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Evaluation of the air density uncertainty: the effect of the correlation of input quantities and higher order terms in the Taylor series expansion

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Abstract
Air density uncertainty is usually evaluated as if its input quantities were uncorrelated and as if the mathematical model was linear. The present work takes the CIPM 81/91 formula as a starting point and proposes arguments in favour or against in order to take into account the correlation components and the higher order terms of the Taylor series expansion in the analysis of air density uncertainty.

Keywords: air density uncertainty, correlation

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

1. Introduction

Air density influences many different areas of measurement, including mass, solid and liquid density, volume, etc. Therefore, it is important to correctly evaluate air density and its associated uncertainty.

The present work shows a process of evaluating the uncertainty associated with calculating the air density.

2. Development

Air density is not usually measured directly but it is calculated using the experimental measurements of air temperature, atmospheric pressure and dew point temperature or relative humidity.

The values of such environmental conditions are introduced in the CIPM 81/91 formula for air density determination [1, 2]:

$$\rho = \frac{pM_a}{ZRT}\left[1 - x_v\left(1 - \frac{M_v}{M_a}\right)\right] - \varepsilon_{\text{fitting}} \qquad (1)$$

where ρ is the air density (kg m^{-3}), M_a the molar mass of dry air (kg mol^{-1}), M_v the molar mass of water (kg mol^{-1}), R the universal constant of ideal gases (J mol^{-1} K^{-1}), p the atmospheric pressure (Pa), Z (x_v, p, p_{sv}, f) the compressibility factor, T the air temperature (K), x_v (p_{sv}, f, p) the molar fraction of water vapour, $\varepsilon_{\text{fitting}}$ the fitting error of the formula, $\varepsilon_{\text{fitting}} = 0$ kg m^{-3} $\pm$ 1 $\times$ 10^{-4} (relative uncertainty)

The variables Z, x_v, f, and p_{sv} are obtained from the following formulae:

$$Z = 1 - \frac{p}{T}\{a_0 + a_1(T - 273.15) + a_2(T - 273.15)^2 + [b_0 + b_1(T - 273.15)]x_v + [c_0 + c_1(T - 273.15)]x_v^2\} + \frac{p^2}{T^2}(d + ex_v^2) \qquad (2)$$

$$x_v = f(p, T_{dp}) \cdot \frac{p_{sv}(T_{dp})}{p} \qquad (3)$$

$$f = \alpha + \beta p + \gamma(T_{dp} - 273.15)^2 \qquad (4)$$

$$p_{sv} = 1\,\text{Pa} \cdot \exp\left(AT_{dp}^2 + BT_{dp} + C + \frac{D}{T_{dp}}\right) \qquad (5)$$

where f is the enhancement factor, p_{sv} is the saturation vapour pressure (Pa), T_{dp} is the dew point temperature (K), exp is the exponential function with base e = 2.718 . . . .

The values of the constants are shown in table 1 [2].

For the evaluation of the air density uncertainty, atmospheric pressure, air temperature, dew point temperature

Table 1. Constants for the air density calculation.

M_a[a]	$0.028\,963\,512\,440$ kg mol^{-1}
M_v	$0.018\,015$ kg mol^{-1}
R	$(8.314\,510 \pm 7 \times 10^{-5})$ J mol^{-1} K^{-1}
a_0	$1.581\,23 \times 10^{-6}$ K Pa^{-1}
a_1	-2.9331×10^{-8} Pa^{-1}
a_2	1.1043×10^{-10} K^{-1} Pa^{-1}
b_0	5.707×10^{-6} K Pa^{-1}
b_1	-2.051×10^{-8} Pa^{-1}
c_0	1.9898×10^{-4} K Pa^{-1}
c_1	-2.376×10^{-6} Pa^{-1}
d	1.83×10^{-11} K^2 Pa^{-2}
e	-0.765×10^{-8} K^2 Pa^{-2}
α	$1.000\,62$
β	3.14×10^{-8} Pa^{-1}
γ	5.6×10^{-7} K^{-2}
A	$1.237\,8847 \times 10^{-5}$ K^{-2}
B	$-1.912\,1316 \times 10^{-2}$ K^{-1}
C	$33.937\,110\,47$
D	$-6.343\,1645 \times 10^3$ K

[a] For M_a value, the mole fraction of carbon dioxide was assumed as $x_{CO_2} = 0.04\%$ and it is calculated from the values of M_a/R and R given in [2]. If the concentration of CO_2 in the air were measured, M_a could be calculated accurately [1].

and the fitting error of the formula (uncertainty of the formula) are the sources of uncertainty [3].

This uncertainty of the formula itself derives from the uncertainties of the values of M_a, M_v, R, and the calculation of Z, x_v, f and p_{sv}.

The uncertainty evaluation according to the GUM [4] uses the next formula to include uncorrelated variables when the mathematical model is approximately linear:

$$u_\rho = \sqrt{\sum_i^n [c_i \cdot u(x_i)]^2} \tag{6}$$

where u_ρ is the standard uncertainty of air density, c_i the sensitivity coefficient due to the uncertainty source i, $u(x_i)$ the standard uncertainty of input quantity i.

In this particular example, the sensitivity coefficients are obtained from partial derivation of formula (1) [4] with respect to the input quantity i, because the mathematical model that relates all input quantities to the air density is known:

$$c_i = \frac{\partial \rho}{\partial x_i}. \tag{7}$$

As the input quantities (T, T_{dp} and p) are related to the air density by intermediate variables (Z, x_v, f and p_{sv}) it is helpful to use the chain rule for calculating the sensitivity coefficients.

Once the sensitivity coefficients and the standard uncertainty of the input quantities are estimated, the standard uncertainty of the air density is evaluated using formula (6).

An important part of the uncertainty evaluation is the evaluation of degrees of freedom because this value is used to choose the coverage factor of the expanded uncertainty according to the desired level of confidence.

The effective degrees of freedom are obtained from the Welch–Satterthwaite formula [4]:

$$\nu_{eff} = \frac{u_\rho^4}{\sum_i^n \frac{u(x_i)^4}{\nu_i}} \tag{8}$$

where ν_{eff} is the degrees of freedom of the uncertainty evaluation of air density and ν_i is the degrees of freedom of the uncertainty evaluation of input quantity i.

Using the degrees of freedom obtained in formula (8), the coverage factor is selected according to the desired confidence level for the expanded uncertainty:

$$U_\rho = k \cdot u_\rho. \tag{9}$$

3. Numerical example

Considering the following environmental condition values and their respective standard uncertainties and degrees of freedom, the air density can be evaluated:

atmospheric pressure $p = 80\,628$ Pa $\pm$ 14 Pa, $\nu_p = 200$

temperature $T = 294.15$ K $\pm$ 0.06 K (21.00 °C $\pm$ 0.06 °C), $\nu_T = 200$

dewpoint temperature $T_{dp} = 280.89$ K $\pm$ 0.10 K (7.74 °C $\pm$ 0.10 °C), $\nu_{Tdp} = 200$.

Fifty degrees of freedom were estimated for the fitting error of formula, corresponding to a 90% level of confidence according to [4].

Introducing these values for the environmental conditions into formulae (1)–(5), the air density is obtained as

$$\rho = 0.950\,40 \text{ kg m}^{-3}.$$

Evaluating the sensitivity coefficients, the following values are obtained:

$$c_p = 1.18 \times 10^{-5} \text{ kg m}^{-3} \text{ Pa}^{-1}$$
$$c_T = -324 \times 10^{-5} \text{ kg m}^{-3}\, {}^\circ\text{C}^{-1}$$
$$c_{T_{dp}} = -32.1 \times 10^{-5} \text{ kg m}^{-3}\, {}^\circ\text{C}^{-1}$$
$$c_{\varepsilon_{fitting}} = -1.$$

Once the sensitivity coefficients and the standard uncertainties of input quantities were obtained, their values were introduced into formula (6) to evaluate the air density uncertainty as

$$u_\rho = 0.000\,27 \text{ kg m}^{-3}.$$

The evaluation of degrees of freedom is $\nu_{eff} = 452$. With this value, the coverage factor is selected in order to expand the confidence interval of the uncertainty to approximately 95.45% ($k \cong 1.97$):

$$U_\rho = 0.000\,54 \text{ kg m}^{-3} (\cong 95.45\%).$$

4. Correlation between input quantities

Input quantities could be correlated by a common traceability origin, but in some cases the correlation could be due to physical relationships.

In section 3 the parameters pressure, temperature and dew point temperature have been considered uncorrelated. This situation is usual for laboratories where the automatic control of the environmental conditions (temperature and humidity mainly) reduces the physical correlation that does exist between the pressure, temperature and volume of the air, as well as the rest of the gases. In some special cases, it is possible to assume a correlation between them, for example for air density determinations inside sealed chambers (often used for high accuracy mass determination), where the air density is constant[1], and the input quantities inside the chamber remain correlated.

For the numerical example of section 3, let us assume for the correlation coefficients between the environmental conditions values as $r(T, p) = 0.9$, $r(T, T_{dp}) = -0.2$ and $r(p, T_{dp}) = 0.2$. The standard uncertainties of this example were evaluated as the combination of type A and type B contributions; however, type A contributions were considered dominant (see section 8); then substituting these values in the correlation term of the combined uncertainty, the next value is obtained:

$$2\sum_{i=1}^{N-1}\sum_{j=i+1}^{N} c_i c_j u(x_i)u(x_j)r(x_i, x_j) = -6.26 \times 10^{-8}\,\mathrm{kg}^2\,\mathrm{m}^{-6}, \tag{10}$$

this value (10) is combined with the contributions that were evaluated earlier to calculate a new value for the standard uncertainty of the air density,

$$u_\rho = 0.000\,11\,\mathrm{kg\,m}^{-3}.$$

The result for the above example shows a decrease of 0.000 16 kg m^{-3} with respect to the value of uncertainty without correlations. This reduction means approximately 59% of the difference between both uncertainties. In this case, a reduction of the uncertainty when the correlation is taken into account appears because the product of sensitivity coefficients with the correlation factors results with a negative sign that reduces the standard uncertainty of the air density.

5. Higher order terms in the Taylor series expansion

The GUM states that when the nonlinearity of the model is significant; in the CIPM 81/91 formula for air density, the higher-order terms in the Taylor series expansion must be included in the expression of the combined standard uncertainty (u_ρ). The GUM also states that, when the distribution of each variable is symmetrical about its mean, the most important terms of next highest order must be added to the terms in the equation as shown in formula (11). Application of this to the numerical example of section 3 gives the next value:

$$\sum_{i=1}^{N}\sum_{j=1}^{N}\left[\frac{1}{2}\left[\frac{\partial^2 f}{\partial x_i \partial x_j}\right]^2 + \frac{\partial f}{\partial x_i}\frac{\partial^3 f}{\partial x_i \partial x_j^2}\right]u^2(x_i)u^2(x_j) = 9.58 \times 10^{-14}\,\mathrm{kg}^2\,\mathrm{m}^{-6}. \tag{11}$$

The last component, combined with the rest of the contributions (except the correlation contribution), results in the value $u_\rho = 0.000\,27$ kg m^{-3}. This result does not show a significant difference against the standard uncertainty evaluated without term (11), which means that the nonlinearity of the mathematical model is negligible.

[1] Mean air density is constant, but there could be density gradients inside the sealed chamber.

Figure 1. Sealed chamber of the CENAM mass laboratory. The chamber is open to show a balance inside.

6. Evaluation of the air density uncertainty by a numerical simulation method (Monte Carlo simulation)

In order to validate the uncertainty evaluation by the GUM method of the air density, especially for the nonlinearity of the mathematical model, the air density uncertainty was evaluated by the Monte Carlo simulation (MCS) [5] using the CIPM 81/91 formula as the mathematical model for the numerical simulation.

The input quantities were considered with normal probability density distribution $N(\mu, \sigma)$, with the following parameters (uncorrelated):

$$p \sim N(80\,628\,\mathrm{Pa};\ 14\,\mathrm{Pa})$$
$$T \sim N(294.15\,\mathrm{K};\ 0.06\,\mathrm{K})$$
$$T_{dp} \sim N(280.89\,\mathrm{K};\ 0.10\,\mathrm{K})$$
$$\varepsilon_{\mathrm{fitting}} \sim N(0\,\mathrm{kg\,m}^{-3};\ 9.5 \times 10^{-5}\,\mathrm{kg\,m}^{-3}).$$

The results of the numerical simulation ($n = 10\,000$) are as follows: mean $\bar{\rho}_a = 0.950\,40$ kg m^{-3}, standard deviation $s = 0.000\,27$ kg m^{-3} and a confidence interval for 95.45% of $\rho_{a(95.45\%)}$ (0.949 84; 0.950 94) kg m^{-3} (see figure 2).

Introducing the correlation coefficients given in section 4, $r(T, p) = 0.9$, $r(T, T_{dp}) = -0.2$ and $r(p, T_{dp}) = 0.2$, and running the numerical simulation, it throws the following results: mean $\bar{\rho}_a = 0.950\,40$ kg m^{-3}, standard deviation $s = 0.000\,11$ kg m^{-3} and a confidence interval for 95.45% of $\rho_{a(95.45\%)}$ (0.950 18; 0.950 62) kg m^{-3} (see figure 3).

The numerical simulation results do not show a significant difference in relation to the results evaluated by the GUM method (considering the input quantities as uncorrelated and correlated) (see table 2).

Table 2. Results of the numerical example of the air density determination and its uncertainty evaluated by both the GUM method and by the Monte Carlo simulation (MCS).

		GUM method	Numerical simulation (MCS)
Uncorrelated input quantities	Mean value	0.950 40 kg m^{-3}	0.950 40 kg m^{-3}
	Confidence interval for approximately 95.45%	(0.949 85; 0.950 95) kg m^{-3}	(0.949 84; 0.950 94) kg m^{-3}
Correlated input quantities	Mean value	0.950 40 kg m^{-3}	0.950 40 kg m^{-3}
	Confidence interval for approximately 95.45%	(0.950 17; 0.950 62) kg m^{-3}	(0.950 18; 0.950 62) kg m^{-3}

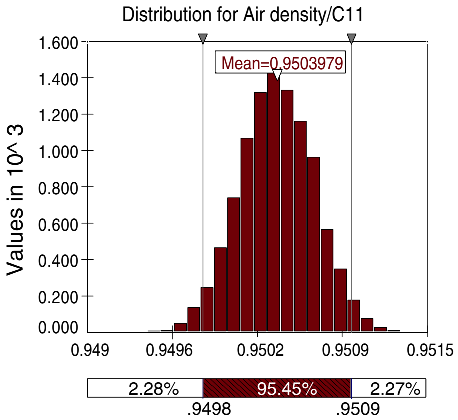

Figure 2. Histogram of air density values obtained from the numerical simulation, considering the input quantities as uncorrelated.

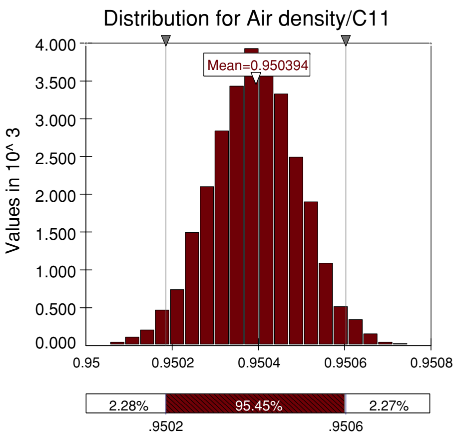

Figure 3. Histogram of air density values obtained from the numerical simulation, considering the input quantities as correlated.

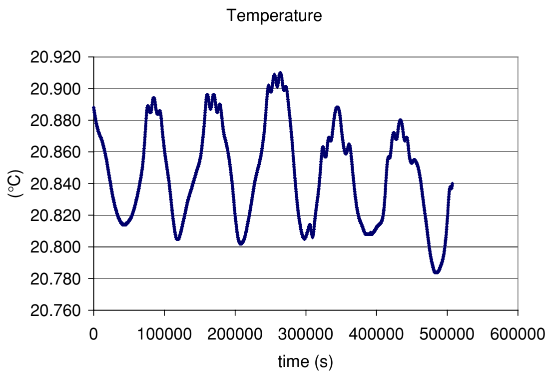

Figure 4. Temperature measured inside the sealed chamber.

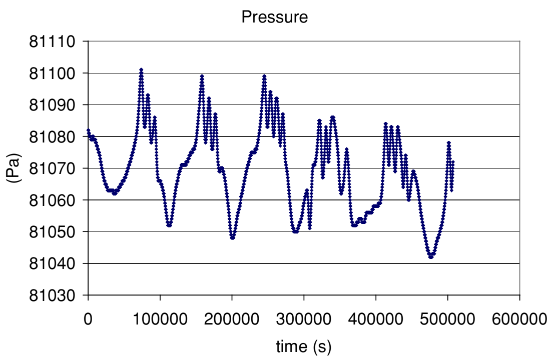

Figure 5. Pressure measured inside the sealed chamber.

7. Experimental measures inside the sealed chamber in order to evaluate the correlation between pressure and temperature

Measurements of pressure, temperature and dew point temperature inside the sealed chamber (see figure 1) were carried out simultaneously during a period of 507 240 s (about 141 h), and the air density $\rho_i = f(T_i, p_i, T_{dpi})$ was calculated from those measurements. The values of the input quantities were gathered in periods of 90 s each.

The characteristics of the measuring instruments are listed in table 3.

5637 readings were taken of each input quantity. Some statistical parameters of these series of measurements and the estimated correlation coefficients between the readings of the input quantities are shown in tables 4 and 5.

Graphs of the measured values of temperature, pressure and dew point temperature are shown in figures 4–6, and the corresponding air density calculated values are shown in figure 7.

The air density and its uncertainty can be expressed with different approaches as shown in table 6.

It can be noticed from table 6 that the third approach gives the same uncertainty value as the first approach which is considered as the best estimation. The discrepancy between approaches 2 and 1 arises due to fact that approach 2 does not take into account the randomness of the distributions of the input quantities. Approach 2, even though it does not take into account the randomness of distributions, is often used in everyday measurements.

Table 3. Sensors used for the measurements inside the sealed chamber.

	Temperature	Pressure	Dew point temperature
Manufacturer	MINCO	DHI	General Eastern
Model		RPMJ	112
Sensor	Platinum resistance	Quartz sensor	Platinum resistance
Display resolution	0.001 °C	1 Pa	0.1 °C
Calibration uncertainty ($k = 1$)	0.01 °C	2 Pa	0.1 °C

Table 4. Statistical parameters of simultaneous measurements inside the sealed chamber. The air density values were calculated for each of the $n = 5637$ data and the standard deviation is evaluated as the dispersion of these 5637 air density values. The standard deviation of the mean is evaluated as the standard deviation over the square root of the number of data. The standard deviation and the standard deviation of the mean concern only type A contributions without considering correlations.

	Dew point T (°C)	Temperature (°C)	Pressure (Pa)	Air density (kg m^{-3})
Mean	8.575 73	20.846 09	81 068.96	0.955 8473
Max	8.8	20.910	81 101	0.956 1280
Min	8.5	20.784	81 042	0.955 6242
Standard deviation	0.066	0.032	12.80	0.000 093
Standard deviation of the mean	0.000 88	0.000 43	0.17	0.000 0012
n (number of data)	5637	5637	5637	5637

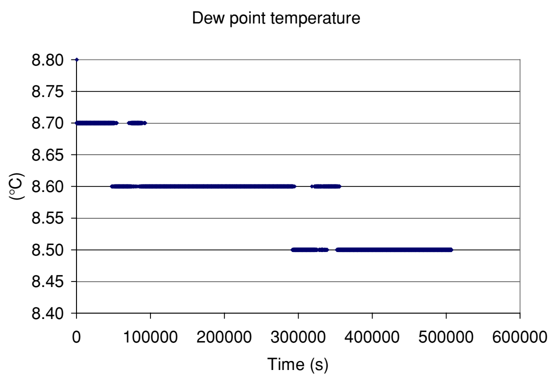

Figure 6. Dew point temperature measured inside the sealed chamber.

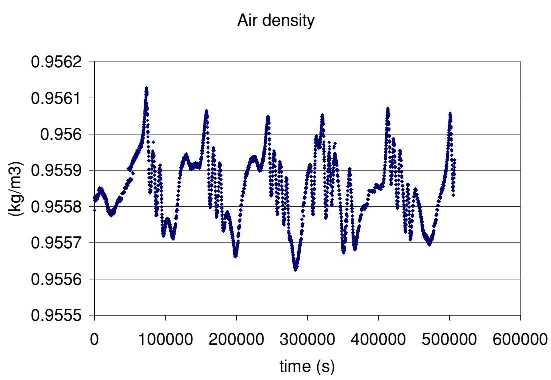

Figure 7. Air density estimated by the simultaneous measurement of T, p and T_{dp}.

In relation to figures 4–7, it is important to remark that the measurements of pressure and dew point temperature are representative for the whole of the inside of the chamber. The measurements of temperature correspond to only one point inside the sealed chamber (where the temperature sensor is placed). According to this, the calculated air density corresponds to only one point inside the sealed chamber. The average air density should remain constant.

Table 5. Correlation coefficients for temperature, pressure and dew point temperature evaluated from the simultaneous series of measurements.

	T_{dp}	T	p
T_{dp}	1	0.31	0.36
T		1	0.78
p			1

8. Discussion

In this particular case, the component of nonlinearity of the CIPM formula does not affect the standard uncertainty of the air density (sections 5 and 6). Correlations between input quantities are avoided as much as possible when making measurements. However, there are many measurements that have correlated input quantities and it is difficult to control these factors and impossible to eliminate them.

For air density uncertainty evaluation, the standard uncertainty of the input quantities (T, p and T_{dp}) should be evaluated at least from the following contributions:

- type B contribution, calibration uncertainty (usually, this uncertainty includes the resolution contribution)
- type A contribution, dispersion of readings.

The correlation between input quantities discussed in sections 4 and 7 for sealed chambers affects only the type A contribution for each input quantity, because the correlation does not apply for the type B contribution.

If the type A contribution (for correlated quantities) is smaller than the type B contribution, then the effect of the correlation is negligible, but if the type A contribution is equal or larger than the type B contribution, then the effect of the correlation on the standard uncertainty of the air density is significant. A possibility for the appearance of the latter

Table 6. Comparison of different approaches for the calculation of the air density and its uncertainty.

	Approach	ρ (kg m^{-3})	u_ρ (kg m^{-3})
1	Air density shown as the mean value of table 4. Air density uncertainty evaluated as the standard deviation of the mean shown in table 4	0.955 8473	0.000 0012
2	Air density calculated applying formula (1) using the mean values of the input quantities shown in table 4 Air density uncertainty evaluated taking as the uncertainty of each input quantity the standard deviation of the mean (shown in table 4).	0.955 8473	0.000 0025
3	Air density calculated applying formula (1) using the mean values of the input quantities shown in table 4 Air density uncertainty evaluated taking as the uncertainty of each input quantity the standard deviation of the mean (shown in table 4). For this evaluation the correlation coefficients between input quantities of table 5 were used	0.955 8473	0.000 0012

situation is when there exists large variation of temperature outside the sealed chamber. This temperature variation outside the sealed chamber produces temperature and pressure variations inside the sealed chamber.

The Welch–Satterthwaite formula is presented in the GUM for measurements that have uncorrelated variables and when the nonlinearity of the mathematical model is not significant. However, it could be understood that if contributions of the terms due to the correlation between input quantities and nonlinearity of the mathematical model have significant values for the standard uncertainty, they must be included into the degrees of freedom evaluation in order to have a good estimation of the confidence interval of the measurement result. It should be recognized that no degrees of freedom were taken into account when dealing with the correlation of input quantities.

The correlation factors used in sections 4 and 6 are hypothetical. The correlation factors shown in section 7 were estimated for a specific place and time period inside the sealed chamber.

Picard *et al* [6] and Park *et al* [7] have presented evidence for a new value of the mole fraction of argon in air, which could change the calculated value of M_a and therefore the calculation of ρ_a. The relative difference between the new calculations of M_a and ρ_a is about 6.4×10^{-5} evaluated with a relative standard uncertainty of 1.2×10^{-5}.

This change of M_a added to the new CODATA value for R which has a relative uncertainty of 1.7×10^{-6} (see http://physics.nist.gov/cuu/Constants/index.html) may reduce the relative uncertainty of the air density formula itself to about 1.2×10^{-5}, and therefore the contribution to the air density uncertainty due to the correlation between temperature and pressure (specially for sealed chambers) may become significant.

9. Conclusions

For future evaluations of air density uncertainty, sufficiently similar to those treated here, it will not be necessary to include the component due to higher order terms in Taylor series expansion for air density uncertainty evaluations because the contribution is negligible (the nonlinearity of the mathematical model is not significant.)

In a sealed chamber, the component due to the correlation between input quantities should be considered in air density calculations because there are correlations between environmental parameters such as T and p. The correlation factors should be characterized for each particular case and period of time, and once the correlation is present, its effect tends to modify the air density uncertainty. This effect will be more significant for air density calculations using formula (1) if the uncertainty of the formula itself is decreased.

Where degrees of freedom estimation are concerned, there is still much work to be done, especially in the evaluation of the contributions of the input quantities correlation and the nonlinearity of the mathematical model.

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