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An Updated Edlén Equation for the Refractive Index of Air

K. P. Birch and M. J. Downs

Abstract. The Edlén equation for the refractive index of air, published in 1966, is still widely used. Subsequent to its formulation, however, improved data have become available on the density of air and the refractivity of water vapour. The practical temperature scale has also been revised and the carbon dioxide content of normal laboratory air has increased. These effects result in a discrepancy of typically 1×10^{-7} . The consequent revision of the equation brings the agreement between calculation and experiment within an experimental uncertainty of $\pm 3 \times 10^{-8}$.

1. Introduction

Interferometric and time-of-flight techniques are widely used for the precise measurement of length and, following the invention of lasers with their intense collimated beams and narrow bandwidths, a greatly extended range and accuracy is achievable using these systems.

In order to achieve the optimum performance from these techniques when they are applied in the free atmosphere it is essential to correct the wavelength of the radiation for the refractive index of air. There are two techniques for determining the refractive index of air. A value may be calculated using the Edlén equation [1] by using suitable sensors to measure atmospheric pressure, air temperature and humidity; the index may be measured directly with a refractometer.

The original Edlén equation, published in 1966 [1], was

$$(n-1)_{tp} = \frac{p(n-1)_s}{720,775} \cdot \frac{1 + p(0,817 - 0,0133t)10^{-6}}{(1 + 0,0036610t)} \quad (1)$$

Here $(n-1)_{tp}$ is the refractivity of standard air, the temperature t is expressed in degrees Celsius and the atmospheric pressure p in torr. In homogeneous form

this is

$$(n-1)_{tp} = \frac{(p/\text{torr})(n-1)_s}{720,775} \times \frac{[1 + (p/\text{torr})(0,817 - 0,0133t/^\circ\text{C})10^{-6}]}{(1 + 0,0036610t/^\circ\text{C})} \quad (1')$$

The value of $(n-1)_s$, the refractivity of standard air at 1 atmosphere and 15°C , is calculated from the dispersion formula which was given as

$$(n-1)_s \times 10^8 = 8\,342,13 + 2\,406\,030(130 - \sigma^2)^{-1} + 15\,997(38,9 - \sigma^2)^{-1}, \quad (2)$$

where σ is the vacuum wavenumber and is expressed in μm^{-1} . Alternatively,

$$(n-1)_s \times 10^8 = 8\,342,13 + 2\,406\,030[130 - (\sigma/\mu\text{m}^{-1})^2]^{-1} + 15\,997[38,9 - (\sigma/\mu\text{m}^{-1})^2]^{-1}. \quad (2')$$

Equations (1) (1'), (2) and (2') are valid for standard air which is defined to be dry air having the following composition by molar percentage: 78,09 % nitrogen, 20,95 % oxygen, 0,93 % argon and 0,03 % carbon dioxide [2].

For the difference in the refractive index of moist air, containing f torr of water vapour, and dry air at the same total pressure, Edlén derived the following expression:

$$n_{tpf} - n_{tp} = -f(5,7224 - 0,0457\sigma^2) \times 10^{-8}. \quad (3)$$

In this, the partial pressure f of water vapour is expressed in torr. The corresponding homogeneous equation is:

$$\begin{aligned} n_{tpf} - n_{tp} \\ = -(f/\text{torr}) [5,7224 - 0,0457(\sigma/\mu\text{m}^{-1})^2] \times 10^{-8}. \end{aligned} \quad (3')$$

The refractivity of ambient air is readily calculated using these equations which, Edlén estimated, have a total uncertainty of about $\pm 5 \times 10^{-8}$ and are valid for visible radiations and over the normal range of atmospheric conditions.

Since the time of the original publication, there has been the acceptance of the SI system of units and improved data on both the density of air and the refractivity of water vapour. In addition, the practical temperature scale has been revised twice and there has been an increase in the carbon dioxide levels of laboratory air. All of these developments now make it advisable to revise the Edlén equation. This paper describes these developments and their effect upon the refractive index of air, derives the revisions and compares the original and revised versions.

2. Review of Developments Since 1966

2.1 The adoption of the SI system of units

In 1960 the International System of Units (SI) was agreed by the Conférence Générale des Poids et Mesures (CGPM) [3]. Since the agreement, this system of units has been progressively accepted throughout most of the world and is likely to remain the primary world system for the foreseeable future. It rationalizes the main metric units of measurement and standardizes their names and symbolic representations.

The adoption of this system of units affects the Edlén equation through his choice of the torr, which is not an SI unit, as the unit of pressure. Therefore the constants in (1) and (3) need to be revised to convert the unit of pressure from the torr to the accepted SI unit, the pascal.

2.2 Comparisons with the original Edlén equation

Subsequent to the publication of the Edlén equation a number of comparisons were made between directly measured values of the refractive index of air and values calculated from the equation [4-9]. These studies show differences of up to 2×10^{-7} between the measured and calculated values.

Of particular significance was an international comparison of interference air refractometers [9]. The participants were: the Eindhoven University of Technology, the Netherlands; the Physikalisch Technische Bundesanstalt, Germany; the National

Physical Laboratory, UK; and the Van Swinden Laboratory, the Netherlands. Refractive index measurements were made using common air samples with refractometers developed by each participant and the results were compared with values calculated from the Edlén equation. It was found that during the period of the comparison the level of carbon dioxide increased to about 800 ppm. * Only when corrections for these excess levels were applied to calculated values of refractivity using the Edlén equation, was agreement to 5×10^{-8} obtained with direct measurement. As shown below, the correction for a 1 ppm increase in carbon dioxide corresponds to an increase in the refractive index of air of $1,45 \times 10^{-10}$.

This comparison, therefore, indicates both that any errors in the Edlén equation are relatively small, and that ambient carbon dioxide levels are a significant factor in the calculation of the refractive index of air.

2.3 Experimental evaluation of the Edlén equation

The discrepancies noted above, although small, are increasingly significant for standards work and for high technology industries requiring length measurement accuracies of better than 1 part in 10^7 . Uncertainty in the determination of the refractivity of air contributes nearly 1 part in 10^8 to the uncertainty of such measurements. Therefore the National Physical Laboratory undertook a programme of work to investigate the validity of the Edlén equation.

This investigation involved the development of a high precision gas refractometer which used a helium-neon laser operating at 633 nm to achieve an instrument uncertainty of 1×10^{-8} . The refractometer was used to compare a measured value of the refractive index of standard air with a calculated value derived from the Edlén equation over the pressure and temperature ranges of 20 kPa to 115 kPa and 10°C to 30°C [10].

The comparison showed that for dry air there was excellent agreement between the measured and calculated values to within the uncertainty of the measurements, which was $\pm 3 \times 10^{-8}$. However when values for moist air were compared, the measured values were found to be greater than those calculated by up to 13×10^{-8} for fully saturated air at 20°C . This difference was attributed to physiosorption effects in the original Barrell and Sears apparatus [11], the results from which Edlén used in the derivation of his equation. Consequently the water vapour constants in (3) were revised in 1988 [12].

* 1 ppm = 1 part per million.

2.4 Comparisons of the original and 1988 versions of the Edlén equation

Since the 1988 revision further comparisons have been reported between directly measured values of the refractive index of air and values derived from both the original Edlén equation and the 1988 version [13–15]. The results from these comparisons confirm the higher accuracy of the 1988 version.

2.4.1 BCR comparison

Of particular significance is the comparison data which were obtained during a project funded by the Bureau Communautaire de Référence (BCR) of the European Community to evaluate the effect of variations in the refractive index of air on the uncertainties of industrial length measurement [13]. The project required a measurement system to be developed which incorporated an air refractometer with calibrated atmospheric sensors so that calculated and measured values of the refractive index of air could be obtained. About 6 500 refractive index measurements were made during the project from thirteen industrial locations in the UK and Germany. In addition several air samples were collected from each location and subsequently analysed for hydrocarbon levels.

The mean results from this project show differences between the measured values and those calculated from the 1966 and 1988 versions of the Edlén equation, at a wavelength of 633 nm, of $+5.9 \times 10^{-8}$ and $+1.1 \times 10^{-8}$ respectively, after application of a correction to account for the excess levels of carbon dioxide measured in the industrial environments. The results of the hydrocarbon analyses show that insignificant levels were present in each of the collected air samples which indicates that carbon dioxide was the main source of changes in air composition.

2.4.2 NIST comparison

Verification of the accuracy of the 1988 equation has also been reported by the National Institute of Standards and Technology (NIST) [15]. This was obtained from the interferometric length measurement of a one metre graduated Invar scale using a stabilized helium-neon laser operating at 633 nm. The overall length of the scale was measured during a period when there was a gradual increase in the relative humidity of the ambient air. The length measurements were corrected for values of the air refractive index derived using both the 1966 Edlén equation and the 1988 version.

The two sets of differences (δL) between the observed and the expected length of the one metre interval were plotted as a function of the partial pressure of water vapour, f , in the interferometer path. A linear regression fit to each set of data yields

the following equations:

$$\delta L/\text{nm} = 0,0572 (f/\text{Pa}) - 3 \quad (4a)$$

$$\delta L/\text{nm} = 0,0006 (f/\text{Pa}) - 3 \quad (4b)$$

for the original Edlén equation and the 1988 version, respectively.

The first expression shows a progressive offset in δL with the increase in the partial pressure of water vapour. This offset is equivalent to an error in the original Edlén equation of $5,72 \times 10^{-11}$ per pascal of water vapour. This is close to the $5,66 \times 10^{-11}$ per pascal found during the investigation at the NPL [10]. The second expression shows a hardly significant offset of 6×10^{-13} per pascal of water vapour. The constant term of 3 nm in each equation shows that there is no significant systematic offset from the dry-air terms of the Edlén equation.

2.5 The ITS-90 temperature scale

In 1966 Edlén would have used the International Practical Temperature Scale of 1948 (IPTS-1948); but since that time there have been two revisions of the scale. A revision to the International Practical Temperature Scale was agreed in 1968 (IPTS-68) [16] and a further revision was made in 1990. This resulted in the establishment of the International Temperature Scale of 1990 (ITS-90) [17].

Examples of the differences in the refractivity of air, $\Delta(n-1)$, which result from these decisions are

Table 1. Changes of refractivity resulting from temperature differences between the ITS-90 and the IPTS-1948.

$t/^\circ\text{C}$	$(t_{90} - t_{48})/^\circ\text{C}$	$10^8 \times \Delta(n-1)$
10	-0,006	0,6
20	-0,012	1,1
30	-0,016	1,5

shown in Table 1 for an ambient range of temperatures. For most practical temperature measurements the effect of these revisions is small. For measurements of the highest accuracy, however, these temperature differences are significant and hence, as in the case of the Edlén equation, revisions are required.

2.6 Air density

The refractive index of air is directly dependent on the density of air. Edlén used the data of Hilsenrath [18] to derive his equation. Since 1966, however, there have been several improvements to the equation for the density of moist air [19, 20] of which the most recent (designated as the 1981/91 equation) was accepted by the Comité International des Poids et Mesures (CIPM) [21]. In particular, this equation has been revised by Davis to include, among other developments, the introduction of the ITS-90

temperature scale and an improved value for the molar gas constant R .

3. Revision of the Edlén Equation

This section discusses the revision of the constants. A derivation of the various correction factors employed may be found in Appendix A.

3.1 Conversion to the SI system of units

As noted above, the torr, which is the unit of pressure used in the original Edlén equation, requires to be changed to the SI unit of the pascal. Since $1 \text{ torr} = 133,32 \text{ Pa}$, (1') and (3') become

$$(n-1)_{tp} = \frac{(p/\text{Pa})(n-1)_s}{96\,095,43} \times \frac{[1 + 10^{-8}(0,613 - 0,00998 \text{ } t/^{\circ}\text{C})] p/\text{Pa}}{(1 + 0,003\,661\,0 \text{ } t/^{\circ}\text{C})}, \quad (5)$$

$$n_{tpf} - n_{tp} = -(f/\text{Pa}) \times [4,292\,2 - 0,034\,3 (\sigma/\mu\text{m}^{-1})^2] \times 10^{-10}. \quad (6)$$

3.2 Revision of the dispersion term

3.2.1 Increased carbon dioxide levels

As mentioned earlier, carbon dioxide concentrations were also measured during many of the recent comparisons of values for the refractive index of air. These concentrations have always been found to be in excess of that assumed by Edlén. Since the refractive index of carbon dioxide is higher than that of air, these excess concentrations, if uncorrected, will have contributed to the differences between the measured and calculated values for the refractive index of air.

During the BCR-funded project discussed above [13], for each measurement of the refractive index of air a corresponding value for the concentration of carbon dioxide was also obtained. The mean concentration, derived from 6 500 measurements, was found to be 444 ppm with a standard deviation of 57 ppm. For the purposes of this revision, therefore, a concentration of 450 ppm is assumed for normal laboratory conditions.

Edlén gave the following expression for the refractivity of air containing x parts by volume of carbon dioxide:

$$(n-1)_x = [1 + 0,540 (x - 0,000\,3)](n-1)_s, \quad (7)$$

where $(n-1)_s$ is obtained from the Edlén dispersion equation.

From a recent measurement of the refractivity of dry air and carbon dioxide [22], it was found that an increase of 1 ppm of carbon dioxide in ambient

air increases the refractive index by $1,45 \times 10^{-10}$. By proportion, an increase in refractivity of $2,18 \times 10^{-8}$ will result from an extra 150 ppm of carbon dioxide in atmospheric air. This value agrees very closely with that derived from the Edlén equation. For carbon dioxide levels of 300 ppm and 450 ppm, (7) gives refractivity values of $276,5175 \times 10^{-6}$ and $276,5399 \times 10^{-6}$ respectively (for a wavelength of 633 nm) and a difference of $2,24 \times 10^{-8}$. If the mean value of $2,21 \times 10^{-8}$ is used, the correction factor to be applied to the dispersion terms in the Edlén equation is 1,000 079 9.

3.2.2 ITS-90 temperature scale

It is appropriate to revise the Edlén equation to reflect the currently accepted ITS-90 temperature scale. This change of temperature scale is most significant when applied to the dispersion formula which is used to calculate the refractivity of standard air at 101 325 Pa and 15 °C. As a result of the two revisions to the temperature scales, a temperature correction of $-0,009^{\circ}\text{C}$ is required at 15 °C and therefore a correction factor of 1,000 030 for the change to the ITS-90 scale should be applied to the constants.

3.2.3 Correction factor

Combining the correction factors for the increased carbon dioxide levels and the ITS-90 temperature scale results in the factor 1,000 109 9 which, when applied to (2'), produces the following:

$$(n-1)_s \times 10^8 = 8\,343,05 + 2\,406\,294 [130 - (\sigma/\mu\text{m}^{-1})^2]^{-1} + 15\,999 [38,9 - (\sigma/\mu\text{m}^{-1})^2]^{-1}. \quad (8)$$

3.3 Revision for dry air

Edlén used air density data to derive his equation and, in particular, values for dry air tabulated by Hilsenrath [18]. Edlén's expression for the compressibility factor Z for air may be written, in homogeneous form, as

$$Z - 1 = -10^{-6} (0,750 - 0,013\,04 \text{ } t/^{\circ}\text{C}) p/\text{torr}. \quad (9)$$

When the unit of pressure is changed to the accepted SI unit of the pascal the relationship becomes

$$Z - 1 = -10^{-9} (5,625 - 0,097\,81 \text{ } t/^{\circ}\text{C}) p/\text{Pa}. \quad (10)$$

As noted above, there have been further improvements to the air density equation producing, in particular, a more reliable expression for the compressibility factor. The constants of (10) have therefore been modified to provide a better fit to this new

data giving

$$Z - 1 = -10^{-9} (5,513 - 0,095\,26\,t_{90}/^{\circ}\text{C})p/\text{Pa}. \quad (11)$$

This revision modifies the constants of (5), which becomes

$$(n-1)_{tp} = \frac{(p/\text{Pa})(n-1)_s}{96\,095,43} \times \frac{[1 + 10^{-8} (0,601 - 0,009\,72\,t_{90}/^{\circ}\text{C})p/\text{Pa}]}{(1 + 0,003\,661\,0\,t_{90}/^{\circ}\text{C})}. \quad (12)$$

3.4 Revision for water vapour

Following the 1988 revision of the water vapour constants, (6) becomes

$$n_{tpf} - n_{tp} = -(f/\text{Pa}) [3,7209 - 0,0343 (\sigma/\mu\text{m}^{-1})^2] \times 10^{-10}. \quad (13)$$

However, a further small improvement may be made by deriving an absolute value for the refractivity of water vapour at 633 nm and using the relative refractivity values of Erickson [23] to derive suitable constants for use over visible wavelengths. The results of this derivation are shown in Table 2.

Table 2. Comparison of the refractivity of water vapour and dry standard air.

$\lambda_{\text{vac}}/\text{nm}$	Relative refractivity of water vapour (after Erickson)	$[10^9 \delta(n-1)/\partial p]/\text{Pa}^{-1}$			$10^9 [\delta'(n-1) - \delta(n-1)]/\text{Pa}^{-1}$
		Water vapour (derived value)	Dry air	$10^9 \delta(n-1)/\text{Pa}^{-1}$	Residuals
644,025	0,981 967	2,317 336	2,681 018	0,363 681	0,000 101
632,991	0,982 672	2,319 000	2,682 334	0,363 334	0,000 108
546,227	0,989 796	2,335 811	2,695 730	0,359 918	0,000 092
508,724	0,994 093	2,345 952	2,703 854	0,357 901	0,000 054
480,125	0,998 059	2,355 311	2,711 441	0,356 129	-0,000 070
467,946	1,000 000	2,359 892	2,715 128	0,355 235	-0,000 090
435,956	1,005 923	2,373 869	2,726 425	0,352 555	-0,000 200
404,771	1,013 228	2,391 108	2,740 325	0,349 216	-0,000 240
361,154	1,027 347	2,424 428	2,766 766	0,342 337	0,000 369

The first two columns in the table show values for the relative refractivity of water vapour obtained by Erickson for each wavelength. From (13), the difference, at a wavelength of 633 nm, in the variation with pressure of the refractivities, $\partial(n-1)/\partial p$, of dry standard air and water vapour is $3,6353 \times 10^{-10} \text{ Pa}^{-1}$. Similarly, from (5), the rate of change of refractivity with pressure of dry standard air at 20 °C is $2,68232 \times 10^{-9} \text{ Pa}^{-1}$ giving a value for water vapour of $2,319 \times 10^{-9} \text{ Pa}^{-1}$. Corresponding values for water vapour at each of the listed wavelengths have been derived from Erickson's relative values and are listed in column 3. Values for the refractivity of dry standard air at 20 °C have been derived from the 1966 Edlén equation and are shown in column 4 for a pressure of 101,325 kPa; differences

in the variation with pressure of the refractivity of dry air and water vapour, $\delta(n-1)$, are listed in column 5.

Finally the $\delta(n-1)$ data have been fitted to σ^2 using a linear regression of the form $\delta'(n-1) = a + b\sigma^2$. From this

$$a = 0,373\,451 \times 10^{-9} \text{ Pa}^{-1}$$

and

$$b = 0,004\,01 \times 10^{-9} (\mu\text{m})^2 \text{ Pa}^{-1}.$$

The residuals resulting from this regression, $\delta'(n-1) - \delta(n-1)$, are shown in the final column.

These residuals represent very small differences of refractivity. For example, the largest indicated residual of $3,69 \times 10^{-13} \text{ Pa}^{-1}$ corresponds to a difference of only $8,6 \times 10^{-10}$ in the refractivity of fully saturated air at 20 °C. Consequently the fitted constants are adequate for the purpose of this revision.

The revised version of (6) is given below:

$$n_{tpf} - n_{tp} = -(f/\text{Pa}) \times [3,734\,5 - 0,040\,1 (\sigma/\mu\text{m}^{-1})^2] \times 10^{-10}. \quad (14)$$

A comparison of (14) and (13), the 1988 version, shows differences of up to $8,1 \times 10^{-9}$ for fully saturated air at 20 °C over the visible range of wavelengths. Therefore, for ambient air, this difference is small and the conclusions regarding the accuracy of the 1988 version also apply to this revised version.

4. Discussion

Incorporation of all the revisions to the Edlén equations discussed in the previous sections gives

$$(n-1)_{tp} = \frac{(p/\text{Pa})(n-1)_s}{96\,095,43} \times \frac{[1 + 10^{-8} (0,601 - 0,009\,72\,t_{90}/^{\circ}\text{C})p/\text{Pa}]}{(1 + 0,003\,661\,0\,t_{90}/^{\circ}\text{C})}, \quad (12)$$

Table 3. Comparison equations for refractivity of air at $\lambda = 633$ nm.

Physical conditions			$10^8 \times (n-1)$		
p/kPa	$t/^\circ\text{C}$	Relative humidity/%	Original Edlén	Revised Edlén	Difference
80	20	0	21 456,8	21 459,0	+ 2,2
100	20	0	26 823,2	26 826,0	+ 2,8
120	20	0	32 190,5	32 193,8	+ 3,3
100	10	0	27 773,3	27 776,1	+ 2,8
100	30	0	25 935,7	25 938,5	+ 2,8
100	20	25	26 798,5	26 804,6	+ 6,1
100	20	50	26 773,9	26 783,4	+ 9,5
100	20	75	26 749,1	26 761,9	+ 12,8

Table 4. Comparison of refractivity determination at $\lambda = 633$ nm for ambient air.

Physical conditions				$10^8 \times (n-1)$				
$t_{90}/^\circ\text{C}$	p/kPa	f/Pa	x/ppm	Measured	Calculated		Measured - calculated	
					Original Edlén	Revised Edlén	Original Edlén	Revised Edlén
19,526	102,094 8	1065	510	27 392,3	27 385,1	27 394,0	+ 7,2	- 1,7
19,517	102,096 8	1065	510	27 394,0	27 386,5	27 395,4	+ 7,5	- 1,4
19,173	102,993	641	450	27 683,4	27 677,7	27 684,2	+ 5,7	- 0,8
19,173	103,006	642	440	27 686,9	27 681,2	27 687,7	+ 5,7	- 0,8
19,188	102,918 8	706	450	27 659,1	27 653,5	27 660,4	+ 5,6	- 1,3
19,189	102,927 8	708	440	27 661,4	27 655,9	27 662,7	+ 5,5	- 1,3
19,532	103,603 2	986	600	27 802,1	27 793,2	27 801,7	+ 8,9	+ 0,4
19,534	103,596 2	962	600	27 800,3	27 792,0	27 800,4	+ 8,3	- 0,1
19,534	103,599 2	951	610	27 801,8	27 793,4	27 801,6	+ 8,4	+ 0,2

where $(n-1)_s$ is given by the revised dispersion equation

$$(n-1)_s \times 10^8 = 8\,343,05 + 2\,406\,294 [130 - (\sigma/\mu\text{m}^{-1})^2]^{-1} + 15\,999 [38,9 - (\sigma/\mu\text{m}^{-1})^2]^{-1}. \quad (8)$$

For the difference in the refractive index of moist air, containing a partial pressure f of water vapour, and dry air at the same total pressure, the following revised expression has been obtained:

$$n_{tpf} - n_{tp} = -(f/\text{Pa}) \times [3,734\,5 - 0,040\,1 (\sigma/\mu\text{m}^{-1})^2] \times 10^{-10}. \quad (14)$$

The 3σ uncertainty associated with these equations is $\pm 3 \times 10^{-8}$ (mainly due to pressure, temperature and humidity measurement) and applies to ambient atmospheric conditions over the range of wavelengths from 350 nm to 650 nm.

5. Comparison of Equations

The original Edlén equations in the SI form (5), (6) and (2) and the revised forms (12), (14) and (8) are compared in Table 3 over the indicated range of

atmospheric conditions. The results show that, for typical laboratory conditions of 100 kPa, 20 °C and 50 % relative humidity, the revised equation gives a value of refractivity about 1×10^{-7} higher.

Finally, Table 4 demonstrates the effect of these revisions on determinations of the refractivity of ambient air made at the NPL by direct measurement and calculation. The table shows the atmospheric conditions in which the measurements were performed, all temperatures being expressed in terms of the ITS-90 scale. The final two columns list the derived differences between the measured values of refractivity and those calculated from the original and revised forms of the Edlén equation. The data in the table were computed on the assumption that no corrections were applied for the temperature differences between the ITS-90 and the IPTS-1948. However, these corrections would have increased the value of the measured temperatures and so reduced the calculated values of refractivity, using the Edlén equation, by $1,1 \times 10^{-8}$. The table clearly shows a marked improvement in the calculation of refractivity using the revised form.

It should be noted, however, that this revision of the Edlén equation still requires a correction where

the levels of carbon dioxide differ from the assumed value of 450 ppm.

6. Conclusions

This paper describes a revision of the Edlén equation and includes a detailed derivation of the various factors used so that any future amendments may easily be implemented. A comparison between the original and revised versions shows that an improvement, typically of 1×10^{-7} , in the calculated value of the refractive index is obtained for ambient air, although an additional correction must be made for levels of carbon dioxide which differ from the assumed 450 ppm if the highest accuracy is required. The appropriate carbon dioxide correction for this purpose is included.

Limitations in the measurement uncertainties of pressure, temperature and humidity, etc. result in a 3σ uncertainty of $\pm 3 \times 10^{-8}$ for the revised Edlén equation. The equation is valid for ambient atmospheric conditions over the wavelength range of 350 nm to 650 nm. Evidence from a variety of experimental results suggests however that this revised equation may have an improved uncertainty approaching $\pm 1 \times 10^{-8}$.

When the equation is used in practice, the total uncertainty associated with the calculated value of the refractive index of air could be increased to about $\pm 1 \times 10^{-7}$ due to the additional individual accuracy of each atmospheric sensor employed. Where a higher accuracy is required, direct measurement using a suitable refractometer is recommended.

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Appendix A

This appendix derives the correction factors which have been applied in the revision of the Edlén equation.

A.1 Carbon dioxide

From the Edlén dispersion (2), for a wavelength of 633 nm, $(n-1)_s = 276,5175 \times 10^{-6}$. This value is calculated for standard air which contains 300 ppm carbon dioxide.

From (7) the refractivity of dry air containing 450 ppm carbon dioxide is $276,5399 \times 10^{-6}$. Consequently the difference of refractivity between air containing 300 ppm and 450 ppm of carbon dioxide is $2,24 \times 10^{-8}$ while direct measurement [22] gives a value of $2,18 \times 10^{-8}$. For this reason, a mean value of $2,21 \times 10^{-8}$ was chosen for this revision.

The correction factor to be applied to the constants in the dispersion equation is therefore the ratio of the refractivities of dry air containing 450 ppm carbon dioxide and 300 ppm carbon dioxide, i.e. $276,5399/276,5175 = 1,0000799$.

A.2 Air density

Edlén introduces the equation of state in the following format:

$$\frac{pV}{RT} = 1 - \varepsilon_t p,$$

where V is the molar volume, R is the universal gas constant and T is the absolute temperature: ε_t is calculated from an expression derived from the data of Hilsenrath [18]:

$$\varepsilon_t = (0,750 - 0,01304 t/^\circ\text{C}) \times 10^{-6}.$$

Since $pV/RT = Z$, the compressibility factor, by combining the two equations above:

$$Z - 1 = -10^{-6} (0,750 - 0,01304 t/^\circ\text{C}) p/\text{torr}.$$

This is (9) in the main text.

Edlén showed that the constants 0,750 and 0,01304 should be increased to 0,817 and 0,0133, respectively, to allow refractivity to be calculated over a wide range of wavelengths.

Using more recent density data [21], the following expression for the compressibility factor has been derived in SI units, (11) in the main text:

$$Z - 1 = -10^{-9} (5,513 - 0,09526 t_{90}/^\circ\text{C}) p/\text{Pa}.$$

In order to derive the new constants for the Edlén equation the values 5,513 and 0,09526 are increased respectively by the factors 0,817/0,750 and 0,0133/0,01304 to give 6,010 and 0,0972. These are the constants used in (12).

A.3 ITS-90

From Table 1, the difference in temperature between the ITS-90 and the IPTS-1948 is $-0,009^\circ\text{C}$ at 15°C . Since $\partial(n-1)_{tpf}/\partial t = 9,24 \times 10^{-7} ^\circ\text{C}^{-1}$ [24], this temperature difference corresponds to an increase in the refractivity of dry air of $8,31 \times 10^{-9}$.

The correction factor to be applied to the constants in the dispersion equation is therefore $276,5258/276,5175$, where the numerator is the refractivity of dry air increased by $8,31 \times 10^{-9}$ and the denominator is the refractivity of dry air. This calculation produces a correction factor of 1,000030.

A.4 Water vapour term

For a wavelength of 633 nm (13) becomes

$$n_{tpf} - n_{tp} = -(f/\text{Pa}) 3,6353 \times 10^{-10}.$$

For dry standard air at a pressure of 100 kPa and temperature of 20°C,

$$(n-1)_{\text{p}} = 268,232 \times 10^{-6},$$

therefore the rate of change of refractivity with pressure is $2,682\,32 \times 10^{-9}/\text{Pa}^{-1}$ and the refractivity of water vapour is

$$\begin{aligned} [2,682\,32 - 0,363\,53] \times 10^{-9} \text{Pa}^{-1} \\ = 2,318\,79 \times 10^{-9} \text{Pa}^{-1}. \end{aligned}$$

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