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HYDROSTATIC WEIGHING SYSTEM AT THE INRiM FOR CALIBRATING HYDROMETERS

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Abstract:

Hydrometers are simple but effective instruments for measuring the density of liquids. In this work, we present the new hydrostatic weighing system developed at the INRiM, formerly IMGC – CNR, for the calibration of hydrometers in the range 500 kg.m^{-3} to 2000 kg.m^{-3}.

The apparatus which uses a method to automatically align specific scale-marks for the calibration of hydrometers, makes easy the whole calibration procedure and allows to reduce the former uncertainty declared by laboratory. It consists of a vision system, a stepping motor, and software to control the system. The vision system, composed of a CCD camera and a frame grabber, is used to acquire images. The overall performance of the apparatus is illustrated by the assessment of the uncertainty for some usual kinds of hydrometers sent to the Institute for calibration.

Keywords: Hydrometer, Calibration, Artificial vision

1. Introduction

Hydrometers are exposed to extended immersion times in various liquids which may attack the glass, plus they are subjected to mechanical stress and abrasion through handling and cleaning. Moreover, the natural ageing process of the glass further results in minute changes to the dimensions of the instrument. The sum of these factors, although not visible to the eye, may result in slight changes in the weight and/or displacement of the instrument and cause it to change its indication.

The correctness of measurements and measuring instruments is one of the most important prerequisites for the assurance of the quality and quantity of products and services, and the accuracy of the instruments must be consistent with their intended use.

The relatively low price of hydrometers doesn't exclude the need of their periodic regular calibration and, if requested, periodic verification. Those two different actions, although established through separate rules and metrological infrastructures and activities, are mostly based on the same measuring procedures, that as are essential to assure the integrity of the readings, the traceability to international standards in the areas of density measurements and to comply with the requirements of the quality systems.

Differently from the direct comparison method where different standards, such as liquids or solutions with known density are used, the multipoint procedure to calibrate hydrometers based on hydrostatic weighing (well know as Cuckow's method) is in use at most national standards laboratories, that provide a calibration services for reference hydrometers generally used as laboratory standards [1].

2. Outline of the hydrometer calibration

Hydrometers of any range can be calibrated at different selected graduation marks, by measuring the buoyancy force when the hydrometer is placed in air and partially immersed in a reference liquid. At first, the hydrometer to be calibrated is weighed in air and then it is sunk into a reference liquid, whose density is known at the reference temperature, with the stem connected to an upper balance through a metal wire (figure 1). The depth of immersion of the hydrometer is adjusted by a mechanical device so that the middle of the graduation mark under calibration is aligned with the horizontal surface of the reference liquid. To detect correctly the alignment of the hydrometer scale the vision by a magnifier or by a monitor is commonly used.

In those situations where the range of the hydrometer to be calibrated is lower than the density of the reference liquid, a supplementary weight, in the shape of a stainless steel ring is added to the hydrometer to cause it to sink.

The hydrometer reading is then compared with a reference value ρ_x calculated from the difference in the weighing results

$$\rho_x \cong (\rho_L - \rho_a)\times \frac{\left[M_a\left(1-\frac{\rho_a}{\rho_s}\right)+\pi D\gamma_x g^{-1}\right]}{\left[M_a\left(1-\frac{\rho_a}{\rho_s}\right)-M_L\left(1-\frac{\rho'_a}{\rho_s}\right)+\pi D\gamma_L g^{-1}\right]}\times \left[1+\beta(T-T_0)\right]+\rho_a \quad (1)$$

where

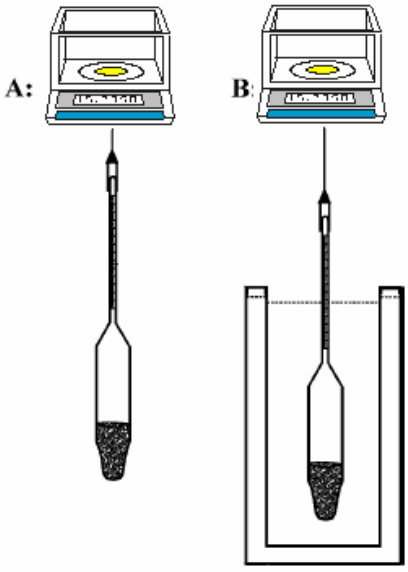

Figure 1. The priciple of the hydrometer calibration procedure in the first (A) and second (B) step.

M_a, M_L = reading of the balance when weighing in air and in the liquid immersed up to the measurement point, respectively;

ρ_a, ρ'_a = density of air during weighing in air and in liquid, respectively;

ρ_s = reference density for weights (8000 kg m^{-3});

ρ_L = density of the calibration liquid;

γ_L, γ_x = surface tension of the calibration liquid and the liquid in which the hydrometer is normally used, respectively;

d = stem diameter of the hydrometer at meniscus level

g = acceleration due to gravity;

β = volumetric thermal expansion coefficient of the glass from which the hydrometer is made;

T, T_0 = the air temperature at the time the weighing was done and the reference temperature, respectively.

3. The experimental set-up

Two main aspects were taken into account in setting up the new INRiM calibration station for hydrometers: the former is to make more easy and accurate all measuring procedures by means of an extensive automation of the calibration process, the latter is to eliminate as much as possible operator's mistakes in detecting correctly the alignment of the hydrometer scale mark to be calibrated.

The adoption of an automatic alignment system [2] composed of a CCD camera (pixel matrix of 604 H x 576 V) and a frame grabber, which is used to acquire images by means of a home-made image processing software, has allowed us to design a hydrostatic weighing station suitable to calibrate hydrometers in the range between 500 kg m^{-3} up 2000 kg m^{-3}.

From our previous station [3] only the weighing system, consisting of a commercially available electronic balance for hydrostatic weighing of 405 g capacity, and the environmental equipment (a portable pressure gage and a thermo-hygrometer) are unchanged.

A lift unit has been installed underneath the concrete base plate upon which the balance and the environmental equipments are installed (figure 2).. The unit comprises a vertical feed ball screw used as a single axis actuator, providing translation up to 67 cm with micrometer resolution. A carriage holding a thermostatic tank is moved vertically together with the CCD camera by the feed ball screw actuator. A computer-controlled stepping motor is coupled to the feed ball screw; its allows the translation to the desired position without overshoot, oscillation, or steady-state error. To achieve this, the actuator moves very regularly in order not to disturb the horizontal plane surface of the reference liquid; when the liquid level is close to the mark to be calibrated, the number of steps made at a time is reduced to 3 correspond to 6 μm.

The 3 litres of reference liquid are contained in a glass vessel surrounded by 30 litres of temperature-controlled circulating water at 20 °C, although different temperatures between 10 °C and 50 °C can be set and maintained by an external thermostat bath. A resistance thermometer is housed inside the glass vessel, close to bulb of the hydrometer to be calibrate, in order to ensure an accurate measurement of the liquid temperature during the calibration. Moreover a commercially available tensiometer is used for measuring the surface tension of the reference liquid. To measure the temperature during the weighing of hydrometers, both in air and in liquid, two calibrated platinum resistance thermometers (Pt100) are linked to an a.c. bridge, finally the mean diameter of the hydrometer stem is determined by an accurate calliper, by measuring it at four different levels, approximately at each select mark.

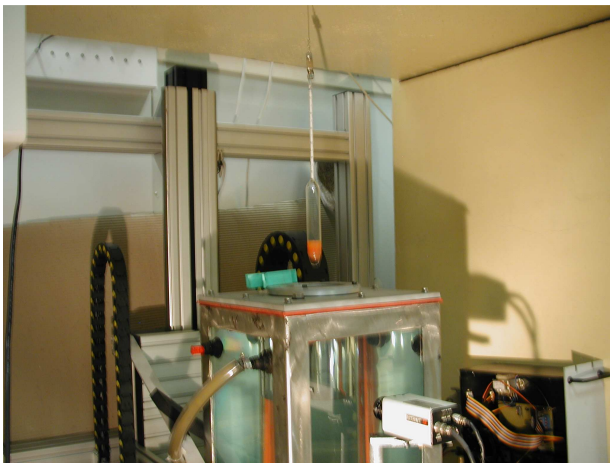

Figure 2. Detail of the hydrometer calibration station before the lift unit is moved towards the hydrometer to be calibrated..

The procedure of calibration is managed by the operating program which has the functions: i) to control the stepping motor and adjust by the movement of the glass vessel for the alignment of the horizontal plane with the particular scale-mark and ii) to process images from the camera by the analysis of the image profile controlled to an accuracy of 0,1 pixel (figure 3).

In short, after the hydrometer has been hung up below the balance and has been weighed in air, the thermostatic bath with the reference liquid is moved towards the hydrometer, thus allowing its partial immersion. The hydrometer reading ρ_r by CCD camera consists in observing the marks of the hydrometer under calibration from below the surface of the liquid and in aligning the middle of the mark to be calibrated with the horizontal plane tangential to the liquid surface. The adjustment allows for the most accurate alignment that is required and removes the operator's mistakes in detecting correctly the alignment of the hydrometer mark to be calibrated.

In the current procedure, five independent weighing-in-air sequences and five independent hydrostatic weighings at each one of the stated levels of immersion are made respectively. The density of the reference liquid is determined as a function of temperature over the range 18 °C to 22 °C by hydrostatic weighing of a zerodur sphere of known mass and volume. In order to check the stability of the density over the time and the possible contamination, the density of the liquid is measured before and after the calibration of each hydrometer by means of a vibrating tube densimeter.

4. Uncertainty budget

Usually hydrometers are calibrated at several graduation marks of the scale (normally three or four) and for each of them the deviation, or the correction *C* is calculated

$$C = \rho_x - \rho_r \qquad (2)$$

where ρ_x is calculated by the equation (1) which is related to the density of the liquid in which the hydrometer would freely float at the scale reading ρ_r. Consequently the best accuracy achieved in the calibration of hydrometers is mainly due to how both the quantities ρ_x and ρ_r are estimated.

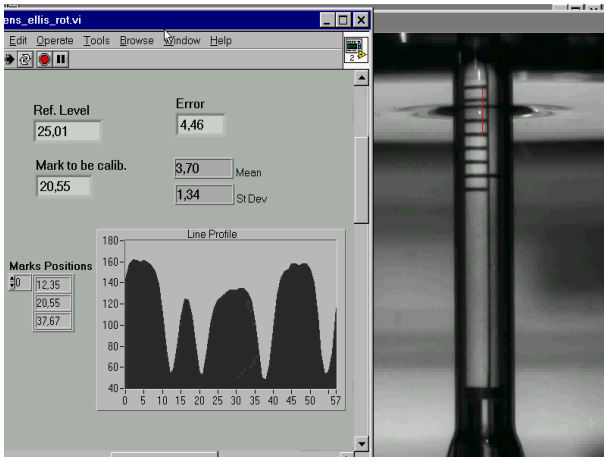

Figure 3. Digital acquired image of hydrometer to be calibrated and analysis of profile around the designed mark.

The correction, as given in equation (2), may be either positive, negative, or zero, and the standard uncertainty associated with the estimate of correction can be expressed as

$$u_c(C) = \sqrt{\sum_{i=1}^{n} \left(\frac{\partial C}{\partial x_i} \right)^2 u^2(x_i)} \qquad (3)$$

where the input estimates x_i of the input quantities in the equations (1) and (2) are assumed to be uncorrelated [4]. Reliability of calibration as well as the level of uncertainty is strictly connected with the hydrometer to be calibrated, as well as with equipment and procedure used in the measurement.

The evaluation of the input quantities are detailed as follows on the base of the INRiM equipments:

a) *Weighing of the hydrometer in air and in the liquid.* The weighings of the hydrometer in air and in the reference liquid are performed by means of an available commercial balances with a resolution of 0,01 mg. To reduce the influence of linear drifts, several weighing cycles can be carried out with different subsequent weighings; the usual standard uncertainties in the weighings are $u(M_a) = 0{,}10$ mg in air and $u(M_L) = 0{,}15$ mg in the liquid respectively. The standard uncertainty associated with the weight of the calibrated hydrometer both in air and in the liquid is obtained from contributions due to the balance calibration and the reference standards calibration, but also from the repeatability, linearity, hysteresis, drifting of the measurements. Moreover in agreement with the equation (1) the standard uncertainty associated with the density of the standard weights must be considered.

b) *Atmospheric buoyancy.* The measurement of air density is necessary to allow buoyancy corrections to be made when comparing weights of different volume, of different material or when making mass measurements to the highest accuracy. In general the air density is calculated by means of environmental measurement of temperature, pressure and humidity, determined during the weighings, using the equation recommended by the CIPM (*Comité International des Poids et Mesures*) [5]. The carbon dioxide concentration is not measured, the value of 0,04 % with an uncertainty of 0,02 % (rectangular probability distribution) is adopted.

The standard uncertainty contribution of the density of air usually results to be $u(\rho_a) = 0{,}003$ kg m^{-3}.

c) *Temperature influence*. Thermal conditions play an important role during the whole procedure, liquid density changes and density gradients due to non-uniform temperature might have a significant effect on hydrometer measurement results even in a temperature controlled set-up. Unfortunately, significant temperature gradients cannot always be avoided for practical reasons, e.g. insufficient uniformity and stability of the reference liquid and differences between the liquid and ambient temperature [6]. The temperature effect should be changes the apparent weight of the hydrometer and the density of the reference

liquid. In the present apparatus, the standard uncertainty contribution of the temperature, considering also its stability and uniformity around the hydrometer to be calibrated, results to be $u(T) =$ 0,01 °C.

d) *The reference liquid*. The density of the buoyant liquid depends mainly on temperature. The density uncertainty contribution of the reference liquid mainly depends on the method used for measuring the density, other minor contributions include the evaporation effect and the compressibility which are usually taken to be negligible. However the standard uncertainty contribution of the Nonane used as the buoyant liquid is usually $u(\rho_L) = 0{,}005$ kg m^{-3}. Its surface tensions is determined from direct measurement by using the plate or the ring method with standard uncertainty $u(\gamma_L) =$ 0,2 mN m^{-1}.

e) *Stem diameter*. An accurate caliper or a suitable instrument with a resolution between 0,01 and 0,1 mm is usually used to measure the diameter of the stem of the hydrometer to be calibrated. The uncertainty contribution, taking into account the uncertainty of the calliper and the experimental standard deviation of the measurements of the diameter at the scale mark, is $u(D) = 0{,}1$ mm.

f) *Expansion coefficient of hydrometers*. Hydrometers are usually made of a glass material with a nominal cubic coefficient of thermal expansion β of 25x10^{-6} °C^{-1} with an uncertainty of 2x10^{-6} °C^{-1} (rectangular distribution).

g) *Gravity influence*. The calibrated hydrometers are weighed in air and in the liquid at different heights. It is not normally necessary to make corrections for variations in gravitational acceleration, the standard uncertainty contribution due to the gravitational acceleration is $u(g) = 1\text{x}10^{-5}$ m s^{-2}.

h) *Operator effects and reading errors*. *Human errors* which can include inaccurate readings or misalignments of the scales on the stem of hydrometer are not present because an automatic alignment is adopted to adjust the vertical position of the hydrometer (or of the bath) so that the designed mark intersects the liquid surface correctly. The automatic vision system makes better the repeatability in the correct alignment being able to discriminate the same position in 0,1 pixel. The main components in the reading uncertainty can come from the sensitivity of hydrometers, the repeatability in the correct alignment and from the perspective error. The alignment introduces an uncertainty contribution (reading error) $u(\rho_r) = 0{,}02$ mm which is not dependent from the distance between the marks.

5. Experimental results

The assessment of the individual contributions allows us to evaluate the uncertainty for some usual kinds of hydrometers sent to INRiM for their calibration.

In obtaining the combined standard uncertainty different results are expected, that mainly comes from the value of the least scale division and the range of hydrometer to be calibrated. Generally, for each kind of hydrometer, the distance between marks is approximately constant over the whole range.

Several features of interest emerge from this, in particular about the weight that the contributions due to the density of reference liquid, the temperature of calibration and the readings exhibit in the whole assessment of uncertainty. Table 1 compares the value of the individual components of the relative uncertainty as function of the combined standard uncertainty for hydrometers having different scale division values from 0,1 kg/m^3 to 1 g/m^3 and mark distance about 1 mm.

The temperature strongly affects the uncertainty through the thermal expansion coefficient of the reference liquid, so that only the density uncertainty and the reading uncertainty have the greatest importance. It is interesting also to realize that for high resolution hydrometers (division of 0,1 kg/m^3) the density uncertainty contribution of the liquid is the main

Relative components of the uncertainty $u'(x_i)$	**Division** / kg m^{-3}			
	0,1	0,2	0,5	1
Weighing in air, $u'(M_a)$	0,002	0,002	0,005	0,006
Weighing in the liquid, $u'(M_L)$	0,027	0,025	0,058	0,084
Air density, $u'(\rho_a)$	0,010	0,008	0,003	0,001
Temperature of liquid around hydrometer, $u'(T)$	0,577	0,474	0,210	0,070
Density of the buoyant liquid, $u'(\rho_L)$	0,333	0,274	0,121	0,040
Diameter of the hydrometer stem, $u'(D)$	0,008	Negligible	Negligible	0,024
Surface tension of the buoyant liquid, $u'(\gamma_L)$	0,016	0,023	0,034	0,041
Gravitational acceleration, $u'(g)$	Negligible	Negligible	Negligible	Negligible
Readings error, $u'(\rho)$	0,027	0,204	0,569	0,734
Combined standard uncertainty $u_c(C)$ / kg m^{-3}	0,012	0,013	0,020	0,035

Table 1. Evaluation of the relative individual uncertainty contributions to the combined standard uncertainty in calibrating hydrometers with different scale division values: from 0,1 kg/m^3 to 1 kg/m^3 and mark distance about 1 mm in the density range close to 1000 kg/m^3.

Relative components of the uncertainty $u'(x_i)$	Range / kg m^{-3}		
	600 - 650	800 - 850	1000 - 1050
Weighing in air, $u'(M_a)$	Negligible	0,001	0,005
Weighing in the liquid, $u'(M_L)$	0,028	0,046	0,058
Air density, $u'(\rho_a)$	Negligible	Negligible	0,003
Temperature of liquid around hydrometer, $u'(T)$	0,117	0,173	0,210
Density of the buoyant liquid, $u'(\rho_L)$	0,068	0,100	0,121
Diameter of the hydrometer stem, $u'(D)$	Negligible	Negligible	Negligible
Surface tension of the buoyant liquid, $u'(\gamma_L)$	0,029	0,027	0,034
Gravitational acceleration, $u'(g)$	Negligible	Negligible	Negligible
Readings error, $u'(\rho)$	0,756566	0,651092	0,569
Combined standard uncertainty $u_c(C)$ / kg m^{-3}	0,017	0,019	0,020

Table 2. Evaluation of the relative individual uncertainty contributions to the combined standard uncertainty in calibrating hydrometers with scale division value 0,5 kg/m^3 and mark distance about 1 mm in the density ranges of 600 - 650 kg/m^3, 800 - 850 kg/m^3, and 1000 - 1050 kg/m^3

source leading to total uncertainty, but its importance fall under about 50 % for hydrometers with division of 0,5 kg/m^3 and becomes somewhat negligible for hydrometers with division of 1 kg/m^3, for which the reading uncertainty is the predominant part of the whole uncertainty. The Table also shows that the combined standard uncertainty values are reduced about of 50 % compared with those obtained by means of the former apparatus [3]; that mainly depends on the automatic alignment.

Table 2 considers the values of the individual components of the relative uncertainty as function of the combined standard uncertainty for hydrometers having same scale division value of 0,5 kg/m^3, mark distance about 1 mm and density ranges of 600 - 650 kg/m^3, 800 – 850 kg/m^3, and 1000 – 1050 kg/m^3 respectively. The Table also shows that the relative uncertainties due to the liquid density, the weighing in the liquid and the temperature are increasing with the density range while the relative uncertainty due to the readings error decreases. That determines a substantial constancy of the relative combined standard uncertainty for the whole range. This last consideration are also applicable to hydrometers having different scale divisions.

5. Conclusion

The measurement by hydrometers and the accuracy of measured data depend by the usual conditions under which they are used, their regular calibration is the most important prerequisite for exact and traceable measurement of density. The calibration apparatus here presented has been designed at the INRiM to make easier and more accurate all measuring procedures. The automatic alignment method introduced in calibrating hydrometers reduces errors caused by limited operator skills or attention when calibration is performed manually and, in particular, a reduction of the overall uncertainty.

In obtaining the combined standard uncertainty different results are expected, that mainly come from the value of the least scale division and the range of hydrometer to be calibrated. Generally, for each kind of hydrometer, the distance between marks is approximately constant over the whole range.

The the hydrostatic apparatus of the INRiM has been evaluated for some kinds of hydrometers usually calibrated at the Institute. Calibration uncertainty is mainly affected by the individual contributions of the density of the reference liquid, the temperature of calibration and the repeatability in the alignment of the mark to be calibrated. The density uncertainty of the reference liquid is the most important term for high resolution hydrometers (div. 0,1 kg/m^3), but its importance falls under about 50 % for hydrometers with division of 0,5 kg/m^3 and becomes somewhat negligible for hydrometers with division of 1 kg/m^3, for which the alignment (reading uncertainty) is the predominant contribution of the total uncertainty.

Considering hydrometers with the same scale division and different density ranges, the relative uncertainty results about constant over the whole range. The best relative uncertainty in the commercial hydrometers usually calibrated at the INRiM results to be between about $3 \cdot 10^{-5}$ for hydrometers with division 1 kg m^{-3} and $12 \cdot 10^{-6}$ for hydrometers with division 0,1 kg m^{-3}.

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