The Refractivity of Air

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The air density equation of Jones, Edlen's dispersion formula for standard air, and Edlen's empirically-derived expressions for the effects of CO$_2$ abundance and water vapor partial pressure on refractivity have been combined into a simplified equation for the refractivity of air, and estimates have been made of uncertainties in calculated refractivity. Under ambient conditions typical of metrology laboratories, the agreement between the simplified equation and Edlen's formulation is well within the uncertainty in each. The simplified equation is valid in the visible region.

Key words: Air density; index of refraction of air; refractivity of air; wavelength of light in air.

1. Introduction

In metrological applications of wavelengths of light in air, it is necessary to calculate the wavelength at ambient conditions of temperature ($T$), pressure ($P$), effective water vapor partial pressure ($e'$), and CO$_2$ abundance ($x_{CO_2}$), using the refractive index of air under these conditions. The relation between $\lambda_{vac}$ the vacuum wavelength, $\lambda_{air}$, the wavelength in air, and $n$, the refractive index of air, is $n = \lambda_{air}/\lambda_{vac}$. Edlen [1] has derived a dispersion formula for standard air ($T = 288.15$K, $P = 101325$ Pa, $e' = 0$, $x_{CO_2} = 0.0003$ by volume) and a formulation for the refractivity of ambient air, $(n-1)_{tp}$. Edlen's formulation is in general use in metrology. Jones [2] has recently published a reformulation of the equation for the density of air and applied it to the transfer of the mass unit. It is the purpose of the present paper to combine the air density equation, Edlen's dispersion formula for standard air, and Edlen's empirically-derived expressions for the effects of CO$_2$ abundance and water vapor partial pressure on refractivity, and in so doing to develop a simpler formulation and to estimate uncertainties in the calculated refractivity.

The Edlen 1966 [1] dispersion formula for standard air is

$$ (n-1) \times 10^8 = 8342.13 + 2406030 (130 - \sigma)^{-1} + 15997 (38.9 - \sigma)^{-1}, \quad (1) $$

where $n$ is the refractive index, $\sigma$ is the vacuum wave number, $(1/\lambda_{vac})$, in $\mu m^{-1}$ and standard air is dry air at 288.15K, 101325 Pa and a CO$_2$ abundance of 0.0003 by volume. Edlen [1] expressed the refractivity, $(n-1)_{tp}$ of dry air at temperature $t$ (in °C) and pressure $p$ (in torr) as

$$ (n-1)_{tp} = K_x D_{tp}, \quad (2) $$

where $K_x$ [3] is a dispersion factor which is independent of $t$ and $p$, and the density factor, $D_{tp}$, is

$$ D_{tp} = p \{ 1 + \epsilon_x p / [(1 + \alpha t)\{1 - (n-1)_{tp}/6\}] \}, \quad (3) $$

where $\alpha = 1/273.15$ and $\epsilon_x$ is a factor which multiplies $p$ in an expression for the nonideality of the gas. By substituting suitable values, (3) becomes

$$ D_{tp} = p \{ 1 + p [0.817 - 0.0133 t] \times 10^{-6}] / [(1 + 0.0036610 t) \}. \quad (4) $$

For air with a CO$_2$ abundance of $x$ by volume, Edlen derived

$$ (n-1)_{x} = [1 + 0.540 (x - 0.0003)] (n-1)_{tp}, \quad (5) $$

and,

$$ n_{tp} - n_p = -h (5.7224 - 0.0457 \sigma^2) \times 10^{-8} \quad (6) $$

for the difference in refractive index of moist air holding $h$ torr of water vapor at a total pressure $p$. (To avoid using the same symbol for two different quantities, in the present work $h$ has been substituted for Edlen's $j$).

From (4) and the relation

$$ (n-1)_{tp} = (n-1), D_{tp}/D_n \quad (7) $$

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Edlén’s general formula is

\[ (n-1)_p = \frac{p (n-1)_r}{720.775} \cdot \left[ \frac{1 + p \left(0.817 - 0.0133 \times 10^{-6}\right)}{1 + 0.0036610 \times 10^{-6}} \right], \]  

(8)

where \( D_s \) is the density factor for standard air.

Equations (5), (6), and (8) are generally combined in the calculation of the refractivity of moist air, in the visible region.

### 2. Present Formulation

In the following, the air density equation derived by Jones [2] will be incorporated into a refractivity equation. The density of moist air, \( \varrho \), is given by

\[ \varrho = \frac{PM_s}{RTZ} \left[ 1 - \left( \frac{18.0152}{M_a} \right) \frac{U}{100} \frac{f \epsilon_r}{P} \right], \]  

(9)

where \( P \) is the pressure in Pa, \( M_s \) is the apparent molecular weight of dry air, \( R \) is the universal gas constant, \( T \) is the temperature in kelvins, \( Z \) is the compressibility factor (the non-ideality of the air-water vapor mixture is reflected in the departure of \( Z \) from 1), \( U \) is the relative humidity in percent, and \( f \) is the enhancement factor (a factor which expresses the fact that the effective saturation vapor pressure of water in air is greater than the saturation vapor pressure, \( \epsilon_r \), of pure phase over a plane surface of pure ordinary liquid water). Tables of \( Z \), \( \epsilon_r \), and \( \varrho \) are provided in the appendix of the present paper.

The Lorentz-Lorenz [4,5] formulation of the Clausius-Mossotti [6,7] equation can be expressed as

\[ \frac{n^2 - 1}{n^2 + 2} = C \frac{\varrho_s}{M_a}, \]  

(10)

the left side of which can be approximated [1] by \( \frac{2}{3} (n - 1)/6 \). Therefore,

\[ (n-1) = C' \frac{\varrho_s}{M_a} \left[ 1 - \frac{(n-1)}{6} \right]^{-1}, \]  

(11)

where \( \varrho_s \) and \( M_a \) are the density and apparent molecular weight, respectively, of dry air and \( C \) and \( C' \) are constants. Since \( \varrho_s = PM_s/RTZ \) [2], (11) becomes

\[ (n-1) = \frac{C'P}{RTZ} \frac{1}{1 - \frac{(n-1)}{6}}, \]  

(12)

and for standard air,

\[ (n-1)_p = \frac{C'P}{RTZ} \frac{1}{1 - \frac{(n-1)_r}{6}}. \]  

(13)

By dividing (12) by (13),

\[ (n-1) = \frac{\left[ 1 - \frac{(n-1)_r}{6} \right]}{\left[ 1 - \frac{(n-1)_p}{6} \right]} \frac{P}{P/TZ} (n-1)_r. \]  

(14)

By substituting the appropriate values of \( P \), \( 101325 \), \( T \), (288.15K) and \( Z \), (0.99958 from table 1 in the appendix), (14) becomes

\[ (n-1) = 0.0028426 \frac{P}{P/TZ} \left[ 1 - \frac{(n-1)_r}{6} \right] \frac{1}{1 - \frac{(n-1)_p}{6}} (n-1)_r. \]  

(15)

which, when rearranged, becomes

\[ (n-1)^3 - 6(n-1) + 0.0170586 (n-1) \cdot \frac{P}{TZ} \left[ 1 - \frac{(n-1)_r}{6} \right] \frac{1}{1 - \frac{(n-1)_p}{6}} = 0. \]  

(16)

The appropriate square root of (16) is

\[ (n-1) = 3 - \left[ 9 - 0.00028426 (n-1) \cdot \frac{P}{TZ} \left[ 1 - \frac{(n-1)_r}{6} \right] \right]^{1/2}. \]  

(17)

We shall return now to Edlén’s development and combine (2) with (3):

\[ (n-1)_p = K_s D_p = \frac{K_s p \left( 1 + \epsilon_r \right)}{(1 + \alpha \epsilon_r) \left[ 1 - \frac{(n-1)_r}{6} \right]} \]  

(18)

\((1 + \epsilon_r)\) is recognized to be \(1/Z\), \((1 + \alpha \epsilon_r) = T/273.15\), and \( p = 760 P/101325 \); therefore,

\[ (n-1)_p = \frac{760 \times 273.15}{101325} \frac{K_s P}{TZ} \frac{1}{1 - \frac{(n-1)_r}{6}}. \]  

(19)

By comparing (19) with (12), \( K_s R(760 \times 273.15)/101325 \) is seen to correspond to \( C' \).

It remains now to combine (17) with Edlén’s empirically-derived expressions for the effects of \( CO_2 \) abundance, (5), and water vapor partial pressure, (6), to arrive at the general expression:

\[ (n-1) = 3 - \left[ 9 - (n-1)_r \left[ 6 - (n-1)_r \right] \right] \cdot \frac{0.0028426 \frac{P}{TZ} \left[ 1 - \frac{(n-1)_r}{6} \right]}{\left[ 1 - \frac{(n-1)_p}{6} \right]^{1/2}} - \frac{\epsilon_r U}{100} \left[ 0.042922 \ - 0.000343 \sigma^2 \right] \times 10^{-6}, \]  

(20)

where \( \epsilon \) is in Pa. Equation (20) corresponds to (8) combined with (5) and (6), i.e. Edlén’s formulation [1]. The agreement between the refractivity of moist air calculated using (20)
and Edén’s formulation is illustrated for \( T = 293.15 \text{K}, P = 101325 \text{Pa}, U = 50, x_{\text{CO}_2} = 0.00043, Z = 0.99963 \) (from table 1), \( f = 1.0041 \) (from table 2), \( e_l = 2338 \text{Pa} \) (from table 3) and \( \lambda_e = \sigma^{-1} = 0.6329912714 \mu\text{m} \) for an iodine stabilized helium-neon laser [8]. Using (20), \( (n-1) = 27131.4 \times 10^{-8} \); using Edén’s formulation \( (n-1)_{\text{ph}} = 27131.3 \times 10^{-8} \). For a more extreme case \( T = 288.15 \text{K}, P = 70000 \text{Pa}, U = 50, x_{\text{CO}_2} = 0.00080, Z = 0.99971, f = 1.0030, e_l = 1705 \text{Pa} \), (for the same wavelength), (20) gives \( (n-1) = 19069.6 \times 10^{-8} \) and the Edén formulation gives \( (n-1)_{\text{ph}} = 19068.1 \times 10^{-8} \). As will be demonstrated in the next section, the difference between the results for the two formulations is well within the uncertainty of each.

Equation (15) can be approximated by

\[
(n-1) = 0.0028426 \frac{P}{TZ} (n-1)_i.
\]

(21)
in the first of the above examples, the resulting change is \( 0.02 \times 10^{-8} \) which is negligible. Equation (20) then becomes

\[
(n-1)_{\text{trr}}' = 0.0028426 \frac{P}{TZ} (n-1)_i - f e_l \frac{U}{100}(0.042922 - 0.000343 \sigma^2) \times 10^{-8},
\]

(22)
where the subscript \( TPd' \) follows Edén’s convention, \( e' = f e_l U/100 \). For a \( \text{CO}_2 \) abundance of 0.0003 by volume and a vacuum wavelength of 0.6329912714 \( \mu\text{m} \) (22) becomes

\[
(n-1)_{\text{trr}}' = (78.603 \frac{P}{TZ} - 0.042066 f e_l \frac{U}{100}) \times 10^{-8}.
\]

(23)
The variation of \( \text{CO}_2 \) abundance, \( x \), can be incorporated in (23) by multiplying 78.603 by \( [1 + 0.540 (x - 0.0003)] \). At NBS, a constant value of 1.0042 can be used for \( f \) [2] with negligible effect on calculated \( (n-1)_{\text{trr}}' \). Equation (23) then becomes

\[
(n-1)_{\text{trr}}' = (78.603 \frac{P}{TZ} - 0.042243 e_l \frac{U}{100}) \times 10^{-8}.
\]

(24)

3. Estimation of Uncertainties

We follow the suggested practice of Eisenhart [9, 10] in stating separately the random and systematic components of the estimated uncertainties. The stated random component is one standard deviation; the stated systematic component is one-third of the half-width of the interval between the bounds of the systematic error.

The uncertainties in calculated \( (n-1)_{\text{trr}}' \) due to estimated uncertainties [2] in \( P, T, Z, U, f, e_l, \) and \( x \) can be estimated from equation (22). We shall not attempt to estimate the uncertainties in Edén’s [1] dispersion formula for standard air and his expressions for the effects of \( \text{CO}_2 \) abundance and water vapor partial pressure. The state-of-the-art in pressure measurement [11] permits the measurement of pressure in a laboratory with a random relative uncertainty of less than \( \pm 0.02 \) percent, calibration of pressure measuring instruments against a primary standard of pressure contributes a systematic relative uncertainty of about \( \pm 0.003 \) percent. The corresponding uncertainties in \( (n-1)_{\text{trr}}' \) in the first example above are \( \pm 5.4 \times 10^{-8} \) and \( \pm 0.8 \times 10^{-8} \).

The measurement of temperature in the air path is potentially as critical as the pressure measurement, in terms of its effect on the uncertainty in the calculated \( (n-1)_{\text{trr}}' \); it is possible to make only a rough estimate of the uncertainty in the temperature measurement. If the vicinity of the path were instrumented with a network of thermopile junctions, the measurements would be expected to have a standard deviation of about \( \pm 0.05K \) [12] and a systematic uncertainty of the order \( \pm 0.01K \). The corresponding uncertainties in \( (n-1)_{\text{trr}}' \) in the first example are \( \pm 4.6 \times 10^{-8} \) and \( \pm 0.9 \times 10^{-8} \).

The estimated systematic relative uncertainty in the compressibility factor, \( Z \), for the first example is \( \pm 0.0017 \) percent. The corresponding uncertainty in \( (n-1)_{\text{trr}}' \) is \( \pm 0.5 \times 10^{-8} \).

The uncertainty in calculated \( (n-1)_{\text{trr}}' \) due to humidity measurement can be estimated from the second term in (22). The state-of-the-art in humidity measurement [13] permits the measurement of relative humidity, \( U \), with a random uncertainty of \( \pm 0.5 \) percent relative humidity and a systematic uncertainty of \( \pm 0.3 \) percent relative humidity. The corresponding uncertainties in \( (n-1)_{\text{trr}}' \) in the first example are \( \pm 0.5 \times 10^{-8} \) and \( \pm 0.3 \times 10^{-8} \). The uncertainties contributed by uncertainties in \( f \) and \( e_l \) are negligible [2].

The uncertainty in calculated \( (n-1)_{\text{trr}}' \) due to a variation in \( \text{CO}_2 \) abundance, \( x \), can be estimated from (5). In the first example, a variation in \( x \) of \( \pm 0.0001 \) corresponds to a systematic uncertainty in \( (n-1)_{\text{trr}}' \) of \( \pm 1.5 \times 10^{-8} \).

The overall random uncertainty in \( (n-1)_{\text{trr}}' \), estimated by combining the random uncertainties by quadrature, is \( \pm 7.1 \times 10^{-8} \). The overall systematic uncertainty, estimated by combining the addition, is \( \pm 2.5 \times 10^{-8} \). The systematic uncertainty due to variation in \( \text{CO}_2 \) abundance is necessarily not included. It should be emphasized that these uncertainties are based on the best possible measurements of \( P, T \) and \( U \).

4. Direct Determination of Air Density

In 1967, Bowman and Schoonover [14] used a pair of stainless steel weights (one of which was hollow) of nearly equal mass but of grossly different volume to make direct
determination of the air density in a balance case, thus avoiding the uncertainties in the parameters and environmental variables in air density calculations. A similar scheme will be used in the transfer of the mass unit [15].

Having estimated the uncertainty in calculated \((n - 1)_{TPR}\) due to the uncertainties in the various variables to be about \(\pm 1 \times 10^{-7}\) at the level of the equivalent of 1 standard deviation, it is of interest to estimate how much improvement would result from the direct determination of air density, \(\varrho\), if practicable. From (9),

\[
\frac{P}{TZ} = \frac{\varrho R}{M_a} \left[ 1 - \frac{1}{1 - \frac{18.0152}{M_a}} \frac{U}{100} f e_r \right],
\]

where \(M_a = 28.963 + 12.011 (x_{CO_2} - 0.00033)\); recalling that \(\varrho\) is the density of moist air. By substituting (25) in (22),

\[
(n - 1)_{TPR} = 0.0028426 \frac{\varrho R}{M_a} \left[ 1 - \frac{1}{1 - \frac{18.0152}{M_a}} \frac{U}{100} f e_r \right] - f e_r \frac{U}{100} \left(0.042922 - 0.000343 \sigma^2\right) \times 10^{-8}. \tag{26}
\]

The uncertainties in the various parameters in (25), other than \(\varrho\) and \((n - 1)_a\), are taken from [2]. The resulting overall uncertainty in the calculated \((n - 1)_{TPR}\) are \(\pm 1.9 \times 10^{-8}\) random and \(\pm 1.8 \times 10^{-8}\) systematic. The uncertainty due to the effect on \(M_a\) of a variation of \(x_{CO_2} 1.1 \times 10^{-8}\) per 0.0001, has necessarily not been included. It can be concluded that even it the uncertainty in a direct determination of \(\varrho\) were negligible, the uncertainty in \((n - 1)_{TPR}\) due to the uncertainties in the various variables and parameters would be reduced by a factor of about 2.5. The major contributors to the uncertainty in \((n - 1)_{TPR}\) are the uncertainties in \(R, M_a\) and \(U\).

5. Conclusions

Jones’s air density equation [2], Edlén’s [1] dispersion formula for standard air, and Edlén’s empirically-derived expressions for the effects of \(CO_2\) abundance and water vapor partial pressure on refractivity have been combined into a simple refractivity of air equation, and estimates have been made of uncertainties in calculated refractivity.

The general equation is (22), which is valid in the visible region; tables of \(Z, f\) and \(e_r\) have been included in the appendix of this paper. The overall estimated uncertainty is about \(\pm 1 \times 10^{-7}\) at the level of the equivalent of 1 standard deviation. The major contributors to the uncertainty in refractivity are the uncertainties in the measurements of pressure and temperature. The magnitude of the uncertainty due to variation in \(CO_2\) concentration can approach that of the uncertainties due to the pressure and temperature measurements. Therefore, the \(CO_2\) concentration should be treated as a variable and should be observed.

If it were practicable to make a direct measurement of air density representative of the air path, the uncertainty in calculated refractivity due to the uncertainties in the various variables and parameters would be reduced by a factor of about 2.5.

The author is pleased to express his thanks to John S. Beers at whose suggestion this work was undertaken, and to Catherine DeLeonibus for typing the manuscript.

6. References

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<th>Pressure (pascals)</th>
<th>Relative Humidity in Percent</th>
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### Table 1: Compressibility factor, $z$, for air containing reasonable amounts of CO₂ [2]

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### 7. Appendix

Relative Humidity in Percent

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TABLE 2. Values of enhancement factor, \( f \), calculated \([2]\) from Hyland's data \([16]\)

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TABLE 3. Values of saturation water vapor pressure, \( e_s \), calculated using formulation of Wesler and Greenspan \([17]\)

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