



# National Institute of Standards & Technology

## Certificate

### Standard Reference Material<sup>®</sup> 211d

#### Toluene Liquid Density—Extended Range

This Standard Reference Material (SRM) is intended for use as a calibration material for densimeters. SRM 211d is liquid toluene characterized for density,  $\rho(t,p)$ , in the temperature range of  $-50\text{ }^{\circ}\text{C}$  to  $150\text{ }^{\circ}\text{C}$ , with pressures up to 30 MPa. A unit consists of four flame-sealed glass ampoules, each containing approximately 5 mL of toluene. Certified values and uncertainties are given for two cases: a special case for near-ambient conditions and the general case covering a wide range of temperature and pressure for degassed and air-saturated samples.

**Certified Values and Uncertainties:** A NIST certified value is a value for which NIST has the highest confidence in its accuracy and that all known or suspected sources of bias have been investigated or accounted for by NIST. The certified values are based on instrumental measurements implementing absolute methods for density determination. These determinations are directly traceable to SI quantities of mass, length, temperature, and pressure. Reference 1 describes the hydrostatic weighing apparatus and procedures for the near-ambient measurements. References 2 and 3 describe the two-sinker densimeter used for the measurements over wide ranges of temperature and pressure and the statistical analysis of these data. The expanded uncertainties are approximate 95 % intervals for toluene density that incorporate standard uncertainties for random measurement variability, day-to-day measurement variability, variability in toluene density from ampoule-to-ampoule, uncertainties in instrument calibration, and, for the wide-ranging measurements, also variability in toluene density resulting from exposure to high temperature during the measurements and varying degrees of air saturation. The true density of each ampoule of this material will lie within the associated uncertainty interval with high probability within the certified temperature and pressure range.

**Expiration of Certification:** The certification of this SRM is valid within the measurement uncertainties specified, until **31 December 2018**, provided that the SRM is used in accordance with the instructions given in this certificate (see "Instructions for Use"). The certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

**Maintenance of SRM Certification:** NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

The overall direction and coordination of the technical measurements leading to certification were provided by M.O. McLinden of the NIST Thermophysical Properties Division.

Characterization of this SRM was performed by M.O. McLinden of the NIST Thermophysical Properties Division. Characterization of this SRM at the near-ambient conditions ( $t = 15\text{ }^{\circ}\text{C}$  to  $25\text{ }^{\circ}\text{C}$ ,  $p = 0.10\text{ MPa}$ ) was performed by J.F. Houser and V.E. Bean of the NIST Process Measurements Division.

Daniel G. Friend, Chief  
Thermophysical Properties Division

Gaithersburg, MD 20899  
Certificate Issue Date: 12 August 2009

Robert L. Watters Jr., Chief  
Measurement Services Division

Statistical analysis was provided by J.D. Splett of the NIST Statistical Engineering Division. W.F. Guthrie of the NIST Statistical Engineering Division provided the statistical analysis of the near-ambient conditions ( $t = 15\text{ }^{\circ}\text{C}$  to  $25\text{ }^{\circ}\text{C}$ ,  $p = 0.10\text{ MPa}$ ) and also the analysis of the ampoule-to-ampoule variability.

The support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the NIST Measurement Services Division.

## NOTICE AND WARNING TO USERS

**Handling:** This material should be handled with care. Use proper disposal methods.

**Storage:** Sealed ampoules, as received, should be stored in the dark at temperatures lower than  $30\text{ }^{\circ}\text{C}$ .

## INSTRUCTIONS FOR USE

The sample tube of the densimeter being calibrated should be cleaned according to the manufacturer's instructions. When an ampoule is to be opened, the area of the stem where the prescored band is located (~5 mm below the encircling metallic band) should be carefully wiped with a clean, damp cloth, then dried, and the body of the ampoule wrapped in absorbent material. Then, wearing gloves and holding the ampoule upright and steady and with thumb and forefinger grasping the stem at the metallic band, **minimal** thumb pressure should be applied to the stem to snap it. (Correctly done, the stem should break easily where prescored. Use of a metal file to break the stem is not recommended.) After opening the ampoule, the entire contents should be transferred immediately to a clean glass syringe. Injection of the toluene into the densimeter should be done according to the densimeter manufacturer's instructions. A plastic syringe should **NOT** be used as the toluene may dissolve the plastic.

Exposure to air should be minimized and/or the sample degassed before use. The sample can be degassed by transferring it to a separate container, freezing by immersing it in liquid nitrogen, and evacuating the vapor space; the sample is then allowed to thaw, and the freeze/pump/thaw procedure is repeated a total of three times. If exposed to the atmosphere, the SRM will dissolve air, changing its density and increasing the uncertainty of the density value. If it is not possible to keep the sample in a degassed state, it should be stored in a dry environment, such as a dessicator, once the vial is opened; the correction for an air-saturated sample (Equation 4 and/or Table 5) should then be applied.

**Source and Preparation of Material:** The toluene used to produce this SRM was obtained from a commercial source. It was flame-sealed in glass ampoules, each containing approximately 5 mL of the liquid.

## SPECIAL CASE: NEAR-AMBIENT CONDITIONS

For the special case of the temperature range of 15 °C to 25 °C and normal atmospheric pressure (0.10 MPa), the certified values of the density and their expanded uncertainties are given in Table 1 and by the interpolation equation, valid between 15 °C and 25 °C:

$$\rho(t) = 866.828 \left[ 1 - 1.07356 \times 10^{-3} (t - 20) - 2.26227 \times 10^{-7} (t - 20)^2 \right] \quad (1)$$

where  $\rho$  is the density in kg/m<sup>3</sup>, and  $t$  is the sample temperature in °C.

Table 1. Certified Values and Expanded Uncertainties ( $k = 2.01$ ) for Liquid Density of SRM 211d at Three Near-Ambient Sample Temperatures and Normal Atmospheric Pressure

Temperature (°C)	Density (kg/m <sup>3</sup> )
15.000	871.476 ± 0.025
20.000	866.828 ± 0.025
25.000	862.170 ± 0.025

The expanded uncertainties listed in Table 1 are based on a coverage factor of  $k = 2.01$  from the Student's  $t$ -distribution with 46 effective degrees of freedom [4]. The uncertainty in results obtained using the interpolation equation will also depend upon the uncertainty in the user's temperature measurement. The expanded uncertainty  $U$  ( $k = 2$ ) associated with values obtained from Equation 1 is

$$U = 2 \cdot \left[ 1.6 \times 10^{-4} + 0.9 \{u(t)\}^2 \right]^{0.5} \quad (2)$$

where  $u(t)$  is the standard ( $k = 1$ ) uncertainty in °C for the user's measurement of the sample temperature. Table 2 gives the expanded uncertainty computed using Equation 2 for some example values of  $u(t)$ . If the uncertainty of the user's temperature measurement is not based on a large number of effective degrees of freedom ( $> 30$ ), then the user should replace the coverage factor,  $k = 2$ , in Equation 2 with a coverage factor obtained from the Student's  $t$ -distribution using the methods in the ISO Guide [4].

Table 2. Expanded Uncertainties from the Interpolation Equation for Some Examples of Uncertainties in Measurement of the Sample Temperature

$u(t)$ (°C)	$U$ (kg/m <sup>3</sup> )
0.001	0.025
0.01	0.032
0.1	0.19

## GENERAL CASE: WIDE RANGES OF TEMPERATURE AND PRESSURE

The general case represents the density at any point within the temperature range of  $-50\text{ }^{\circ}\text{C}$  to  $150\text{ }^{\circ}\text{C}$ , with pressures up to 30 MPa. The certified values of the density are given by Equation 4.

### Interpolating Equation (Model Surface)

The density values for degassed samples have been computed using the following empirical model:

$$\rho = \sum_{i=1}^8 a_i \left( \frac{t + 273.15}{100} \right)^{b_i} p^{c_i} \quad (3)$$

where  $\rho$  is the density in  $\text{kg}/\text{m}^3$ ,  $t$  is temperature in  $^{\circ}\text{C}$ , and  $p$  is pressure in MPa. The model parameter values  $a_i$ ,  $b_i$ , and  $c_i$  in Equation 3 were determined based on 975 density measurements collected on degassed material over a range of temperatures and pressures, as reported in Reference 3. Estimated parameter values are given in Table 3.

A correction is added to Equation 3 to adjust the computed density values for any air dissolved in the sample at the time of measurement, so that the interpolating equation becomes

$$\rho_{\Delta} = \rho + \Delta \quad (4)$$

where  $\Delta = F_{\text{air}} \cdot g$ . The quantity,  $F_{\text{air}}$ , is the fraction of air dissolved in the sample relative to a sample saturated with air at  $20\text{ }^{\circ}\text{C}$  and 0.1 MPa pressure and  $g$  is the density *correction* in  $\text{kg}/\text{m}^3$  for an air-saturated sample. The value of  $g$  is determined by an empirical function:

$$g = -0.054910 - 3.1589 \times 10^{-4} \cdot t + 5.6019 \times 10^{-5} \cdot p - 2.32 \times 10^{-6} \cdot t \cdot p \quad (5)$$

where  $t$  is temperature in  $^{\circ}\text{C}$ , and  $p$  is pressure in MPa.  $F_{\text{air}}$  is zero for a degassed sample and 1.0 for toluene saturated with air at  $20\text{ }^{\circ}\text{C}$  and 0.1 MPa pressure. The SRM 211d material, as shipped, has  $F_{\text{air}} = 0.59$ . It is the user's responsibility to determine the appropriate value of  $F_{\text{air}}$  for their measurements.

For a degassed sample, the empirical model (Equation 4 with  $\Delta = F_{\text{air}} \cdot g = 0.0$ ) can be used to calculate the density for any temperature in the range of  $-50\text{ }^{\circ}\text{C}$  to  $150\text{ }^{\circ}\text{C}$  and any pressure up to 30 MPa. Table 4 lists certified densities for convenient temperatures and pressures based on Equation 4 with  $\Delta = F_{\text{air}} \cdot g = 0.0$ .

The density correction  $g$  represents the change in density resulting from toluene saturated with dry air at a temperature of  $20\text{ }^{\circ}\text{C}$  and pressure of 0.1 MPa compared to degassed toluene. While Equation 5 is valid over a range of  $t$  and  $p$ , it represents only the case of toluene equilibrated with dry air at  $20\text{ }^{\circ}\text{C}$  and 0.1 MPa and then measured over a range of  $t$  and  $p$ . The value of  $g$  is  $-0.0612\text{ kg}/\text{m}^3$  at  $t = 20\text{ }^{\circ}\text{C}$  and  $p = 0.1\text{ MPa}$ ; it ranges from  $-0.0357\text{ kg}/\text{m}^3$  at  $t = -50\text{ }^{\circ}\text{C}$  and  $p = 20\text{ MPa}$  to  $-0.0900\text{ kg}/\text{m}^3$  at  $t = 100\text{ }^{\circ}\text{C}$  and  $p = 20\text{ MPa}$ . The estimated uncertainty in  $g$  is  $0.007\text{ kg}/\text{m}^3$  with 224 degrees of freedom. Equation 5 is valid over the temperature range  $-50\text{ }^{\circ}\text{C}$  to  $100\text{ }^{\circ}\text{C}$  and pressures up to 20 MPa. There is evidence that toluene reacts with air at temperatures above  $100\text{ }^{\circ}\text{C}$ , and thus Equation 5 does not apply at higher temperatures.

Table 4 lists densities for convenient temperatures and pressures based on Equation 4 for a *degassed* sample of toluene ( $\Delta = 0.0$ ). Table 5 gives the density *correction*,  $g$ , for a sample saturated with air at  $t = 20\text{ }^{\circ}\text{C}$  and  $p = 0.1\text{ MPa}$  based on Equations 4 and 5 with ( $F_{\text{air}} = 1.0$ ). Finally, Table 6 lists densities for convenient temperatures and pressures based on Equations 4 and 5 for the SRM 211d *as shipped* ( $F_{\text{air}} = 0.59$ ).

Table 3. Coefficients to Equation 3 — Model Surface for the Density of *Degassed* Toluene Over the Temperature Range of  $-50\text{ }^{\circ}\text{C}$  to  $150\text{ }^{\circ}\text{C}$  (with Pressures up to 30 MPa)

$i$	$a_i$	$b_i$	$c_i$
1	$0.118648 \times 10^4$	0	0
2	$-0.133648 \times 10^3$	0.80	0
3	$-0.119260 \times 10^{-1}$	5.34	0
4	0.229402	0.10	1.00
5	$0.187212 \times 10^{-4}$	7.60	1.00
6	$0.661127 \times 10^{-1}$	2.20	1.15
7	$-0.249953 \times 10^{-1}$	2.24	1.30
8	$-0.280091 \times 10^{-5}$	7.93	1.30

Table 4. Certified Values for Liquid Density ( $\text{kg}/\text{m}^3$ ) of *Degassed* SRM 211d ( $F_{\text{air}} = 0.0$ ) Over the Temperature Range of  $-50\text{ }^{\circ}\text{C}$  to  $150\text{ }^{\circ}\text{C}$  (with Pressures up to 30 MPa)

Temperature ( $^{\circ}\text{C}$ )	Pressure (MPa)								
	0.1	1.0	2.0	5.0	10.0	15.0	20.0	25.0	30.0
-50	931.655	932.100	932.605	934.118	936.595	939.011	941.370	943.678	945.937
-40	922.362	922.833	923.366	924.963	927.573	930.114	932.592	935.012	937.377
-30	913.101	913.598	914.162	915.848	918.600	921.274	923.877	926.415	928.893
-20	903.860	904.386	904.982	906.763	909.665	912.481	915.216	917.879	920.475
-10	894.627	895.184	895.815	897.699	900.762	903.726	906.602	909.397	912.118
0	885.392	885.982	886.651	888.645	891.878	895.002	898.027	900.962	903.813
10	876.142	876.769	877.478	879.589	883.006	886.300	889.482	892.564	895.554
20	866.864	867.531	868.284	870.522	874.136	877.610	880.960	884.198	887.334
30	857.545	858.255	859.056	861.432	865.257	868.924	872.453	875.856	879.145
40	848.170	848.929	849.782	852.307	856.359	860.233	863.952	867.530	870.982
50	838.726	839.537	840.448	843.134	847.432	851.529	855.450	859.215	862.838
60	829.195	830.065	831.038	833.902	838.466	842.802	846.939	850.902	854.706
70	819.562	820.496	821.539	824.597	829.450	834.043	838.413	842.586	846.581
80	809.808	810.815	811.935	815.205	820.373	825.244	829.863	834.260	838.458
90	799.916	801.003	802.208	805.713	811.225	816.397	821.283	825.919	830.330
100	789.865	791.043	792.342	796.106	801.994	807.492	812.665	817.556	822.194
110	779.634	780.914	782.318	786.369	792.669	798.521	804.005	809.167	814.044
120	*	770.596	772.118	776.486	783.239	789.478	795.295	800.748	805.878
130	*	760.069	761.722	766.443	773.694	780.353	786.531	792.294	797.691
140	*	749.309	751.110	756.222	764.022	771.140	777.707	783.803	789.481
150	*	738.293	740.259	745.808	754.214	761.832	768.820	775.270	781.246

\* above the normal boiling-point temperature (liquid phase not stable at  $p = 0.1\text{ MPa}$ )

Table 5. Values for the Liquid Density Correction  $g$  ( $\text{kg/m}^3$ ) for a Toluene Sample Saturated with Air at  $t = 20\text{ }^\circ\text{C}$  and  $p = 0.1\text{ MPa}$  Over the Temperature Range of  $-50\text{ }^\circ\text{C}$  to  $100\text{ }^\circ\text{C}$  (with Pressures up to 20 MPa).

Temperature ( $^\circ\text{C}$ )	Pressure (MPa)						
	0.1	1.0	2.0	5.0	10.0	15.0	20.0
-50	-0.0391	-0.0389	-0.0388	-0.0383	-0.0374	-0.0365	-0.0357
-40	-0.0423	-0.0421	-0.0420	-0.0415	-0.0408	-0.0400	-0.0393
-30	-0.0454	-0.0453	-0.0452	-0.0448	-0.0442	-0.0435	-0.0429
-20	-0.0486	-0.0485	-0.0484	-0.0481	-0.0476	-0.0471	-0.0465
-10	-0.0517	-0.0517	-0.0516	-0.0514	-0.0510	-0.0506	-0.0502
0	-0.0549	-0.0549	-0.0548	-0.0546	-0.0543	-0.0541	-0.0538
10	-0.0581	-0.0580	-0.0580	-0.0579	-0.0577	-0.0576	-0.0574
20	-0.0612	-0.0612	-0.0612	-0.0612	-0.0611	-0.0611	-0.0610
30	-0.0644	-0.0644	-0.0644	-0.0645	-0.0645	-0.0646	-0.0647
40	-0.0675	-0.0676	-0.0676	-0.0677	-0.0679	-0.0681	-0.0683
50	-0.0707	-0.0708	-0.0708	-0.0710	-0.0713	-0.0716	-0.0719
60	-0.0739	-0.0739	-0.0740	-0.0743	-0.0747	-0.0751	-0.0755
70	-0.0770	-0.0771	-0.0772	-0.0776	-0.0781	-0.0786	-0.0791
80	-0.0802	-0.0803	-0.0804	-0.0808	-0.0815	-0.0821	-0.0828
90	-0.0834	-0.0835	-0.0836	-0.0841	-0.0849	-0.0856	-0.0864
100	-0.0865	-0.0867	-0.0869	-0.0874	-0.0883	-0.0891	-0.0900

Table 6. Certified Values for Liquid Density ( $\text{kg/m}^3$ ) of SRM 211d *as shipped* ( $F_{\text{air}} = 0.59$ ) Over the Temperature Range of  $-50\text{ }^\circ\text{C}$  to  $100\text{ }^\circ\text{C}$  (with Pressures up to 20 MPa).

Temperature ( $^\circ\text{C}$ )	Pressure (MPa)						
	0.1	1.0	2.0	5.0	10.0	15.0	20.0
-50	931.632	932.077	932.583	934.096	936.573	938.990	941.349
-40	922.338	922.808	923.342	924.939	927.549	930.091	932.569
-30	913.074	913.571	914.135	915.822	918.573	921.248	923.852
-20	903.831	904.357	904.953	906.735	909.637	912.453	915.189
-10	894.597	895.154	895.785	897.669	900.732	903.697	906.573
0	885.360	885.950	886.619	888.612	891.846	894.971	897.995
10	876.108	876.735	877.444	879.555	882.972	886.266	889.449
20	866.828	867.495	868.248	870.486	874.100	877.574	880.924
30	857.507	858.217	859.018	861.394	865.219	868.886	872.414
40	848.131	848.889	849.742	852.267	856.319	860.193	863.911
50	838.684	839.495	840.406	843.092	847.390	851.487	855.408
60	829.152	830.021	830.995	833.858	838.422	842.757	846.895
70	819.516	820.451	821.494	824.551	829.404	833.997	838.366
80	809.761	810.768	811.887	815.157	820.325	825.196	829.814
90	799.867	800.954	802.159	805.663	811.175	816.346	821.232
100	789.814	790.991	792.291	796.054	801.941	807.439	812.612

## Combined Standard Uncertainty of Fluid Density

The combined standard uncertainty associated with a fluid density  $\rho_{\Delta}$  from Equation (4) is:

$$u_c = \left[ u^2(\rho) + u^2(V) + u^2(e) + u^2(x) + u^2(\Delta) + u^2(tp) \right]^{0.5} \quad (6)$$

where  $u(\rho)$  is the uncertainty associated with the empirical model, Equation 3;  $u(V)$  is the uncertainty associated with the variability between the SRM ampoules (vials), as determined by measurements carried out at near-ambient conditions;  $u(e)$  is the uncertainty associated with a single experimental density measurement, which we can think of as method/apparatus error; and  $u(x)$  is the uncertainty associated with any possible degradation (*i.e.*, change in chemical composition) of the sample resulting from exposing it to high temperatures. The uncertainty associated with an air-saturated sample (if applicable) is  $u(\Delta)$ . The final uncertainty component  $u(tp)$  represents the uncertainty associated with the user's temperature and pressure measurements.

The value of  $u(\rho)$  is  $0.0086 \text{ kg/m}^3$ , and can be thought of as model error. The value of  $u(V)$ ,  $0.0114 \text{ kg/m}^3$ , represents the combined ampoule-to-ampoule, day-to-day, and apparatus uncertainties provided in the report of analysis for near-ambient conditions [1]. We assume the uncertainty due to ampoule measurement errors is the same for all temperatures and pressures. The value of  $u(x)$  is estimated to be less than  $0.003 \text{ kg/m}^3$ , based on replicate measurements at  $40 \text{ }^\circ\text{C}$  made before and after heating a sample of degassed toluene to a maximum temperature of  $200 \text{ }^\circ\text{C}$ ; the sample was at  $100 \text{ }^\circ\text{C}$  or higher for a total of 238 hours. The value of  $u(e)$  was computed for each of the 975 density measurements using the procedures described in Reference 3. To predict  $u(e)$  for given values of temperature and pressure, a polynomial equation was fitted to the  $u(e)$  surface:

$$u(e) = \begin{cases} 0.0267 + 2.064 \times 10^{-6} \cdot t + 2.468 \times 10^{-6} \cdot t^2 - 1.88661 \times 10^{-8} \cdot t^3 + 4.56257 \times 10^{-11} \cdot t^4 \\ + 4.6622 \times 10^{-5} \cdot p + 3.415 \times 10^{-6} \cdot p^2 \end{cases} \quad (7)$$

where  $u(e)$  is the estimated uncertainty in the density in  $\text{kg/m}^3$ ,  $t$  is temperature in  $^\circ\text{C}$ , and  $p$  is pressure in MPa. The error introduced into  $u(e)$  by using Equation 7 is negligible compared to the magnitude of  $u(e)$ .

The uncertainties due to the sum of the “model,” “vial,” “method,” and “degradation” error sources

$$u_N = \left[ u^2(\rho) + u^2(V) + u^2(e) + u^2(x) \right]^{0.5} \quad (8)$$

are given in Table 7 for the same temperatures and pressures as Table 4. Because  $u(e)$  depends on temperature and pressure, the value of  $u_N$  and its degrees of freedom also depend on temperature and pressure. The degrees of freedom associated with the values of  $u_N$  given in table 7 range from 10 at higher temperatures to 15 at lower temperatures. A conservative estimate of the degrees of freedom associated with  $u_N$  is 10.

The value of  $u(\Delta)$  depends on the user's level of air saturation in the sample and is computed using

$$u(\Delta) = \left[ \left( g \cdot u(F_{\text{air}}) \right)^2 + \left( F_{\text{air}} \cdot u(g) \right)^2 \right]^{0.5} \quad (9)$$

where  $g$  is computed using Equation 5, and  $F_{\text{air}}$  is specified by the user. The quantity  $u(g)$  is estimated to be  $0.007 \text{ kg/m}^3$  (with 224 degrees of freedom), if the sample has been exposed to air, while  $u(F_{\text{air}})$  is determined by the user. For a degassed sample, both  $\Delta$  and  $u(\Delta)$  are zero.

The final uncertainty component,  $u(tp)$ , depends on the *user's* temperature and pressure uncertainties. Since each user's measurement apparatus is different, we performed a sensitivity study for the density (Equation 3) by varying temperature and pressure at nine combinations of uncertainty levels and quantifying the effect on density; the resulting  $u(tp)$  are given in Table 8. It is ultimately left for the user to estimate  $u(tp)$  and its associated degrees of freedom.

Table 7. Standard Uncertainties  $u_N$  ( $k = 1$ ) in Liquid Density ( $\text{kg/m}^3$ ) of SRM 211d  
Over the Temperature Range of  $-50$  °C to  $150$  °C (with Pressures up to 30 MPa)  
Due to “Model,” “Vial,” “Method,” and “Degradation” Error Sources.

Temperature (°C)	Pressure (MPa)								
	0.1	1.0	2.0	5.0	10.0	15.0	20.0	25.0	30.0
-50	0.038	0.038	0.038	0.039	0.039	0.040	0.040	0.041	0.042
-40	0.035	0.035	0.035	0.035	0.036	0.036	0.037	0.038	0.039
-30	0.033	0.033	0.033	0.033	0.034	0.034	0.035	0.036	0.037
-20	0.031	0.031	0.031	0.032	0.032	0.033	0.033	0.034	0.035
-10	0.031	0.031	0.031	0.031	0.031	0.032	0.033	0.034	0.035
0	0.030	0.030	0.031	0.031	0.031	0.032	0.032	0.033	0.034
10	0.031	0.031	0.031	0.031	0.031	0.032	0.033	0.034	0.035
20	0.031	0.031	0.031	0.031	0.032	0.033	0.033	0.034	0.035
30	0.032	0.032	0.032	0.032	0.033	0.033	0.034	0.035	0.036
40	0.033	0.033	0.033	0.033	0.034	0.034	0.035	0.036	0.037
50	0.034	0.034	0.034	0.034	0.035	0.036	0.036	0.037	0.038
60	0.035	0.035	0.035	0.036	0.036	0.037	0.037	0.038	0.039
70	0.037	0.037	0.037	0.037	0.037	0.038	0.039	0.040	0.041
80	0.038	0.038	0.038	0.038	0.039	0.039	0.040	0.041	0.042
90	0.039	0.039	0.039	0.039	0.040	0.040	0.041	0.042	0.043
100	0.040	0.040	0.040	0.040	0.041	0.041	0.042	0.043	0.044
110	0.041	0.041	0.041	0.041	0.042	0.042	0.043	0.044	0.045
120	*	0.042	0.042	0.042	0.043	0.043	0.044	0.045	0.046
130	*	0.043	0.043	0.043	0.044	0.044	0.045	0.046	0.047
140	*	0.044	0.044	0.044	0.044	0.045	0.046	0.047	0.048
150	*	0.044	0.045	0.045	0.045	0.046	0.047	0.048	0.049

\* above the normal boiling-point temperature (liquid phase not stable at  $p = 0.1$  MPa)

Table 8. Estimated Standard Uncertainty in Density  $u(tp)$  Due to User’s Temperature and Pressure Uncertainty

$u(t)$ (°C)	$u(p)$ (MPa)	$u(tp)$ ( $\text{kg/m}^3$ )
0.001	0.001	0.001
0.001	0.01	0.005
0.001	0.1	0.051
0.01	0.001	0.005
0.01	0.01	0.007
0.01	0.1	0.051
0.1	0.001	0.053
0.1	0.01	0.054
0.1	0.1	0.075

## Expanded Uncertainty of Fluid Density

We recommend computing the effective degrees of freedom associated with the combined standard uncertainty  $u_c$  to determine the appropriate coverage factor ( $t$ -table value) for computing the expanded uncertainty. Effective degrees of freedom can be computed using the Welch-Satterthwaite approximation as described in Reference 4. For the case where the samples are degassed and  $u(tp)$  is negligible, the coverage factor for a 95 % uncertainty interval is  $k = 2.228$ , based on our conservative estimate of 10 degrees of freedom.

**Example 1.** We would like to estimate the density and its expanded uncertainty at  $t = 40$  °C and  $p = 10$  MPa; the sample has been degassed. The density calculated by Equation 4 is  $856.359 \text{ kg/m}^3$ . Similarly,  $u(e) = 0.031 \text{ kg/m}^3$  is calculated by Equation 7. Since the sample is degassed, the  $\Delta$  correction and its uncertainty  $u(\Delta)$  are both zero. If the user's temperature and pressure uncertainties are estimated to be  $0.1$  °C and  $0.01$  MPa, respectively, then from Table 8,  $u(tp) = 0.054 \text{ kg/m}^3$ . The combined standard uncertainty of the density is

$$\begin{aligned} u_c &= \left[ u^2(\rho) + u^2(V) + u^2(e) + u^2(x) + u^2(\Delta) + u^2(tp) \right]^{0.5} \\ &= \left[ (0.0086 \text{ kg/m}^3)^2 + (0.0114 \text{ kg/m}^3)^2 + (0.031 \text{ kg/m}^3)^2 \right. \\ &\quad \left. + (0.003 \text{ kg/m}^3)^2 + (0.0)^2 + (0.054 \text{ kg/m}^3)^2 \right]^{0.5} \\ &= 0.064 \text{ kg/m}^3 \end{aligned} \quad (10)$$

The density can also be found in Table 4, and we can simplify the uncertainty calculations by using the information in Table 7 so that

$$\begin{aligned} u_c &= \left[ u_N^2 + u^2(tp) \right]^{0.5} \\ &= \left[ (0.034 \text{ kg/m}^3)^2 + (0.054 \text{ kg/m}^3)^2 \right]^{0.5} \\ &= 0.064 \text{ kg/m}^3 \end{aligned} \quad (11)$$

The conservative estimate of the degrees of freedom associated with  $u_N$  is 10, and assuming  $u(tp)$  has 30 degrees of freedom, the effective degrees of freedom, calculated using the Welch-Satterthwaite approximation, are

$$df_{\text{eff}} = \frac{u_c^4}{\frac{u_N^4}{df_N} + \frac{u^4(tp)}{df_p}} = \frac{(0.064 \text{ kg/m}^3)^4}{\frac{(0.034 \text{ kg/m}^3)^4}{10} + \frac{(0.054 \text{ kg/m}^3)^4}{30}} = 40.2 \quad (12)$$

which truncates to 40. From the  $t$ -table, a coverage factor of  $t_{1-\alpha/2, df} = t_{0.975, 40} = 2.021$  is appropriate for a 95 % uncertainty interval. The expanded uncertainty  $U$  is obtained by multiplying  $u_c$  by 2.021 so that  $U = 0.129 \text{ kg/m}^3$ .

**Example 2.** Suppose the sample in Example 1 is measured *as shipped* so that  $F_{\text{air}} = 0.59$ . From Table 5, the  $g$  correction is given as  $-0.0679 \text{ kg/m}^3$ , and  $\Delta = F_{\text{air}} \cdot g = 0.59(-0.0679 \text{ kg/m}^3) = -0.041 \text{ kg/m}^3$ . The corrected density value is

$$\rho_{\Delta} = \rho + \Delta = 856.359 \text{ kg/m}^3 - 0.041 \text{ kg/m}^3 = 856.319 \text{ kg/m}^3 \quad (13)$$

which can also be found in Table 6. Next, we compute the value of  $u(\Delta)$  from Equation 9. The value of  $u(g)$  was given previously as  $0.007 \text{ kg/m}^3$  (with 224 degrees of freedom), and we will assume  $u(F_{\text{air}}) = 0.058$  (with 8 degrees of freedom). The uncertainty of the  $\Delta$  correction is

$$\begin{aligned}
u(\Delta) &= \left[ (g \cdot u(F_{\text{air}}))^2 + (F_{\text{air}} \cdot u(g))^2 \right]^{0.5} \\
&= \left[ ((-0.0679 \text{ kg/m}^3) \cdot (0.058))^2 + ((0.59) \cdot (0.007 \text{ kg/m}^3))^2 \right]^{0.5} \\
&= 0.006 \text{ kg/m}^3
\end{aligned} \tag{14}$$

with degrees of freedom

$$df_{\Delta} = \frac{u_c^4}{\frac{[g \cdot u(F_{\text{air}})]^4}{df_{F_{\text{air}}}} + \frac{[F_{\text{air}} \cdot u(g)]^4}{df_g}} = \frac{(0.006 \text{ kg/m}^3)^4}{\frac{(-0.0679 \text{ kg/m}^3 \cdot 0.058)^4}{8} + \frac{(0.59 \cdot 0.007 \text{ kg/m}^3)^4}{224}} = 41.3 \tag{15}$$

which truncates to 41. The combined standard uncertainty of the final density estimate is

$$\begin{aligned}
u_c &= \left[ u_N^2 + u^2(\Delta) + u^2(tp) \right]^{0.5} \\
&= \left[ (0.034 \text{ kg/m}^3)^2 + (0.006 \text{ kg/m}^3)^2 + (0.054 \text{ kg/m}^3)^2 \right]^{0.5} \\
&= 0.064 \text{ kg/m}^3
\end{aligned} \tag{16}$$

The effective degrees of freedom, calculated using the Welch-Satterthwaite approximation, are

$$df_{\text{eff}} = \frac{u_c^4}{\frac{u_N^4}{df_N} + \frac{u^4(\Delta)}{df_{\Delta}} + \frac{u^4(tp)}{df_{tp}}} = \frac{(0.064 \text{ kg/m}^3)^4}{\frac{(0.034 \text{ kg/m}^3)^4}{14} + \frac{(0.006 \text{ kg/m}^3)^4}{41} + \frac{(0.054 \text{ kg/m}^3)^4}{30}} = 44.3 \tag{17}$$

which truncates to 44. From the *t*-table, a coverage factor of  $t_{1-\alpha/2, df} = t_{0.975, 44} = 2.015$  is appropriate for a two-sided 95 % uncertainty interval. The expanded uncertainty *U* is obtained by multiplying  $u_c$  by 2.015 so that  $U = 0.129 \text{ kg/m}^3$ . Although the uncertainty of the  $\Delta$  correction is negligible for this example, it is important to perform the analysis since  $u(\Delta)$  depends on both *g*,  $F_{\text{air}}$ , and their associated uncertainties.

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