Hydrometer calibration by hydrostatic weighing with automated liquid surface positioning

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Abstract
We describe an automated apparatus for calibrating hydrometers by hydrostatic weighing
(Cuckow's method) in tridecane, a liquid of known, stable density, and with a relatively low
surface tension and contact angle against glass. The apparatus uses a laser light sheet and a
laser power meter to position the tridecane surface at the hydrometer scale mark to be
calibrated with an uncertainty of 0.08 mm. The calibration results have an expanded
uncertainty (with a coverage factor of 2) of 100 parts in 10^6 or less of the liquid density. We
validated the apparatus by comparisons using water, toluene, tridecane and trichloroethylene,
and found agreement within 40 parts in 10^6 or less. The new calibration method is consistent
with earlier, manual calibrations performed by NIST. When customers use calibrated
hydrometers, they may encounter uncertainties of 370 parts in 10^6 or larger due to surface
tension, contact angle and temperature effects.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The National Institute of Standards and Technology (NIST)
provides traceability for liquid density measurements through
standard reference materials and a calibration service for
hydrometers. NIST calibrated hydrometers are used by
secondary labs as working standards and thereby provide
traceability to thousands of hydrometers used in the distilling
and petroleum industries.

Until recently, NIST calibrated customers' hydrometers
by the comparison method. NIST working standard
hydrometers were periodically calibrated by floating the
hydrometer in liquids of measured density, determined by
hydrostatic weighing of a sinker of known mass and volume.
Customers' hydrometers were then calibrated by comparing
them to the NIST hydrometers in several liquids. We sought
to eliminate the collection of unsafe liquids used to carry
out the comparison method (aqueous solutions of acids or

mixtures of volatile hydrocarbons). We also wished to reduce
uncertainty, the labor involved and the cost to the customer
[1–3] by automating the hydrometer calibrations.

Therefore, the NIST Fluid Metrology Group developed
an automated apparatus for the calibration of hydrometers via
Cuckow's method [4], a hydrostatic weighing approach. The
NIST apparatus employs a laser light sheet and a laser power
meter to position the liquid surface at the stem mark to be
calibrated. This apparatus achieves an expanded uncertainty
of 100 parts in 10^6 or less. Of course, larger uncertainties
can be expected during hydrometer application because of
surface tension, contact angle, and temperature effects and we
provide sample uncertainty analyses in this paper to help users
of hydrometers assess the uncertainty of their liquid density
measurements.

2. Cuckow's method

Cuckow derived a method for a calibration laboratory to
determine the density ρ_L represented by a given scale mark on

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the hydrometer stem [4]. Force balance equations are written for a hydrometer in three conditions: (1) when floating freely in a liquid of unknown density (ρ_L), (2) when weighed in air and (3) when weighed while immersed to the same level as case 1, but in a liquid of known density. By solving the three equations simultaneously, one can derive an equation for ρ_L:

$$\rho_L = \frac{\{\rho_T[1 + \beta(T_T - T_0)] - \rho_{a2}\}\left(\alpha O_2 + \frac{\pi D \gamma_L \cos\theta_L}{g}\right)}{\alpha O_2 - \alpha O_3 + \frac{\pi D \gamma_T \cos\theta_T}{g} + m_s - V_s\rho_T[1 + \beta_s(T_T - T_0)]} + \rho_{a2},$$
(1)

with the symbols defined as:

ρ_T: known density of the liquid in the apparatus, in our case, tridecane,

β: volumetric thermal expansion coefficient of the glass from which the hydrometer is made,

T_T: temperature of the tridecane,

T_0:   reference temperature,

ρ_{a2}:   density of the air at the time the hydrometer was weighed in air,

α: calibration coefficient for the balance,

O_2:   output from the balance for the hydrometer in air,

D: diameter of the hydrometer stem at the scale mark to be calibrated,

γ_L: surface tension of the liquid in which the hydrometer is used,

θ_L: contact angle of the liquid on the hydrometer stem,

g: local acceleration due to gravity,

O_3:   output from the balance for the hydrostatic weighing,

γ_T: surface tension of tridecane,

θ_T: contact angle of the tridecane on the hydrometer stem,

m_s: mass of the stainless steel weight added to sink a hydrometer designed to measure densities less than that of tridecane,

V_s: volume of the stainless steel weight, and

β_s: volumetric thermal expansion coefficient of the stainless steel weight.

Equation (1) includes forces due to surface tension, those due to the calibration liquid (tridecane) as well as those due to the liquid in which the hydrometer is used by the customer. For liquids that wet glass, surface tension causes a meniscus to rise on the stem of a hydrometer and the weight of the meniscus pulls the hydrometer deeper into the liquid, causing the hydrometer reading to be too low. Typically, surface tension forces on hydrometers effect density measurements by about 0.2% for aqueous solutions and about 0.1% for hydrocarbon liquids.

If the value of γ_L is not known at the time of calibration (perhaps because the hydrometer will be applied in several liquids with different surface tensions) the result of the calibration can be reported as an equation that gives a correction to be added to each calibrated scale mark:

$$C_L = A + B\gamma_L \cos\theta_L$$
(2)

where

$$A = \frac{\{\rho_T[1 + \beta(T_T - T_0)] - \rho_{a2}\}\alpha O_2}{\alpha O_2 - \alpha O_3 + \frac{\pi D \gamma_T \cos\theta_T}{g} + m_s - V_s[1 + \beta_s(T_T - T_0)]\rho_T}$$
$$+ \rho_{a2} - R$$
(3)

where R is the hydrometer reading at the calibrated scale mark and

$$B = (A + R - \rho_{a2})\frac{\pi D}{\alpha O_2 g}.$$
(4)

The values of A and B are the output of a NIST calibration and in section 6 of this paper, we will give the uncertainty contributed to C_L via A and B. In section 7 of this paper, we will analyze the uncertainties that arise during application of a hydrometer using a NIST calibration. For example, the values of surface tension and contact angle in equation (2) depend on the liquid under test and the cleanliness of the hydrometer when it is used and are not included in the NIST calibration uncertainty.

3. Procedures and apparatus

Hydrometer calibration by Cuckow's method requires that the hydrometer be weighed in air and weighed while immersed to the selected scale marks in a liquid of known density, in our case, tridecane. The hydrostatic weighing process has been automated. In brief, the hydrostatic weighing process is to:

(1) Hang the hydrometer from a hook on the underside of the pan of the balance so that the stem intersects the free surface of the tridecane.

(2) With the tridecane surface below the scale mark to be calibrated, center a horizontal sheet of laser light on that selected scale mark.

(3) Raise the tridecane surface 3 mm above the scale mark and then lower it until the laser power meter mounted opposite the laser indicates a sharp decrease in the laser light intensity due to the tridecane surface being in the same plane as the scale mark to be calibrated (the 'surface positioning process', see figure 2).

(4) Stop the travel of the tridecane surface, pause for the balance readings to stabilize, and record the tridecane temperature, the reading of the balance, and the reading of the encoder that monitors the travel of the tridecane surface.

The hydrostatic weighing of the hydrometer is done with an analytical balance located on top of a cabinet of square cross section, approximately 0.5 m on an edge and 1.5 m high (see figure 1). The balance has a capacity of 205 g and a resolution of 0.0001 g. The hydrometer is hung by a chain from the underside of the pan of the balance, which is centered over a hole in the top plate of the cabinet so as to be directly above the 100 mm diameter tube containing the tridecane. This tube is mounted vertically in a cylindrical, temperature controlled bath, which is mounted on a vertical stage such that the bath-and-tube can be raised and lowered by a motor under computer control. A linear encoder (5 μm resolution) is attached to the vertical stage to monitor the position of the tridecane surface. Although the linear encoder measurements are not needed for density calculations, they are useful for calculating the repeatability of the surface positioning process. An external bath pumps temperature controlled water through the cylinder surrounding the tube of
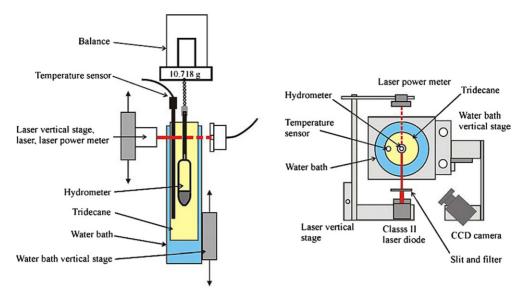
Figure 1. A schematic diagram of the hydrostatic weighing (Cuckow's) apparatus at NIST.
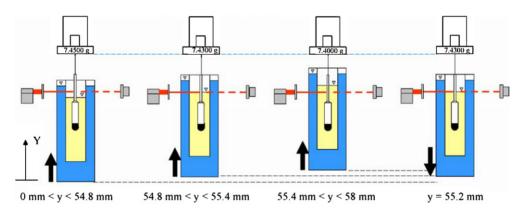

Figure 2. Surface positioning process.

tridecane. A thermometer well mounted within the tridecane supports a calibrated thermistor to measure the temperature.

A CCD camera provides an image of the hydrometer scale on the computer monitor upon which cursors are placed to indicate the scale marks to be calibrated. A self-leveling class II laser (a laser diode mounted on a magnetically dampened pendulum) is located on its own vertical stage with a motor under computer control. The thickness of the laser light sheet (0.2 mm) is defined by a 50 mm long optical slit with a polarizing filter, located between the laser and the bath-and-tube. A laser power meter is mounted on the opposite side of the bath-and-tube from the laser which detects when the tridecane surface and the scale mark to be calibrated are in the same plane by indicating a sharp decrease in the intensity of the laser light. The laser power meter output (in Ω) is acquired by the computer and used along with the bath-and-tube vertical stage by the surface positioning process. A computer program controls the number of replications at each mark and then moves the entire process onto the next mark to be calibrated. The automated hydrometer calibrator is capable of doing the hydrostatic weighing at any number of scale marks on the hydrometer scale without operator intervention. It will operate unattended overnight.

The apparatus can be operated in a semi-automatic mode wherein the operator centers the laser sheet on the scale mark to be calibrated by turning the lead screw by hand while looking directly at the scale or by looking at the CCD camera image of the scale on the computer monitor. Then the automatic features move the tridecane surface, determine when the tridecane surface is at the scale mark to be calibrated, and records the required data. The semi-automatic mode is faster than the fully automatic mode.

4. Surface positioning process

In our apparatus, the laser light sheet is centered on the hydrometer scale mark to be calibrated and the tridecane surface is aligned with the center of the laser light sheet by lowering the tridecane and looking for the decrease in intensity of the laser light measured by the laser power meter. A plot of the laser light intensity versus elevation of the tridecane surface is shown in figure 3. Figure 3 actually shows traces for three measurements at the same calibration mark to demonstrate the repeatability of the surface positioning process. The tridecane surface is raised above the mark to be calibrated by 3 mm and then lowered until the light intensity is at
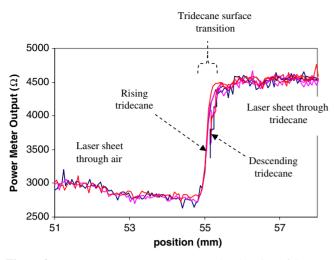
Figure 3. Laser power meter output versus the elevation of the liquid tridecane surface. As the liquid surface traverses the laser light sheet, the power meter registers the transition that we use in the surface positioning process.

the half way point of the transition to ensure a stable and reproducible meniscus on the hydrometer stem. In figure 3, at elevations from 51 mm to 54.8 mm the laser power meter outputs approximately 3000 Ω. At these elevations the laser sheet is passing through the walls of the tube and the bath, the water in the bath, and through air above the tridecane surface. At about 55 mm the light intensity moves through the transition and the power meter output rises from 3000 Ω to 4500 Ω. At tridecane elevations of 55.4 mm and above, the power meter registers the highest intensity (4500 Ω). At these elevations the laser sheet is passing through the container walls, the water and the tridecane. The three traces for the descending surface end at an elevation of about 55.2 where the surface positioning process has determined that the light intensity is at the midpoint of the transition. At this point the tridecane surface is aligned with the scale mark to be calibrated and after a 40 s wait for stabilization of the balance, its readings along with the tridecane temperature are recorded to file for later processing. The vertical stage changing the tridecane surface elevation is operated at a slow speed (0.5 mm min^{-1}) so that the surface does not overrun the desired position due to computer processing or actuation delays.

The shape of the light intensity transition is caused by (1) the lens behavior of the tridecane-filled cylinder, (2) the vertical intensity profile of the laser light sheet, and (3) refraction and reflection of the light sheet by the tridecane meniscus. The large change in intensity is due to the vessel of tridecane acting as a cylindrical lens, focusing the light onto the power meter window. The width of the transition (about 0.2 mm) is due to the width of the laser light sheet. As the tridecane is raised and a larger portion of the light sheet passes through the liquid lens, the power meter readings increase. Therefore, at the midpoint of the transition, the middle of the laser light sheet is aligned with the bottom of the meniscus. Since we align the middle of the light sheet with the hydrometer mark to be calibrated, the bottom of the meniscus is aligned with the hydrometer mark to be calibrated.

The decrease in intensity seen between 51 mm and 55 mm in figure 3 is caused by refraction and reflection of the laser light by the tridecane meniscus inside the cylinder. The angle formed by the tridecane at the cylinder wall refracts or reflects (depending on the angle of the meniscus surface) the laser light away from the power meter window. The hysteresis in the power meter output between the rising versus descending tridecane surface is caused by the non-zero contact angle on the cylinder and hydrometer.

5. Surface tension and contact angle effects

Surface tension and contact angle effects are the primary reason for our selecting tridecane as the liquid of known density. The surface tension of tridecane is relatively low (25 mN m^{-1} at 20 °C) and so all surface tension and contact error effects are about one third the magnitude of those for water. The surface tension of tridecane (and hydrocarbon liquids in general) has low sensitivity to contaminants. Also, we found that the contact angle is effectively zero for simple and safe hydrometer cleaning processes using solvents, i.e. the contact angle (measured by the sessile drop method) for tridecane on glass is only weakly sensitive to glass surface contamination.

Initially we used distilled water as the liquid of known density in our apparatus. We had difficulty obtaining reliable results due to the large sensitivity of water's surface tension and contact angle due to contaminants on the water's surface or on the hydrometer stem.

Water has large surface tension, 73 mN m^{-1} at 20 °C; however only trace contamination by detergents or hydrocarbons will reduce the surface tension by as much as 10 mN m^{-1}. An error in surface tension of 10 mN m^{-1} leads to errors of 150 parts in 10^6 for 1 g cm^{-3} hydrometer.

There is a similar problem caused by the contact angle formed by the water with the glass of the hydrometer stem. The force due to surface tension on the hydrometer stem is $\pi D \gamma \cos \theta$, where θ is the contact angle of the liquid with the hydrometer stem glass surface [5]. Derivations of the equations for Cuckow's method generally assume that the contact angle is equal to zero, so that the surface tension force is simply $\pi D \gamma$. This assumption is made because (1) it is difficult to measure the contact angle (particularly on a curved surface such as a hydrometer stem) and (2) the stem is thought to be cleaned well enough that the contact angle is effectively zero. However, we have found that many cleaning processes are not adequate to justify the zero contact angle assumption and that it is difficult to maintain the stem in a clean condition even over a period of hours. In particular, glass cleaned with solvents, finished with ethanol and air dried does not achieve an effectively zero contact angle. We note that if a hydrometer is cleaned with chromic-sulfuric acid, rinsed with water, air dried, and used immediately, the contact angle is less than 10° and $\cos(\theta)$ can be assumed equal to one. However, the glass will not remain clean for long unless carefully protected from contamination, such as oil droplets in air.

Table 1. Uncertainty analysis for a hydrometer calibrated with the NIST Cuckow's apparatus. See table 2 for extra components that arise during hydrometer usage.

Quantity	x_i	x_i value	dx_i value	Units	S_i	S_i value	$10^6\,S_i\,dx_i$
(1) Density of tridecane	ρ_T	0.756	7×10^{-6}	g cm^{-3}	$\frac{O_2-O_3+m_s}{\rho_T(O_2-O_3+m_s-\rho_T V_s)}$	1.32	9
(2) Hydrometer volume thermal expansion	β	2.5×10^{-5}	5×10^{-6}	K^{-1}	$T_T - T_0$	4.44	22
(3) Temperature of tridecane	T_T	20.0	0.008	°C	$\frac{\beta(O_2-O_3+m_s-\rho_T V_s)+\beta_s V_s \rho_T}{O_2-O_3+m_s-V_s\rho_T}$	2.5×10^{-5}	0
(4) Density of air	ρ_{a2}	1.2×10^{-3}	1×10^{-5}	g cm^{-3}	$\frac{-O_3+m_s-\rho_T V_s}{\rho_T O_2}$	-0.32	-3
(5) Hydrometer weight in air	O_2	48	0.000 15	g	$\frac{-O_3+m_s-\rho_T V_s}{O_2(O_2-O_3+m_s-\rho_T V_s)}$	-6.6×10^{-3}	-1
(6) Hydrometer weight in tridecane	O_3	11.6	0.0003	g	$\frac{1}{O_2-O_3+m_s-\rho_T V_s}$	2.8×10^{-2}	8
(7) Stem diameter	D	0.5	0.001	cm	$\frac{\pi}{g}\left[\frac{\gamma_L \cos(\theta_L)}{O_2}-\frac{\gamma_T \cos(\theta_T)}{O_2-O_3+m_s-\rho_T V_s}\right]$	-2.3×10^{-3}	2
(8) Surface tension of tridecane	γ_T	25	0.5	mN m^{-1}	$-\frac{\pi D \cos(\theta_T)}{g(O_2-O_3+m_s-\rho_T V_s)}$	-4.4×10^{-5}	-22
(9) Contact angle in tridecane	$\cos(\theta_T)$	1	0.015		$-\frac{\pi D \gamma_T}{g(O_2-O_3+m_s-\rho_T V_s)}$	-1.1×10^{-3}	-17
(10) Grav constant	g	980	1×10^{-2}	cm s^{-2}	$\frac{\pi D}{g^2}\left[\frac{\gamma_L \cos(\theta_L)}{O_2}-\frac{\gamma_T \cos(\theta_T)}{O_2-O_3+m_s-\rho_T V_s}\right]$	-1.2×10^{-6}	0
(11) Mass of sinker	m_s	0	0^a	g	$\frac{-1}{O_2-O_3+m_s-\rho_T V_s}$	-2.8×10^{-2}	0
(12) Volume of sinker	V_s	0	0^a	cm^3	$\frac{1}{O_2-O_3+m_s-\rho_T V_s}$	2.8×10^{-2}	0
(13) Volume thermal expansion of sinker	β_s	0	0^a	K^{-1}	$\frac{\rho_T V_s(T_T-T_0)}{O_2-O_3+m_s-\rho_T V_s}$	0.74	0
(14) Laser positioning	–	–	8.3×10^{-3}	cm	$\frac{1}{\rho_L}\frac{\partial \rho_L}{\partial \lambda}$	3.7×10^{-3}	31
(15) Surface positioning	–	–	2×10^{-3}	cm	$\frac{1}{\rho_L}\frac{\partial \rho_L}{\partial \lambda}$	3.7×10^{-3}	7
(16) Repeatability	–	1	1×10^{-5}	g cm^{-3}	–	1	10
Expanded uncertainty of NIST calibration						RSS $\times$ 2	101

^{a} Sinker not used for the hydrometer used in this example.

6. Uncertainty of the NIST hydrometer calibration

We analyzed the uncertainty of a density measurement caused by the NIST hydrometer calibration results (A and B in equation (2)) following the method of propagation of uncertainties [6–8]. This involved obtaining normalized sensitivity coefficients, $S_i = (1/\rho_L)(\partial \rho_L/\partial x_i)$, by partial differentiation. We also obtained standard uncertainties (dx_i) for the calibration inputs from experiments with the instruments in the apparatus. We examined a number of cases and found that the calibration results from our apparatus normally have an expanded uncertainty (coverage factor $k = 2$) of 100 parts in 10^6 or less. In the following section, we consider uncertainty components that arise during application of the hydrometer (temperature effects, the customer's surface tension and contact angle) and find that they can lead to uncertainties of 370 parts in 10^6 ($k = 2$), or larger.

Table 1 gives an uncertainty analysis for a hydrometer that we have used to measure the density of water. This hydrometer is similar in design to those that we receive for calibration. It has a span of 0.05 g cm^{-3} and each scale increment is 1.3 mm long and represents 0.0005 g cm^{-3}. The uncertainty analysis in table 1 includes only the components related to the calibration at NIST using our apparatus. Table 1 has columns for (1) the

input quantities to equation (1), (2) their variable names, (3) their values, (4) the values of the standard uncertainties ($k = 1$), (5) the units for each quantity, (6) the normalized sensitivity coefficients, (7) the values for the sensitivity coefficients and (8) the product of the normalized sensitivity coefficient and the standard uncertainty, expressed as parts in 10^6. Explanations about some of the numbered uncertainty components in table 1 will be given now.

(1) We measured the density of the tridecane used in our apparatus by hydrostatic weighing of a spherical stainless steel sinker of known mass and known volume at temperatures between 15 °C and 23 °C. The standard uncertainty of our equation for tridecane density is 5 parts in 10^6 based on uncertainty analysis of the hydrostatic weighing method. (We also measured the tridecane density with a vibrating tube densitometer that was calibrated with air and distilled water. These results agreed with the hydrostatic weighing density within 37 parts in 10^6, within the uncertainty of the densitometer.) The uncertainty of the temperature of the tridecane in the hydrometer calibration apparatus is 0.008 K and this contributes to the tridecane density uncertainty as well ($\beta_T = 710 \times 10^{-6}$ K^{-1}). The standard uncertainty of the tridecane density is 7×10^{-6} g cm^{-3}.

(2) Hydrometers are made from a variety of glasses, including borosilicate glass and soda-lime glass. The volumetric thermal expansion coefficient of these glasses varies from 9×10^{-6} K^{-1} to 26×10^{-6} K^{-1}. Unless a reliable value is specified, this component has a relatively large standard uncertainty and contributes significantly to the expanded uncertainty of the NIST calibration. This component can be reduced to negligible levels by operating the apparatus at the hydrometer reference temperature. In this example, we have operated the apparatus at 20 °C and used a reference temperature of 15.56 °C (60 °F) to illustrate that the component is significant (22 parts in 10^6 here).

(3) The temperature of the tridecane was surveyed and monitored with a thermister. The tridecane temperature within the tube was uniform within 0.003 K and stable within 0.005 K during the 3 h interval necessary to calibrate a hydrometer. Three annual calibrations of this thermister are consistent within 0.005 K. The root-sum-square (RSS) of these temperature components is 0.008 K; we will use this value as the standard uncertainty of the temperature of the tridecane.

(5) and (6) Zero drift of the balance is the primary source of uncertainty for the hydrostatic weight measurement (0.3 mg). Zero readings are checked before and after hydrometer calibrations and zero readings in error by more than 3 mg trigger re-testing. Repeatability, resolution (0.1 mg), linearity (checked periodically with calibration masses) and the uncertainty of calibration masses are negligible in comparison. For the dry weight measurement, scale resolution and linearity are the most significant components and the standard uncertainty is 0.15 mg.

(8) We measured the surface tension of our tridecane with a DuNouy tensiometer and our measurements differed from literature values [9] by 1 mN m^{-1} or less. We have taken 0.5 mN m^{-1} as the standard uncertainty.

(9) Our experiments showed that the contact angle for tridecane is small for even simple glass cleaning procedures. Our calculations assume the contact angle is zero, but we will use a standard uncertainty of 10° for our uncertainty analysis. For mathematical reasons, we will deal with the uncertainty of the term $\cos(\theta_T)$ and $\cos(\theta_L)$ rather than θ_T and θ_L.

(10) The gravitational constant g at the apparatus is 980.1018 cm s^{-2} with a standard uncertainty of 10 parts in 10^6 or less [10].

(11), (12) and (13) The sinker is needed only when calibrating hydrometers for liquids less dense than tridecane (<0.76 g cm^{-3}). When the sinker is used, the sinker uncertainty components are all less than 6 parts in 10^6, negligible compared to other components.

(14) The largest uncertainty component is one that is not explicitly found in equation (1): the alignment of the laser light sheet with the hydrometer stem mark. The uncertainty for this component depends on the pixel resolution of the camera system that we use during alignment. The standard uncertainty is one half of the pixel dimension (0.016/2 = 0.08 mm). The normalized sensitivity coefficient for this component is $(1/\rho_L)(\partial\rho_L/\partial\lambda)$ where λ is the length along the hydrometer stem. For a hydrometer of the design used in this example (1.3 mm scale increments represent

0.0005 g cm^{-3}), 0.08 mm length uncertainty corresponds to 31 parts in 10^6 density uncertainty. This uncertainty value is not changed when the laser is aligned with the scale mark by the operator instead of by the computer. We have calibrated the same stem mark repeatedly, manually moving the laser light sheet off and back onto the mark each time, and we have found the standard deviation of the calibration results to be 20 parts in 10^6.

(15) We also include a component due to alignment of the tridecane surface with the laser light sheet by the surface positioning process. The process reliably locates the midpoint of the power meter transition within 10% of the transition. The slope of the transition (see figure 3) allows us to translate the 10% uncertainty into a length and then a density uncertainty for the hydrometer stem design (7 parts in 10^6). This value is confirmed by repeatability measurements: when we leave the laser light sheet in a fixed position and use the surface positioning process repeatedly, the liquid surface position (as measured by the linear encoder) has a standard deviation of 0.016 mm, 6 parts in 10^6 for density.

(16) All of the uncertainty components discussed up to now are of type B. For a customer calibration, we include the standard deviation of five repeated measurements made at the same scale mark in the uncertainty analysis (type A). In our experience, this is always less than 10 parts in 10^6 and we have included a component of this size in table 1.

Taking the root-sum-square of the components and multiplying by 2 gives an expanded, approximately 95% confidence level uncertainty. The result is 101 parts in 10^6 ($k = 2$) for a hydrometer of the design type we calibrate most often.

In this example, the laser positioning component is the largest contributor. This component is analogous to the ability to 'read' the position of the liquid surface on the hydrometer scale and we can do this with our apparatus with standard uncertainty of 0.08 mm. This length corresponds to different density uncertainties depending on the design of the hydrometer under test. For a high resolution hydrometer, this component can drop to less than half the value in table 1. Then, the dominant uncertainty components of our apparatus become surface tension, contact angle and the hydrometer thermal expansion coefficient, and the expanded uncertainty of the calibration result falls below 100 parts in 10^6 ($k = 2$).

7. Uncertainty when the hydrometer is used

Table 2 shows uncertainty analyses for hydrometers used to measure the density of water and two hydrocarbon liquids (trichloroethylene and toluene). The table gives sample magnitudes for illustration, but users' values may be quite different. The examples are given to show hydrometer users that uncertainties other than the NIST calibration must be considered and that those extra uncertainties are significant.

Surface tension and contact angle are needed when equations (1) or (2) are used to calculate the density of a liquid. The uncertainty of these values is dependent on the liquid under

Table 2. Uncertainty for hydrometer density measurements in water, trichloroethylene and toluene, using a NIST calibration.

Liquid under test				Water				Trichloroethylene				Toluene			
Quantity	x_i	Units	S_i	x_i	dx_i	S_i	$10^6 \times S_i dx_i$	x_i	dx_i	S_i	$10^6 \times S_i dx_i$	x_i	dx_i	S_i	$10^6 \times S_i dx_i$
NIST calibration	A, B	–	–	–	–	1	50	–	–	1	44	–	–	1	39
User surface tension	γ_L	mN m^{-1}	$\frac{\pi D \cos(\theta_L)}{g O_2}$	68	2.5	3.1×10^{-5}	78	29	1	3.1×10^{-5}	17	28	1	2.7×10^{-5}	27
User contact angle	$\cos(\theta_L)$	–	$\frac{\pi D \gamma_L}{g O_2}$	0.94	0.045	2.3×10^{-3}	-102	1	0.015	5×10^{-4}	8	1	0.015	5×10^{-4}	12
T effects	T_L	°C	$\frac{1}{\rho_L} \frac{\partial \rho_L}{\partial \lambda}$	20	0.1	2×10^{-4}	20	20	0.1	1.7×10^{-3}	167	20	0.1	9×10^{-4}	92
Resolution	ρ_L	g cm^{-3}	–	1.0	1×10^{-4}	–	100	1.46	1×10^{-4}	–	68	0.87	5×10^{-5}	–	58
Expanded uncertainty of hydrometer usage						RSS $\times$ 2	344			RSS $\times$ 2	373			RSS $\times$ 2	238

Table 3. Summary of validation tests using liquids of known density.

Liquid	Density from equation of state (g cm^{-3})	Density from Cuckow's apparatus (g cm^{-3})	Difference (g cm^{-3})	Difference (parts in 10^6)
Tridecane	0.756 95	0.756 92	−0.000 03	−40
Toluene	0.867 79	0.867 78	−0.000 01	−12
Water	0.998 25	0.998 24	−0.000 01	−10
Trichloroethylene	1.465 50	1.465 51	+0.000 01	+6

test. For hydrocarbon liquids, handbook surface tension values are available and uncertainties of 1 mN m^{-1} are reasonable. Simple cleaning procedures will give contact angles of nearly zero with standard uncertainty of 10° for hydrocarbons on glass. For water and aqueous solutions, only certain cleaning procedures will give contact angles less than 20° (for instance chromic-sulfuric acid, water rinsed, air dried) and unless these procedures are used, large uncertainties must be assumed. This problem is compounded by the large values of surface tension for aqueous solutions and their large uncertainties since they are sensitive to contamination.

Uncertainty due to thermometer calibration and temperature non-uniformity of the liquid sample in which the hydrometer is floated can be large. The sensitivity coefficient is proportional to the volumetric thermal expansion coefficient of the liquid under test, about 200×10^{-6} K^{-1} for aqueous solutions, about 1000×10^{-6} K^{-1} for most hydrocarbons and 1670×10^{-6} K^{-1} for trichloroethylene. The temperature uncertainty used in table 2 is half the measurement resolution recommended in an ISO hydrometer procedure and one tenth of the allowed difference between before and after temperature measurements [11].

Two additional uncertainty components deserve mention: the density of air and the gravitational constant. Cuckow's derivation assumes that the air density buoying the emergent stem is equal during calibration and usage. We examined the case where a hydrometer was calibrated at sea level and used at an elevation of 2000 m and found that Cuckow's approximation introduced an error of less than 10 parts in 10^6, negligible relative to the uncertainties in table 2. We also note that the two instances of *g* found in equation (1) may differ since calibration and usage may occur at different latitudes or altitudes. A difference in *g* of 0.25% leads to an error of less than 10 parts in 10^6.

For water, the dominant uncertainty contributors are the surface tension and contact angle. For trichloroethylene, temperature effects dominate all others due to a large thermal expansion coefficient. In the example for a hydrometer used in toluene, the hydrometer scale has twice the resolution of the prior examples. This allows lower uncertainty from our apparatus (77 parts in 10^6, $k = 2$) and during usage (238 parts in 10^6, $k = 2$).

8. Validation with liquids of known density

The performance of the apparatus was validated with a two-step process. First we freely floated a hydrometer in a liquid of known density. We stirred the liquid, measured its temperature, floated the hydrometer and read it by eye, removed the hydrometer, stirred the liquid, and measured the temperature of the liquid again. We then used our apparatus and equation (1) to calculate the density represented by the same stem scale mark read on the freely floating hydrometer. We performed the validation tests in four liquids: tridecane, toluene, water and trichloroethylene. The resolution of the hydrometer scales was 0.0005 g cm^{-3} for all except the toluene hydrometer which had a resolution of 0.0002 g cm^{-3}. The results of the validation tests are listed in table 3. The densities based on temperature measurements and from the Cuckow's apparatus all agree within 0.000 03 g cm^{-3} (40 parts in 10^6).

The density as a function of temperature (at atmospheric pressure) for tridecane and trichloroethylene were determined by hydrostatic weighing of a sinker as described earlier (standard uncertainty 5 parts in 10^6). (The same tridecane was used for the freely floating measurements and the Cuckow's apparatus measurements.) The density as a function of temperature for the toluene sample was measured with a vibrating tube densitometer (standard uncertainty 15 parts in 10^6), using NIST Standard Reference Material 211d (toluene) as a liquid of reference density. The density of the water was calculated using the equation of Patterson and Morris [12]. We compared hydrostatic weighing and vibrating tube densitometer measurements of the density of our distilled water to the equation of Patterson and Morris and found agreement within 10 parts in 10^6. Therefore, the standard uncertainty of the density as a function of temperature equations for the liquids used in the validation experiments is always less than 15 parts in 10^6.

The validation experiments apply hydrometers in much the same way that our calibration customers do. As a result, the validation experiments are subject to the same uncertainty concerns for the freely floating test that are listed in table 2, i.e., the Cuckow's apparatus results, surface tension, contact angle, temperature and resolution, as well as the density as a function of temperature uncertainties given above. We used chromic sulfuric acid to clean the hydrometer stems for the freely floating experiments and this is critical to obtaining low uncertainty for the water validation experiment. The density agreement found in the validation experiments (40 parts in 10^6) is well within our expectations based on an uncertainty analysis (373 parts in 10^6) for the experiment.
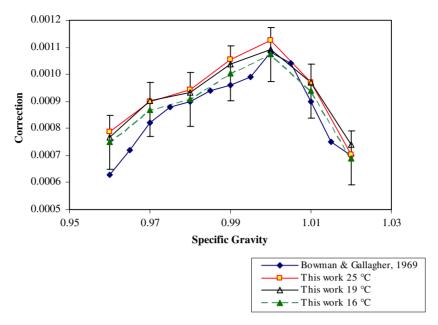
Figure 4. Corrections for hydrometer KNEK 260 from our apparatus (used at three tridecane temperatures) and from Bowman and Gallagher, 1969. Error bars are 100 parts in 10^6 from table 1.

9. Comparison to NIST historical results for a reference hydrometer

NIST has a collection of reference hydrometers that have been used to calibrate customers' hydrometers by the comparison method. The reference hydrometers have been calibrated by placing them in liquids of known density, said density determined by hydrostatic weighing of sinkers of known mass and volume. We have records of the calibration of one of these reference hydrometers (KNEK 260) by Bowman and Gallagher [13] (measured in 1956, published in 1969). We calibrated KNEK 260 in our Cuckow's apparatus at three different tridecane temperatures and the results, along with those of Bowman and Gallagher are shown in figure 4. The old and new calibrations agree within 160 parts in 10^6 over the range of density tested.

The three sets of data from our apparatus differ by as much as 40 parts in 10^6, and appear to be a function of test temperature. We believe the apparent temperature dependence is due to a small error in the value $\beta = 23 \times 10^{-6}$ K^{-1} that Bowman and Gallagher used for the volumetric thermal expansion coefficient of the KNEK 260 hydrometer. If we replace the Bowman and Gallagher value with β of 19×10^{-6} K^{-1}, the temperature dependence vanishes.

10. Summary

We constructed and validated an automated standard that calibrates hydrometers by Cuckow's method. The advantages of the automated hydrometer calibrator include:

(1) It can calibrate any number of hydrometer scale marks with any number of replications while unattended by an operator. Thus a hydrometer can be calibrated overnight.

(2) Any location on the hydrometer scale can be calibrated. This is superior to the comparison method of calibration where the location on the scale of the calibration is dictated by the density of the liquid used for the calibration.

(3) Only one user-friendly calibrating fluid is used. In the comparison method, several mixtures of sulfuric acid/water and volatile organic solvent/oil mixtures are required.

We selected tridecane as the liquid of known density in our Cuckow's apparatus since it has a relatively low surface tension (25 mN m^{-1}) that is not sensitive to contamination, and it forms a contact angle less than 10° with the glass hydrometer stem even with a simple ethanol cleaning process. It has a low vapor pressure, so we do not lose liquid due to evaporation at an unacceptable rate. It is a single component fluid: the liquid that remains will maintain a constant density as some of it evaporates.

The uncertainty of the calibration at NIST is 100 parts in 10^6 for a typical hydrometer design. Usage of a hydrometer to measure an unknown liquid density introduces several significant uncertainty components (surface tension, contact angle, temperature effects and resolution) that lead to uncertainties of 370 parts in 10^6 or more unless great care is taken. This is particularly true for aqueous solutions or liquids with large thermal expansion coefficients.

We validated our automated Cuckow's apparatus using four liquids of known density and found agreement of 40 parts in 10^6 or less, well within our uncertainty specifications. We compared the results of our apparatus with historic calibrations of one of our reference hydrometers (KNEK 260). KNEK 260 is one of the hydrometers we used as a working standard to perform comparison method calibrations of customer hydrometers. We found that the old and new calibrations

agree within 160 parts in 10^6, indicating that changing to our new calibration method should not introduce any significant discontinuity in the results of calibrations performed by NIST. We tested KNEK 260 at tridecane temperatures ranging from 16 °C to 25 °C and obtained consistent results within our uncertainty for the thermal expansion coefficient of the hydrometer.

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