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CALIBRATION OF A REFERENCE VIBRATING TUBE DENSIMETER

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Abstract–This article reports the calibration procedure for a commercial Solartron 7835 densimeter which is currently used as “reference” instrument in an automatic apparatus for the calibration of on-line densimeters. Three different materials (fluids), whose densities are known at the usual working condition of pressure and temperature, are used for characterizing the reference densimeter.

The procedure applied at the INRIM to produce accurate parameter estimates in the densimeter calibrations is described in this papers. It is based on the application of the weighted least square method (WLS), considering together with the uncertainties of the dependent and independent variables also those of the model. The model analysis performed by a Chi-square test and the expected uncertainty computed over the calibration range have shown to be fully consistent with the experimental data.

Keywords: Densimeter, Vibrating tube, Calibration

1. INTRODUCTION

According to the quality management requirements, the knowledge of all fluid properties must be traceable to national or international standards, which necessarily involves the calibration of instruments and the statement of their measurement uncertainty. As regards density, there are many commercially available instruments and apparatuses for the measurement of this quantity, embodying different measuring principles.

Vibrating-tube densimeters are widely used for accurate measurements of fluids: gas and liquids, finding applications in research and industry. High precision, simple operation, low volume of samples needed, and measurements in a flow regime are the main advantages of this kind of instruments.

The well-known principle of vibrating-tube densimeters is based on the theory of vibration and material deformation of mechanical oscillator concerning a U or V-shaped glass or metal tube of constant volume filled with a fluid sample. Stationary oscillations of the tube are maintained by the electromagnetic force, generated by means of a drive system, acting on the tube. The input signal for the drive system is obtained from a pick-up system that converts mechanical oscillations of the tube into an electrical signal. Oscillations are close to the resonant frequency of the tube and are related to the density ρ_f of a fluid filled in. The resonant frequency f of a vibrating tube densimeter, filled with a fluid, can be expressed as:

$$f = \frac{1}{2\pi}\sqrt{\frac{k}{m_r + V_f \cdot \rho_f}} \tag{1}$$

where:

k is the stiffness of the resonant element;
m_r is the mass of the resonant glass or metal tube filled with a fluid sample;
V_f is the volume of the fluid contained in the resonant element.

It is also understood that the density of fluid, the frequency, the stiffness and the sample volume depend upon the same conditions of measurements, i.e. mainly the thermodynamic properties: temperature and pressure and, in addition, several characteristics of the sample like its homogeneity and viscosity. However to deduct the sample's density ρ_f a usual working equation, according to the internal software, takes into account the measurement of the period of the oscillation of the filled tube, τ at the testing temperature, T and pressure, p

$$\rho_f(T,p) = A(T,p)\tau^2 - B(T,p) \qquad (2).$$

where *A(T,p)* and *B(T,p)* are two apparatus constants in which the cell volume and the cell mass are involved as well as the spring constant of the measuring cell. Corrections of non-linearities and those related to the influence of the viscosity are not here considered.

The equation (2) is only a first order approximation to the actual behavior of a vibrating tube densimeter containing a fluid; a second order mathematical model, according to the behaviour of a harmonic damping system, it is usually suggested to correlate density at the designed temperature and pressure when the period τ is the output signal for several commercially available instruments.

In this paper, the procedure applied at the INRIM to produce more accurate parameter estimates in a mathematical model usually suggested to correlate density and temperature-pressure when the period τ is the output signal of a commercially-available vibrating tube densimeter is shown as an example. The example implies the use of at least three reference fluids of “known” density, like air, water and kerosene possibly close to 20 °C and at atmospheric pressure.

The parameter estimation based on the application of the weighted least square method (WLS) has been designed; it considers, together with the uncertainties of the dependent and independent variables, also those of model. The model analysis performed by a Chi-square test and the expected uncertainty computed over the calibration range are also shown.

2. STATEMENT OF THE PROBLEM

Equation (2) is only a first order approximation to the actual behavior of a vibrating tube densimeter containing a fluid; different types of mathematical models for both the calibration of a vibrating tubes and the density calculations can be used, see [1-3] for a non exhaustive but rather recent overview. However a generic equations have been developed for use in the calibration of a specific instrument [4], allowing the user to convert the output periodic time signal from the meter into a better density calculation of the contained fluid at the designed temperature T and the pressure p

$$\rho(T,p) = f(K_0, K_1, \ldots, K_n, \tau) \tag{3}$$

K_0, K_1, …, K_n are the new apparatus constants.

However, a second order mathematical model, according to the behaviour of a harmonic damping system, it is usually suggested to correlate density at the designed temperature and pressure when the period τ is the output signal for several commercially available instruments [5]

$$\rho(T,p) = K_0 + K_1\tau + K_2\tau^2 \tag{4}$$

Differently from (2), the (4) introduces the K_1 term which includes the effect of damping attributed to fluid viscosity on the coupled vibrating tube.

The more conventional way to calibrate the densimeter is then to determine the relationships between the three instrumental constants (parameters) K_0, K_1 and K_2 across the full operational temperature and pressure range with fluids of known density and, possibly, viscosity at those conditions. By this approach the use of n reference fluids and m test repetitions at reference temperature and pressure conditions allows to write down $n \times m$ equations in three variables (K_0, K_1 and K_2) whose parameters can be estimated by the weighted least square method (WLS) [6].

The best solution of the parameter estimates $\hat{\boldsymbol{\beta}}$ is

$$\hat{\boldsymbol{\beta}} = (\tau^T \psi_\rho^{-1} \tau)^{-1} \tau^T \psi_\rho^{-1} \boldsymbol{\rho} \tag{5}$$

with covariance matrix

$$\psi_{\hat{\beta}} = (\tau^T \psi_\rho^{-1} \tau)^{-1} \tag{6}$$

The terms in equations (5) and (6) are

$$\hat{\boldsymbol{\beta}} = \begin{bmatrix} K_0 \\ K_1 \\ K_2 \end{bmatrix}, \quad \boldsymbol{\tau} = \begin{bmatrix} 1 & \tau_{11} & \tau_{11}^2 \\ \vdots & \vdots & \vdots \\ 1 & \tau_{1m} & \tau_{1m}^2 \\ \vdots & \vdots & \vdots \\ 1 & \tau_{n1} & \tau_{n1}^2 \\ \vdots & \vdots & \vdots \\ 1 & \tau_{nm} & \tau_{nm}^2 \end{bmatrix}; \quad \boldsymbol{\rho} = \begin{bmatrix} \rho_1 \\ \vdots \\ \rho_1 \\ \vdots \\ \rho_n \\ \vdots \\ \rho_n \end{bmatrix} \tag{7}$$

and ψ_ρ is the covariance matrix of the fluid density that, assuming that all density values are obtained independently, is a diagonal matrix

$$\psi_\rho = \begin{bmatrix} s_{\rho_1}^2 & 0 & \cdots & 0 \\ 0 & s_{\rho_2}^2 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & s_{\rho_n}^2 \end{bmatrix} \tag{8}$$

The diagonal element of such matrix are the variance $s_{\rho_i}^2$ which, according to the GUM [7], encompass both the uncertainty u_{ρ_i} of each dependent quantity ρ_i, and also the contributions of the uncertainty of the independent variable τ_{ij} such that

$$s_{\rho_i}^2 = u_{\rho_i}^2 + \left(\frac{\partial\rho}{\partial\tau} s_\tau\right)^2 \cong u_{\rho_i}^2 + \rho_i^2 s_{\tau_{ij}}'^2 \tag{9}$$

The uncertainty of the independent variable is obtained by the corresponding relative variance of the period $s_{\tau_{ij}}'^2$ (type A) which takes into account the repeatability of the measurements, given by the standard deviation of repeated measurement of period $u_{repeatibility}$, for each reference fluid, in addition to the accuracy of the frequency counter unit $u_{counter}$. The other term, concerning the uncertainty u_{ρ_i}, is evaluated like a component of type B. At each reference temperature and pressure, the uncertainty u_{ρ_i} is associated to the main contribute of the uncertainty of the fluid samples, used for the calibration of densimeter and given by the certificate of density or by the uncertainty obtained from independent measurements u_{CRMs}, in addition to the influence of temperature and pressure on the standard fluids

	Uncertainty contribute	Uncertainty category (Type)	Distribution
u_{ρ_i}	u_{CRMs}	B	Normal
	u_T	B	Rectangular
	u_p	B	Rectangular
$s'_{\tau_{ij}}$	$u_{repeatibility}$	A	Normal
	$u_{counter}$	B	Rectangular

Table 1. Uncertainty contributions for the combined standard uncertainty of the vibrating tube densimeter under test.

during the calibration u_T and u_p, respectively.

In Table 1 the uncertainty sources mentioned are shown.

Finally, the chi-square test can be used as an indicator of the agreement between the observed (the data) and the predicted values, as well as between the estimated variance of fit and the input uncertainties. The model is consistent with the observed values, if the expected value of the reduced chi-square $\tilde{\chi}^2$ (chi-square per degree of freedom) results

$$\tilde{\chi}^2 = \frac{\chi^2}{\nu} = \frac{(\rho - \hat{\rho})^T \psi_\rho^{-1} (\rho - \hat{\rho})}{\nu} \leq 1 \tag{10}$$

where ν is the number of degrees of freedom

$$\nu = n \text{ x } m - 3 \tag{11}$$

However, if unreasonably large values are obtained because the model is not perfectly correct and it is not possible to revise it by physical considerations, moreover if no mistakes in the data are apparent, then the input uncertainty can be enlarged so as to reach consistency [8]. This can be done by multiplying the matrix ψ_ρ by factor h chosen so that equation (10) becomes equal to unity. Therefore the covariance matrix becomes

$$\psi_{\hat{\beta}} = h\left(\tau^T \psi_\rho^{-1} \tau\right)^{-1} \tag{12}$$

In this way, the estimated parameters remain unchanged, while their uncertainty is enlarged by $\sqrt{h}$.

3. EXPERIMENTAL

As an actual example, the results of the application of the above algorithm have been tested in calibrating a commercially-available on-line vibrating tube densimeter Solartron 7835, previously installed in the “density meter prover” (DMP) apparatus as a secondary standard [8], to be used for reference density measurements of fluids in metrology laboratories or to be installed directly in a plant, Figure 1. The densimeter, during its calibration, was connected to a Fluke PM 6681 Timer/Counter for reading the period τ of vibrating tube during the measurements.

The procedure to evaluate the parameters implies the use of at least three reference fluids of “known” density, possibly near to the range of temperature, pressure and density intended to be used in the apparatus [9]. In this example air, water and kerosene have been selected close to 20 °C and at atmospheric pressure.

The calibration procedure was performed separately with each one of the selected fluids, after that the vibrating tube was empty, cleaned and dried. The procedure consisted in five repeated cycles of 1000 readings each one of the period of oscillation of the filled vibrating tube, yielding fifteen independent equations in three variables, according to the equation (4).

Initially, compressed and dried air was pushed in the apparatus, then kerosene and finally water flew down through a system of three-way valves from one of the three upper tanks respectively, due to the action of a peristaltic pump, through the test line at constant flow rate. A chilled-water heat exchanger controlled by a feedback temperature sensor (thermostat) has been used to remove from the fluids the heat added by the operation of the pump.

The actual temperature has measured by the average of the measurements given by two platinum resistance thermometers (T1, T2), installed upstream and downstream the input and output ports of the densimeter, respectively.

The traceability to SI system is assured by the calibration of the two thermometers and by the three fluids used in the calibration:

- *Air density.* The values of air density inside the densimeter were determined according to the CIPM-2007 air density equation where the combined standard relative uncertainty exclusive of the measured input parameters: pressure, temperature and dew-point temperature (or relative humidity) is $u(\rho_a)/\rho_a \leq 2\text{x}10^{-5}$ [10]. In the equation, the mole fraction of CO_2, χ_{CO2} in atmosphere has been supposed to be equal to 0.0004. Only the ambient pressure P_a, and humidity H_a have been measured in the room where the apparatus was placed, while temperature T_a was the average of temperature measured by two platinum resistance thermometers T_1 and T_2. The air density uncertainty at the measuring conditions has been then evaluated, for each set, taking into account also the contributions of the temperature and pressure stability during the reading of the period.
- *Water density.* The water used in the calibration was purified and bi-distilled, hence showing the quality suitable for the purpose of calibration of densimeter, with a resistivity of >1.0 MΩ (conductivity <1 μS). The value of density of the water at the calibration temperature T_a has been computed according to the

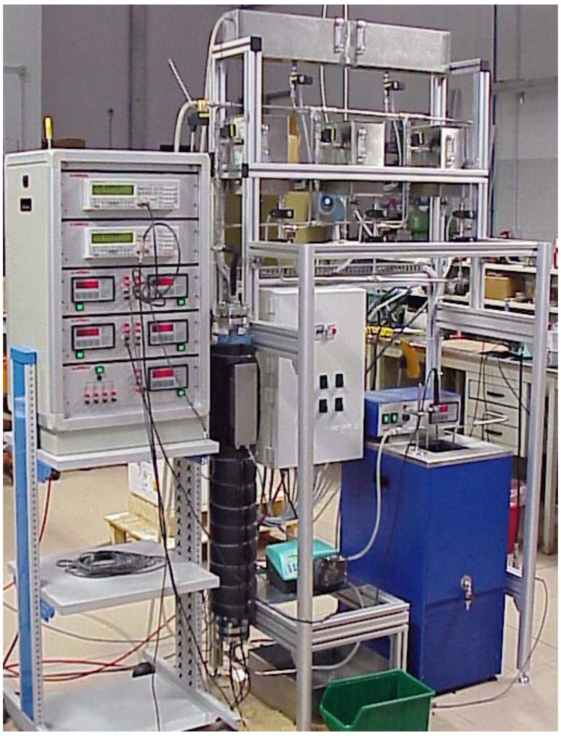

Figure 1. “Density meter prover” (DMP) apparatus for the calibration of on-line densimeter and for density measurements.

water density equations recommended by BIPM for temperatures between 0 °C and 40 °C and at the pressure of 101.325 kPa [11], where the combined standard relative uncertainty is evaluated to be less than 1 × 10^{-6} (coverage factor $k = 1$).

- *Kerosene density.* The density of kerosene has been measured in the range 15 °C and 25 °C at atmospheric pressure by a vibrating tube densimeter Paar DMA 5000 with an uncertainty of 0.015 kg·m^{-3}. The vibrating tube densimeter Paar DMA 5000 were metrological traceable through a previously calibration in the range 10 °C and 60°C, by the use of liquid density standard Certificate materials (CRMs), produced in the INRIM Density and Viscosity laboratory by hydrostatic weighing.

4. DISCUSSION

The experimental results as a function of temperature are reported in Table 2.

The density value ρ_i, with their combined uncertainty s_{ρ_i} (computed by (9)), and the period for each set of measurements are the reference data (input) for the parameters estimation. The combined density uncertainty for each set takes into account the dispersion of the period readings at the measuring conditions, the uncertainty shown in the certificate and also the influence conditions linked to the properties of the tested fluid and the instruments. An important contribution seems to be due to the temperature influence, especially that given by the thermal expansivity of fluids, i.e for the water is β_{water}= 0.2 kg·m^{-3}·K^{-1} and for the kerosene is $\beta_{kerosene}$=1.0 kg·m^{-3}·K^{-1}.

The Table also shows the value of reduced chi-square, the degrees of freedom, the parameter estimates with their uncertainty, according to equation (12).

Although the value of $\tilde{\chi}^2$ is slightly greater than 1, we can however think that the set of observations well fit the used model even if the uncertainty of some of them might have been underestimated. The value found could be reduced by using, in the calibration procedure, a largest number of reference fluids and of measurements. In any case, it is very important to pay careful attention to the estimation of the measurement uncertainties.

5. CONCLUSION

After reviewing the well-known principle of the vibrating-tube densimeters and the implications of the pressure and the temperature dependencies in the usual calibration models, a second order mathematical model has been considered in the calibration procedure related to a commercial Solartron 7835 to correlate the density and the period τ at the designed temperature of 20 °C and at atmospheric pressure.

The parameters estimation based on the application of the weighted least square method (WLS) and the model analysis performed by a Chi-square test have been shown through an actual example concerning the procedure of calibration currently used at INRIM.

Testing Fluid	Av.ge temperature °C	Reference Density, ρ_i kg·m^{-3}	Combined Uncertainty, s_{ρ_i} kg·m^{-3}	Av.ge period reading, τ_i s·10^{-6}
Air	18.351	1.200	0.05	1075.90510
	18.359	1.200	0.05	1075.90490
	18.376	1.200	0.05	1075.90519
	18.381	1.200	0.05	1075.90505
	18.382	1.199	0.05	1075.90495
Kerosene	20.101	744.947	0.60	1345.87690
	20.106	744.950	0.61	1345.88050
	20.105	744.941	0.60	1345.87750
	20.109	744.955	0.71	1345.88020
	20.115	744.931	0.60	1345.87690
Water	20.063	998.129	0.21	1425.06980
	20.051	998.134	0.21	1425.06975
	20.041	998.134	0.21	1425.06985
	20.029	998.138	0.21	1425.06970
	20.016	998.141	0.21	1425.06990
		K_2: 0.00128 kg·m^{-3}·s^{-2} K_1: -0.36 kg·m^{-3}·s^{-1} K_0: -1102.1 kg·m^{-3} $\tilde{\chi}^2 \cong 2$	s_{K1}: 1.2E-05 kg·m^{-3}·s^{-2} s_{K2}: 0.03 kg·m^{-3}·s^{-1} s_{K3}: 18.3 kg·m^{-3} $\nu = 12$	

Table 1. Experimental input data and result of the parameters estimation relating to calibration of the vibrating tube densimeter Solartron 7835, previously installed in the "density meter prover" (DMP) apparatus [8].

The WLS approach provides the information necessary to know how the densimeter or, more generally, the measurement system works, taking into account the uncertainty of the calibration points in the estimation of the parameters. Moreover, the model was demonstrated to be fully consistent with the data, after appropriately decreasing the chi squared value (initially greater then 1), hence leading us to adjust the uncertainty of the evaluated parameters.

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