(f)$ determined by the rheometer (Mars III, ThermoScientific) with a plate-plate (PP35TiL) measurement geometry, for the frequency values, f_ρ , measured by the oscillation-type density meter for each sample.

Samples	Density meter		Viscoelastic character predicted for f_ρ	Frequency sweep tests			
	f_ρ	$\eta_{\text{est. } \rho}$		$\tan \delta$	$\eta'_{\text{ext.}}$	$ \eta^* _{\text{ext.}}$	$\delta\eta_\rho$
	(Hz)	(mPa·s)		(1)	(mPa·s)		(%)
Carbopol	278.62	< 6	$G' \cong G''$	0.89	5.3	8119	13
PVA/ Borax	277.94	10.3	$G' > G''$	0.23	10.7	375	-4
Hydroxymethylcellulose	278.34	48.5	$G'' > G'$	2.16	29.1	34.2	67
Mayonnaise	282.13	> 795	$G' > G''$	0.44	88.5	329	798
Ketchup	270.52	> 795	$G' > G''$	0.60	245.5	313	224

Legend: f_ρ – oscillation frequency produced in the oscillation-type density meter (DMA 5000, Anton Paar) during the density measurement (Hz); $\eta_{\text{est. } \rho}$ – viscosity value estimated by the results of the oscillation-type density meter; $\log(\eta') = a \log(f) + b$ – linear fitting of the dynamic viscosity η' results against frequency, f , obtained in the frequency tests in the rheometer (Mars III, ThermoScientific); $\eta'_{\text{ext.}}$ – dynamic viscosity value extrapolated from the curve; $|\eta^*|_{\text{ext.}}$ – complex viscosity value extrapolated for f_ρ ; $\delta\eta_\rho$ – relative deviation of the $\eta_{\text{est. } \rho}$ in relation to $\eta'_{\text{ext.}}$.

4. Conclusions

Oscillation-type density meters are a very robust, reliable and convenient instruments to measure the density of newtonian liquids in wide range of density, viscosity and temperature with an expanded uncertainty from $1.0 \cdot 10^{-5} \text{ g}\cdot\text{cm}^{-3}$ to $3.0 \cdot 10^{-5} \text{ g}\cdot\text{cm}^{-3}$, by using a proper calibration curve, since the deviations due to viscosity may lead to a maximum density deviation of $6.2 \cdot 10^{-4} \text{ g}\cdot\text{cm}^{-3}$ in the viscosity

interval up to 795 mPa·s [10]. This study showed that the knowledge of the effect of samples' viscoelasticity on the density measurements results using this kind of density meter is limited by the uncertainty of the pycnometer method ($5.0 \cdot 10^{-3} \text{ g}\cdot\text{cm}^{-3}$), since these density meters are able to produce density results with lower uncertainty ($1.0 \cdot 10^{-5} \text{ g}\cdot\text{cm}^{-3}$). Only the mayonnaise sample, with a gel-like structure, showed a density deviation of $1.4 \cdot 10^{-2} \text{ g}\cdot\text{cm}^{-3}$, one order of magnitude higher than the uncertainty of the pycnometer method. With this, and to be safe, one can say that the density of viscoelastic samples may be determinate by using oscillation-type density meters with an expected maximum deviation of $1.4 \cdot 10^{-2} \text{ g}\cdot\text{cm}^{-3}$. Additionally, one should have in consideration that these results may be instrument-dependent. Despite the obtained data one cannot conclude about how the rheological properties of a fluid affect the density measurements and viscosity predictions with an oscillation-type density meter. Additionally, the results showed that the approach used to estimate the dynamic viscosity of newtonian fluids by using the density results given by an oscillation-type density meter [10] cannot be used for non-newtonian fluids.

As already suspected in earlier studies [10], these results are other indication that oscillation of the density meter cell during density measurements can cause modifications in the internal structure and arrangement of the molecules of the non-newtonian samples, leading to a non-well described density deviation trend, which may be essentially due to the elastic portion of the viscoelastic behaviour of these samples. As planned in the 17RPT02-*rhoLiq* EMPIR Project the viscoelasticity effect on density results need to be study by a measurement method with a low uncertainty such as the hydrostatic weighing. This may lead to means of comparison that will be able to use the oscillation-type density meters in their maximum metrological capability also with non-newtonian samples. Or even to know the real limitation of this measuring instrument, to give the most accurate insights for reference documents, such as standards and guides.

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