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# Capability of commercial trackers as compensators for the absolute refractive index of air

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Keywords: Refractometry Precision measurement Air-wavelength Gas metrology	A procedure is presented which calibrates a wavelength/refractive-index tracker, so that it can compensate for the absolute refractive index of air within $3 \times 10^{-8} \cdot n$ . The procedure employs ultrahigh-purity helium and argon as reference gases of known $n(p, T)$ to deduce the two unknown parameters in the working equation of the tracker: gas pathlength and pressure-induced distortion error. The performance of the gas calibration procedure is evaluated by comparing the corrected tracker against a master refractometer based on a Fabry–Perot cavity in nitrogen, a third reference gas of known $n(p, T)$ . In nitrogen, the calibrated trackers demonstrate accuracy at the level of $4 \times 10^{-9} \cdot n$ . Testing in a fourth reference gas—water vapor—reveals that the working equation of the trackers must include a third unknown parameter: an end-effect caused by a moisture-dependence of the reflection phase-shift. Correcting for this moisture-related error represents the largest contribution to measure- ment uncertainty, and explains why performance of the calibrated trackers is an order-of-magnitude worse in moist air than in pure gas. In air, the Fabry–Perot cavity-based refractometer performs within $5 \times 10^{-9} \cdot n$ , but is not a commercially-available device.

## 1. Introduction

When operating outside of vacuum, the accuracy of lengthmeasuring interferometers can be limited by knowledge of the refractive index of air. Therefore, most manufacturers of laser metrology systems offer add-on devices that can compensate for refractive index. These add-on devices are usually classed as wavelength-trackers and refractive-index-trackers [1]. The general measurement equation governing their operation tracks changes in refractive index

$$\Delta n = \frac{\Delta \phi}{8\pi} \frac{\lambda}{L},\tag{1}$$

via changes in interferometric phase  $\Delta \phi$ . This generic (1) is for the typical doublepass configuration. The vacuum-wavelength of the metrology laser is  $\lambda$ . The characteristic length of the cell or etalon is L, which establishes a stable/constant gas pathlength. (Strictly, L is a difference in geometric length between two arms of an interferometer in which there is gas. Changes in the refractive index of this portion of the gas pathlength cause a change in interferometer phase. Throughout this article, the tracker parameter L will be referred to simply as gas pathlength.)

A tracker is a relative device, detecting changes in refractive index

relative to a known *n*-state of air. The reference *n*-state could be estimated by the Edlen equation with measurement of environmental conditions, or established as the scale error in the measurement of an artifact of precisely known length. There are two main reasons which preclude a tracker from measuring absolute refractive index. First, L is not accurately known, and even if determined within 1 µm by coordinate probing, it is not realistic to account for angular and positional misalignments between the axes of the interferometer and tracker at that level. Typically, differences between the mechanical estimate of L and the actual gas pathlength prohibit a measurement of absolute refractive index within  $10^{-7} \cdot n$ . The second factor relegating trackers to relative devices is that the pressure-induced distortion error is unknown. As mentioned, for conventional operation, a tracker defines a reference  $\phi$  at a known *n*-state of air estimated by the Edlen equation. By this action, the tracker becomes relative via  $\Delta \phi$ , and its distortion error is mostly irrelevant for the small  $\Delta p$  around atmosphere. To be used absolutely,  $\Delta \Phi = 2\pi \Delta N + \Delta \phi$  must be established relative to vacuum n = 1. Determining the integer change in fringe number  $\Delta N$  is no problem, but there is a difference in L between atmosphere and vacuum, caused by compressibility and/or a change in optical pathlength between the two states. Consequently, pressure-induced distortion represents an error between  $10^{-7} \cdot n$  and  $10^{-6} \cdot n$  in ambient air.

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**Fig. 1.** Topology of the refractometers studied in this work. (a) An etalon-based wavelength tracker [3,4]. (b) A cell-based refractive-index tracker [5,6]. (c) A Fabry–Perot cavity-based refractometer [12]. Relevant optical components include: helium–neon laser (HeNe), non-polarizing and polarizing beamsplitters (bs, pbs), quarter- and half-waveplates (qwp, hwp), retroreflector (rr), parallel-separating plate (psp), polarizer (pol), mirror (m), photodetector (pd), acoustooptic modulator (aom), lenses (pcx), fiber coupler/collimator (fc).

Approximately, the contribution of this article is a method to precisely determine the gas pathlength of a tracker and its pressure-induced distortion. The focus is on two popular commercial devices [2], but the general principle and approach is applicable to any refractometer. From one viewpoint, the attraction of commercial devices is that they have been robustly engineered, and seamlessly integrate with their respective multiaxis interferometer systems. Further, since the two devices studied are widely used in precision engineering, some tinkering to establish these trackers as absolute and accurate has immediate impact. (This development of single-point "absolute trackers" would be of most interest to length metrology at 1 m and below, which operate in highly uniform air/gas environments.)

The article covers much ground. It begins with a general description of the two trackers studied, and also describes a Fabry–Perot (FP) cavity master refractometer which plays an important crosscheck role throughout. The article then outlines the calibration procedure, which consists of measuring two gases (helium and argon) of known n(p, T) and deducing the unknown tracker parameters by least-squares regression. Comparisons are made between the calibrated trackers and the FP cavity refractometer in nitrogen, which is a third gas of known n(p, T). In a separate test, performance is assessed in water vapor. Taken together, the nitrogen and water vapor tests complete the evaluation, and it is upon these which an uncertainty statement is based. Finally, comparisons are made against the Edlen equation, which are of secondary importance.

## 2. Description of three different refractometers

One objective of this work is to outline a procedure to make a

wavelength/refractive-index tracker absolute and accurate. Two different commercial [2] trackers are evaluated: one based on an etalon, and one based on a vacuum cell. A master refractometer based on an FP cavity is also employed; this master refractometer is the check-standard to which the trackers are compared. All three refractometer topologies have been in use for more than thirty years, and so describing their operation is somewhat redundant. However, a brief description together with their working equation will be useful for what is undertaken in this work. This section therefore begins with a description of each measurement device: (i) an etalon-based refractometer, sometimes called a wavelength-tracker [3,4], (ii) a cell-based refractometer, sometimes called a refractive-index-tracker [5,6], and (iii) an FP cavity-based refractometer, sometimes called an air-wavelength reference [7,8].

## 2.1. Etalon-based wavelength tracker

A schematic for an etalon-based tracker is shown in Fig. 1(a). This topology compares optical pathlength between two unequal arms in a differential, doublepass heterodyne interferometer. The two separate frequencies, which facilitate the heterodyning, are implemented as the Zeeman-split in a dual polarization mode stabilized helium-neon laser [9], and are emitted orthogonally-polarized. The etalon creates an arm imbalance between two mirrored surfaces, which are fixed to a low thermal expansion spacer. Changes in the refractive index of the gas surrounding the etalon causes a change in the optical pathlength difference [3,4].

When the etalon-based tracker measures the change in optical pathlength difference between vacuum and pressure  $\Delta OPD = 4L_e[(n-1) - n \frac{\kappa_e}{2}p]$ , the working equation via  $\Delta \Phi \equiv \frac{2\pi}{2}\Delta OPD$  becomes

$$n-1 = \frac{\Delta \Phi \cdot \lambda + 8\pi L_{\rm e} \frac{\kappa_{\rm e}}{3} p}{8\pi L_{\rm e} \left(1 - \frac{\kappa_{\rm e}}{2} p\right)}.$$
(2)

The change in phase difference  $\Delta \Phi = 2\pi\Delta N + \Delta \phi$  in the interferometer is readout in response to changes in the refractive index of the gas, and must account for the change in integer fringe number  $\Delta N$ . The vacuum-wavelength of the HeNe laser is obtained by frequency calibration against a molecular reference [10], or by consensus [11]. The gas pathlength of the etalon  $L_e$  is unknown. More precisely, the difference between a dimensional estimate of the etalon spacer length versus the actual gas pathlength seen by the laser beam can cause error at the level of  $10^{-7} \cdot n$ . The error term  $\frac{\kappa_e}{3}$  is a distortion term proportional to pressure p, and is also unknown. Since all surfaces of the etalon are exposed to uniform pressure, the distortion error is predominantly compressibility  $\kappa_{\rm e} = \frac{1}{\kappa}$ , and the fractional length of the etalon changes by  $\frac{\Delta L}{L} = -\frac{\kappa_e}{3} \Delta p$ , with *K* being bulk modulus of the material from which the etalon is made. The length of the etalon decreases as pressure increases, and  $\kappa_e$  is signed positive in (2). For the glass-ceramic etalon used in this work  $K \approx 57.9$  GPa, so fractional length change is about 5.8  $\times$  $10^{-12}$ /Pa, which corresponds to error in ambient air of 5.8  $\times$   $10^{-7} \cdot n$ . When an etalon is made of homogeneous material,  $\kappa_e$  can be reliably estimated within  $\pm 5$  % using handbook values for elastic properties.

#### 2.2. Cell-based refractive-index tracker

A schematic for a cell-based tracker is shown in Fig. 1(b). Again, the source is a Zeeman-split polarization-stabilized helium-neon laser, and again a differential, doublepass heterodyne interferometer topology is employed, albeit with some differences in how the beams are separated and directed. The main conceptual difference between a cell-based system compared to an etalon is that now pathlengths are approximately balanced, with a measurement arm passing through gas and a reference arm passing through a cell permanently held at vacuum. Change in the refractive index of the gas surrounding the vacuum-cell causes a change in the optical pathlength difference [5,6].

When the cell-based tracker measures the change in optical pathlength difference between vacuum and pressure  $\Delta OPD = 4[L_c(n-1) - \varepsilon_w p]$ , the working equation

$$n-1 = \frac{\Delta \Phi \cdot \lambda}{8\pi L_{\rm c}} + \frac{\varepsilon_{\rm w} p}{L_{\rm c}} \tag{3}$$

is analogous to (2) with a gas pathlength  $L_c$ , but now must account for an error  $\varepsilon_w$  caused by change in window pathlength plus mirror bending. There is no straightforward analytic expression [13] for  $\varepsilon_w$ , but both its components—changes in window pathlength and mirror bending—can be estimated by finite-element methods. The term is proportional to applied pressure. A calculation procedure is outlined in Ref. [14], and details on the cell used in the present study are given in App. B, which estimates  $\varepsilon_w = -58.2$  fm/Pa. Sign of  $\varepsilon_w$  and its correction to (3) requires care. Given that the cell has a single-pass length of 70 mm, if pressure-induced distortion is uncorrected,  $\varepsilon_w$  represents an error of 4.2  $\times 10^{-8} \cdot n$  in ambient air. Note that  $\varepsilon_w$  is an end-effect, which is an error contribution that can be proportionally reduced by increasing cell length.

## 2.3. Fabry-Perot cavity-based refractometer

A schematic for an FP cavity-based refractometer is shown in Fig. 1 (c). The measurement principle is now based on resonant frequencies of the cavity  $\nu \approx \frac{mc}{2nL}$ , and changes in the refractive index of the gas between the cavity mirrors is directly related to changes in resonant frequency  $\frac{d\nu}{\nu} = -\frac{dn}{n}$ . As such, the laser frequency must be tuned and locked to a resonant frequency of the cavity, and the laser must be frequency-modulated in order to do so; further is the requirement for a stable reference frequency with which to compare and measure the changes in

cavity resonance frequency.

The working equation is based on deducing refractivity from a change in resonance frequency

$$n - 1 = \frac{\Delta f + \nu_{f} \frac{\kappa_{fp}}{3} p}{\nu_{f} \left(1 - \frac{\kappa_{fp}}{3} p\right)},$$
(4)

with  $\Delta f = (\nu_i - \nu_f)(1 + \varepsilon_{\alpha}) + \Delta m \frac{c}{2L_{fb}} + \varepsilon_d$ . Equation (4) above is identical to Eq. (2) in Ref. [12], when the latter is solved for n - 1. The initial  $\nu_{\rm i}$  and final  $\nu_{\rm f}$  resonant frequencies are measured as rf beat frequencies relative to a stable frequency reference, such as an iodine-stabilized laser. The integer change in mode number of the cavity is  $\Delta m$ . The effect of diffraction  $\varepsilon_d$  can be ignored for the accuracy levels that concern this work. The parameter  $\varepsilon_{\alpha}$  accounts for the fact that reflection phase-shift from the cavity mirrors has a frequency dependence. For refractive index measurements near 100 kPa, the effect  $\varepsilon_a$  is a negligible offset effect in (4). However,  $\varepsilon_{\alpha}$  is important when the cavity length  $L_{\rm fp} = \frac{c}{2\Delta\nu_{\rm fer}}/(1+\epsilon_{\alpha})$  is deduced via measurement of a free-spectral range  $\Delta \nu_{\rm fsr}$ , the frequency separation between adjacent resonant modes. The term  $\varepsilon_{\alpha} = \frac{c\alpha}{2\pi L_{\rm fp}}$  for a two mirror cavity is given by the change in reflection phase-shift as a function of frequency  $\alpha = \frac{d\phi_R}{d\nu}$ ; here  $\alpha$  and  $\phi_R$  are for one mirror. For the cavity used in this work,  $\varepsilon_{\alpha} = 7.6 \times 10^{-6}$ , and ignoring it when inferring  $L_{\rm fp} = \frac{c}{2\Delta\nu_{\rm ter}}/(1+\epsilon_{\alpha})$  would result in a 2.1 × 10<sup>-9</sup> · *n* error in atmospheric air.

All surfaces of the cavity are exposed to uniform pressure, so the distortion term is caused by compressibility  $\kappa_{\rm fp} = \frac{1}{K}$ , where *K* is bulk modulus. For the titania-silicate glass cavity used in this work,  $K \approx 34.1$  GPa, so the pressure-induced distortion error  $\frac{\Delta L}{L} = -\frac{\kappa_{\rm fp}}{3} \Delta p$  is about 9.8 ×  $10^{-12}$ /Pa which corresponds to error of 9.8 ×  $10^{-7} \cdot n$  in ambient air.

## 2.4. General contrast and compare

The brief descriptions above have shown much similarity between the three approaches to the measurement of refractive index, the main points are now summarized in general terms.

The etalon- and cell-based trackers both measure changes in interferometric phase, whereas the FP cavity-based refractometer measures changes in resonant frequency. Measurement of a resonant frequency-—effectively, thousands of beam passes through the gas path—affords ultrahigh resolution. But the more important difference is that what is happening outside the etalon and cell can influence the detected phase change, because it is part of the optical pathlength; by contrast, changes in resonant frequency for the cavity depend only on roundtrip phase inside the resonator. Consequently, the cavity is more stable, and more reproducible from setup to setup. Indeed, for the trackers, the initial phase at vacuum  $\phi_i$  should arguably be considered a pseudo-unknown parameter; to operate absolutely, the trackers need a recurring check on  $\phi_i$ . (Which entails a permanent vacuum system and plumbing requirement.)

The etalon and cavity have similar pressure-induced proportional error terms, governed by material compressibility, whereas the cell has an end-effect caused by change in window pathlength (and mirror bending). In general, a cell will have a lower pressure-induced error term compared to a refractometer based on an etalon or cavity. For the systems studied in this work, the pressure-induced distortion error in the cell is more than an order-of-magnitude smaller than the etalon and cavity. However, recent developments [14,15] have shown that the historical account [16] of window pathlength error is incorrect in magnitude and ambiguous in sign. Obviously, the topic is worth further study, if for no other reason than to build confidence in the error model so that correction might be based on calculation rather than measurement.

The cell has n - 1 dependent on cell-length; in contrast, both the etalon and cavity have *n* dependent on separation between mirrors. This difference is not apparent in (2) and (3), but it is implicit in the

#### Table 1

Proportionality coefficients for (5), which relate refractivity at  $\lambda = 632.9908$  nm to a measured gas pressure and temperature. Accuracy valid within  $16 \times 10^{-6} \cdot (n-1)$  for p < 500 kPa and  $T_{90} = (293.15 \pm 0.05)$  K.

gas	$c_1 \ / \big[ 10^{-7} \ (K/Pa) \big]$	$c_2 \ / \Big[ 10^{-13} \ \left( \text{K}/\text{Pa} \right)^2 \Big]$	$c_3 / \Big[ 10^{-18} ({\rm K/Pa})^3 \Big]$
He	0.9385856	-1.3345	0.2301
Ne	1.804466	-2.402	-0.536
Ar	7.569376	16.822	-22.31
Xe	18.74592	316.36	859.03
$N_2$	8.021159	7.050	-19.52
$CO_2$	11.98531	186.87	679.32
$N_2O$	13.52922	225.71	647.94

underlying assumption about pathlength difference. The consequence is that disturbances to the length of the cell during a refractivity measurement are  $10^4$  less significant compared to disturbances in lengths of the etalon and cavity. Example disturbances include thermal expansion, dimensional instability, temporal drift, etc. It is repeated that immunity to disturbance is *during* a measurement: there is no avoiding that  $L_c$  must be known either at vacuum or in gas, and consequently low thermal expansion and dimensionally stable materials remain desirable for cell construction.

The etalon and cell are commercial devices that integrate seamlessly with displacement metrology systems employing a Zeeman-split laser and Michelson interferometry. There is no commercial offering of a FP cavity-based refractometer. On this score, the hassle of modulation and feedback loops evident in Fig. 1(c) is no more complicated than anything internal to a Zeeman-split, dual polarization-stabilized laser: the lack of a commercial FP cavity-based refractometer offering is not because it is complicated. The single-cavity topology of Fig. 1(c) also requires a separate iodine-stabilized laser, but this piece of high-end hardware can be omitted when the refractometer is based on a dual-cavity design [17].

The etalon is unique in that it has two mirrored surfaces "facing the same direction." In principle, any effect disturbing the phase-shift on reflection should cancel in a measurement of refractive index. From past work [12], it is known that exposure to water vapor can affect the optical length of a cavity at the level of several nanometers, causing error at the few  $10^{-8} \cdot n$ . This work revisits the water vapor effect, and makes quantitative estimates for all three systems studied.

The gas pathlength of the cavity can be inferred by measurement of the free-spectral range. Consequently, (4) has only one unknown—distortion  $\frac{\kappa_{ip}}{3}$ . In contrast, there is no equivalent method of determining the gas pathlength of the etalon and cell, so (2) and (3) have two unknown terms—gas pathlength and distortion. Therefore, a cavity can be calibrated by measuring one gas of known n(p, T)-state and deducing  $\frac{\kappa_{ip}}{3}$  as the error term [18]. However, calibration of the trackers requires measurement of two gases of known n(p, T)-state. It is the recent establishment [14,19] of the known n(p, T)-state for several metrology gases that now facilitates this two-gas calibration, as described next.

## 3. Procedure and apparatus

This section first outlines the principle behind calibrating a tracker. The procedure is based on measurement of reference gases, whose refractivity can be calculated as a function of pressure and temperature. The experimental apparatus is then described. The section ends by implementing the calibration procedure, using helium and argon gases to deduce the two unknown parameters in each tracker.

## 3.1. Calibration via reference properties

The approach to calibrate a tracker by measurements of gases of known refractivities is based on solving a system of linear equations. The first step is to recognize that refractivity can be calculated at a known pressure and temperature

$$n-1 = c_1 \left(\frac{p}{T}\right) + c_2 \left(\frac{p}{T}\right)^2 + c_3 \left(\frac{p}{T}\right)^3 + \cdots,$$
 (5)

with

$$c_{1} = \frac{3A_{R}}{2R}$$

$$c_{2} = \frac{3}{8R^{2}} \left( A_{R}^{2} - 4A_{R}B_{\rho} + 4B_{R} \right)$$

$$c_{3} = \frac{3}{16R^{3}} \left[ 5A_{R}^{3} - 4A_{R}^{2}B_{\rho} + 4A_{R} \left( 4B_{\rho}^{2} + B_{R} - 2C_{\rho} \right) + 8(-2B_{R}B_{\rho} + C_{R}) \right].$$
(6)

using proportionality coefficients  $c_1$ ,  $c_2$ , and  $c_3$ , and with R being the gas constant. Equation (5) is based on the Lorentz-Lorenz equation governing the relation between refractive index and gas density via molar polarizability  $A_R$  (and with refractivity virial coefficients  $B_R$ ,  $C_R$ describing small deviations from linear). To replace molar density with  $\frac{p}{r^2}$  (5) also employs an equation-of-state describing deviation from ideal gas behavior (through density virial coefficients  $B_{\rho}$ ,  $C_{\rho}$ ). Details on (5) are given in Ref. [14], where a final series inversion gave an emphasis on  $p(n-1)_T$ . What is most relevant for the present article is that the proportionality coefficients are accurately known for six gases via measurement [14] at 20 °C, and for helium the coefficients are accurately known via first-principles calculation [20]. For reference, these coefficients are listed in Table 1. For nitrogen at 100 kPa and 20 °C, the accuracy of a refractive index calculation using these coefficients corresponds to 4 parts in  $10^9$ . It is likely that both the accuracy and valid (temperature) operating range for some of these gases will be improved in the near future; regardless, the accuracy levels of Table 1 already satisfy the present purposes of calibrating a tracker such that it can outperform the Edlen equation.

The essence of the calibration procedure is to use the tracker, a barometer, and a thermometer to measure n(p, T) for two gases; and then to deduce the two unknown parameters of the tracker by comparing the measured refractivity to what is expected based on calculation in (5). To take the etalon as example, the two unknown parameters are found by minimizing the difference between measurement and calculated refractive indexes

$$\min_{L_{e}, \frac{e_{e}}{3}} \left[ \sum \left( n_{\text{meas}} - n_{\text{calc}} \right)_{\text{He}}^{2} + \sum \left( n_{\text{meas}} - n_{\text{calc}} \right)_{\text{Ar}}^{2} \right].$$
(7)

For each gas,  $n_{\text{meas}}$  is the "instrument equation" defined in (2), and  $n_{\text{calc}}$  is the "reference property equation" given by (5) and Table 1. The two unknown parameters, gas pathlength  $L_{\text{e}}$  and pressure-induced distortion  $\frac{\kappa_{\text{e}}}{3}$ , are optimized to find the minimum of the objective function.

Before next moving onto an experimental demonstration, some caveats on what has just been outlined should be mentioned. The motivational statement is that the accuracy goal in the absolute refractive index of air is  $5 \times 10^{-9} \cdot n$ , but ...

- 1. Equation (5) develops error when operating away from (20.00  $\pm$  0.05) °C, if using the fixed-value coefficients of Table 1. The nonlinear terms  $c_2$  and  $c_3$  are temperature-dependent and, for a molecule,  $c_1$  is also temperature-dependent. In principle, most of this error can be corrected using a reference property calculator (e.g., Ref. [21]). However, for the subset of length metrology applications, where the only practical interest is in the gases helium, argon, and nitrogen at pressures up to 110 kPa, the valid operating range of Table 1 becomes (20  $\pm$  1) °C. Under these (low-density) constraints, error in the refractive index of argon calculated with (5) becomes no larger than  $3 \times 10^{-9}$ . Consequently, the proportionality coefficients in Table 1 meet present accuracy goals for most tracker calibrations.
- 2. The calibration procedure requires accurate measurements of pressure and temperature, corresponding to about 1.8 Pa at 100 kPa and



Fig. 2. Top-level diagram of the experiment. The etalon- and cell-based trackers were compared, in turn, to the Fabry–Perot cavity-based refractometer. Gas pressure was measured with a barometer at the gas inlet, gas temperature was measured with thermistors inside the chamber.

5.4 mK at 20 °C, respectively. Past experience with commercial pressure transducers is that this level of performance is unrealistic unless care is taken in the handling and thermal history of the instrument, the zero-pressure reading is repeatedly recorded and corrected for, and that experimental technique is identical in all gas measurements. Arguably, accuracy requirements on the pressure transducer is the weakest link toward achieving the performance

goal in absolute refractometry. Past experience with commercial thermometer bridges and glass-bead thermistors in a highly isothermal environment is that the temperature requirement is easily met. However, care must be taken to keep all parameters/measurements on the same temperature scale. This article has used the international temperature scale of 1990, and Table 1 is stated as  $T_{90}$ ,



Fig. 3. Steady-state dimensional/temporal stability of the refractometers at vacuum and temperature-stabilized near 20  $^\circ\text{C}.$ 

which is conventional in dimensional metrology. However, (5), and hence (7), must use thermodynamic temperature.

3. The underlying concept that  $c_1$ ,  $c_2$ ,  $c_3$  allows one to calculate the refractivity of a pure gas, requires that a pure gas is used in the calibration procedure. The requirement is not extreme, and can be easily met with 99.9999 %-purity, which is widely-available for the main three metrology gases: helium, argon, and nitrogen. High-purity work is also contingent on a plumbing setup that accommodates turbopumping to high-vacuum (order-of 10 mPa). The gas-purity requirement also extends to compliance with good vacuum practice [22], material choices, and cleanliness.

## 3.2. Experimental arrangement

A top-level view of the experiment is shown in Fig. 2, which compliments the schematics of Fig. 1. The general idea is that either the etalon or cell was characterized beside the cavity: the FP cavity-based refractometer was the crosscheck standard in all measurements. The characterization was performed by filling a chamber with different gases, and analyzing the results as mentioned above. Next follows additional experimental details.

## 3.2.1. Apparatus details

The trackers used their respective Zeeman-split, polarization-stabilized laser (not shown in Fig. 2) and differential interferometer optics. However, there were two notable deviations from standard operating procedure: (i) the etalon/cell was placed inside an aluminum chamber, which could be pumped to vacuum and filled with pure gas, and (ii) custom photodetectors and phasemeter were used to readout the interferometer phase (not shown in Fig. 2). The former is a prerequisite when the interest is absolute refractometry, and this was implemented by forming the base of the vacuum chamber on an oversized aluminum plate, to which the etalon/cell and differential interferometer were both mounted. Custom phasedetection was done to (i) allow a fair comparison of both systems, (ii) ensure readout electronics were not the resolution limit, and (iii) remove any dependence on manufacturer software/processing algorithms, etc. (Here, "custom" means other commercial products which are not part of the tracker metrology system. There were no special characteristics in either the photodetectors or the phasemeter, but the phasemeter is a high-end instrument, holding sub-milliradian precision and linearity on megahertz signals.)

The FP cavity was built in 2016, with D-shaped mirrors stood-off a polished spacer bar. Both mirrors and spacer bar were made of low thermal expansion titania-silicate glass. The mirrors were silicatebonded to the spacer bar when a HeNe laser beam was present, so that resonance was ensured: the resonant mode is within 1 mm of center of the mirrored portion. The cavity length was 150 mm, and configured plano-concave with one mirror having 0.5 m radius of curvature. The mirrors were ion-beam sputter-coated to 99.8 % reflectivity (finesse 2000). As depicted in Fig. 2, the cavity was mounted friction-free by cable suspension, and its beam altitude matched the altitude of the trackers within 2 mm, necessitating a recess into the bottom of the chamber. The cavity system and electronics sketched in Fig. 1(c) closely follow Ref. [12].

The chamber/pressure vessel of Fig. 2 was sized to house the cavity and either the etalon or cell, in turn. The base of the chamber had the necessary fittings for the gas inlet, the vacuum line (gas outlet), and an electrical feedthrough for two thermistors. The chamber/pressure vessel was placed inside an aluminum envelope, temperature-stabilized to  $20.00 \pm 0.01$  °C with foil heaters. The gas inlet and vacuum line were thermally-lagged to the aluminum envelope, to avoid a conductive short to the lab temperature. Windows were glued to the aluminum envelope so that there was no convection with the lab temperature. It should be noted that for the trackers, the windows on the thermal envelope and vacuum chamber become part of the interferometer pathlength: removing them post-calibration will alter the initial (vacuum) phase  $\phi_{i}$ , and may cause large error in the system. Finally, a foam box was placed over the aluminum envelope (the foam box had holes without windows; the foam box is not shown in Fig. 2).

The chamber was pumped with a turbopump station, and achieved vacuum at the level of 20 mPa. Gas pressure was generated with a pressure-balance and recorded with a pressure transducer. The natural reference level of the pressure-balance was within 2 mm of the optical axes of the refractometers. The pressure transducer was calibrated within 16 µPa/Pa by a measurement of helium refractivity at known temperature [14], and is traceable to the SI kelvin. Two thermistors inside the chamber were used to record gas temperature. The thermistors were calibrated within 1 mK on the international temperature scale of 1990 (ITS-90): the thermistors were compared to a standard platinum resistance thermometer which interpolated between resistance measurements made in a water triple-point cell and gallium melting-point cell. All pressure and temperature calibration and instrumentation-comprising a pressure-balance and fixed-point cells with maintenance systems-were carried out in the same lab: Fig. 2 belies the efforts/scope involved in the supporting  $p/t_{90}$  instrumentation.

## 3.2.2. Vacuum stability and precision

Before describing the gas measurements, a few observations are made about the stability of the three systems, steady-state at vacuum. Phase/frequency stability and fringe-resolving capability in vacuum (when temperature-stabilized) is one method of estimating system precision.

One-week vacuum stability data are shown in Fig. 3. To reduce the data to fractional length and allow like-to-like comparison, the

#### Table 2

Highlight results from the two-gas characterization and minimization procedure. The length of the FP cavity  $L_{\rm fp} = 149.864$  mm was obtained by measurement of the free spectral range  $\Delta \nu_{\rm fsr} = \frac{c}{2L}/(1 + \epsilon_a)$ .

ZLip			
	etalon	cell	cavity
Eq. (7) /10 <sup>-15</sup>	3.47	4.48	na
helium $\sigma/10^{-9}$	5.44	7.16	0.17
argon $\sigma/10^{-9}$	7.57	7.86	0.70
$L_{\rm e}, L_{\rm c}/{\rm mm}$	127.159	70.032	na
$\frac{\kappa_{\rm e}}{3}, \ \frac{\varepsilon_{\rm w}}{L_{\rm c}}, \ \frac{\kappa_{\rm fp}}{3} \ /(10^{-12} \cdot {\rm Pa}^{-1})$	5.652	-0.759	9.862



**Fig. 4.** Vacuum zero stability during each measurement campaign for the (a) etalon and (b) the cell. Shaded areas denote the timeline of the gas species being used in the characterization. Note that the ordinate has  $10^{-8}$  for scale, in contrast to the  $10^{-9}$  of Fig. 3.

respective values of  $L_{\rm e}$  and  $L_{\rm c}$  are used; changes in fractional length of the cavity are equivalent to changes in fractional (resonant) frequency. Note the cell data in Fig. 3 have had a large linear drift removed (discussed more in the next section). As is well-known, the precision of a resonant FP interferometer is many orders of magnitude higher than a Michelson interferometer, and Fig. 3 encapsulates that fact. To take total deviation [23] as the figure of merit: for an analysis interval of 24 h, the cavity is almost 200 times more precise than the trackers. Total deviations are  $2.9 \times 10^{-9}$ ,  $1.4 \times 10^{-8}$ , and  $1.5 \times 10^{-11}$  for the etalon, cell, and cavity, respectively.

For the etalon and cell, the steady-state vacuum stability data are initial warning that precision may be a limit in reaching the motivational goal of  $5 \times 10^{-9} \cdot n$  uncertainty in ambient air. Indeed, as

discussed next, steady-state vacuum stability is too optimistic a picture of precision.

## 3.3. Details on the calibration

The calibration procedure was simply to measure n(p, T) of helium gas, followed by n(p, T) of argon gas some time later. The collected data were then ported to an optimization algorithm, which deduced the unknown parameters of (2) or (3). The data and implementation behind the characterization are included in the supplementary material to this article. Table 2 provides an overview of the results. Some features of the calibration are now discussed, but details about overall uncertainty for a calibrated system are confined to Appendix D.

The first entry in Table 2 is the optimized result of the objective function (7). The root-mean-square error (alternately, mean absolute error) is obtained by taking the entries of Table 2, dividing by the number of predictions (80 in this dataset), and finding the square-root: the results are 6.6  $\times$  10<sup>-9</sup> for the etalon and 7.5  $\times$  10<sup>-9</sup> for the cell. It is of interest to evaluate the standard deviations  $\sigma$  for each of the two gases in the dataset. To be clear,  $\sigma$  in Table 2 refers to standard deviation on the 40 predictions of  $n_{\rm meas} - n_{\rm calc}$  for each gas, where  $n_{\rm meas}$  is postcalibration and uses the optimized parameters for gas pathlength and distortion coefficient. The interest in  $\sigma$  for each gas is because, in principle, the ratio of standard deviations should approach the ratio of refractivities (polarizabilities), unless a system is performance limited. For Ar: He the polarizability ratio is 8.1. There are three likely explanations why  $\sigma$  ratios in Table 2 are lower than polarizability ratios: (i) offset errors are dominant effects, (ii) helium permeation into material and/or coatings causes problems, (iii) general instability/hysteresis. These possible explanations will be revisited momentarily. Discussion about the calibration campaign is also well-served by Fig. 4, which shows how the vacuum zero of each refractometer changed over time and in various gases. Here, vacuum zero means the interferometer phase or resonant frequency when turbopumped to p < 20 mPa: the ordinate of Fig. 4 converts changes in the phase or frequency to the equivalent change in refractive index from the n = 1 reference of vacuum. Fig. 4 gives a fuller picture of the stability for a working system over a long period of time, unlike steady-state vacuum stability in Fig. 3.

For the etalon, the  $\sigma$  in Table 2, suggests a general offset effect limiting performance, on the order of  $6\times 10^{-9}$  in refractive index. This limit can be reasonably interpreted as a 0.8 nm variability on  $L_{e}$ , or 30mrad random error on  $\Delta \phi$ . Clearly, the vacuum zero data for the etalon in Fig. 4(a) support the assessment that variability is either in  $L_e$  or  $\phi_i$ . Before the measurement campaign, the etalon had a vacuum bake-out to 85 °C for three days; the relaxation observed in Fig. 4(a) is wellestablished for glass-ceramic [24]. However, on the relaxation trend, there is daily fluctuation on the vacuum zero of  $\pm 10^{-8}$ . Since these fluctuations are larger than steady-state operation in Fig. 3(a), it is reasonable to attribute their origin either to compressibility hysteresis or some other pressure-induced instability in the etalon. A (large) random error proportional to pressure explains why the etalon  $\sigma$  in Table 2 are of similar magnitude, independent of gas species. Note: the etalon characterized in this work is over 15 years old, and there have been advancements in the stability and performance of ceramics [25] in the interim. So, observations in Fig. 4(a) for one specific device should not peremptorily reject the etalon concept in precision refractometry (Note that Ref. [25] describes a pure ceramic, whereas the etalon studied here is a glass-ceramic. For this non-transmissive etalon design, one can imagine improved performance using a low CTE pure ceramic without thinfilm coatings. This remark about the benefit of no thinfilm coatings will become apparent later in the article.).

In terms of  $\sigma$ , the cell performance is similar to the etalon, and this is impressive because the  $L_c$  is 45 % shorter than  $L_e$ . The similar  $\sigma$  results in helium and argon can also be attributed to instability. The  $\sigma$  performance demonstrated in Table 2 was only possible because the vacuum zero was checked immediately before every measurement of refractive



**Fig. 5.** Agreement between the measured refractive index of nitrogen and its calculation. Errorbars span one standard deviation on 10 repeat measurements. For clarity, at each of the four generated pressures the datasets for each refractometer are separated by 1.5 kPa. Shaded area denotes uncertainty in the calculated n(p, T).

index. The necessity of this frequent checking is evinced by the instability of the vacuum zero in Fig. 4(b): the cell-based system had a large, inexplicable drift. With balanced-pathlengths reflected off the same mirror, the cell pathlength drift should be almost independent of drift in the invar vacuum tubes. The magnitude of the trend in Fig. 4(b) corresponds to 17.6  $\times$  10  $^{-9}/d,$  which is arguably too large to arise from second-order effects, such as material mismatch drift-rates bending the mirror. For example, the landmark study by Jacobs et al. [26] showed variations in the temporal drift rates among thirteen invar samples of between 4.1  $\times$  10  $^{-9}/d$  and 20.6  $\times$  10  $^{-9}/d.$  The cell is constructed of two separate invar vacuum tubes tack-welded together: if the two tubes were drifting at different rates, distortion across the mirror surface would be a complicated phenomenon, but explaining Fig. 4(b) would require perhaps unreasonable dissimilarity [26] in tube stock. Regarding a possible moment induced by fixturing the cell assembly to the chamber base: the three-point fixturing is kinematic, and all manufacturer hardware was used. It must also be noted that how the glass window is bonded to the invar vacuum tube is unknown. Seeking other explanations, an alternative to changing dimensions would be a compromised vacuum cell. The cell trend in Fig. 4(b) implies decreasing pressure inside the vacuum cell, but again the magnitude of the change puzzles: about 0.6 Pa/h, and Fig. 4(b) implies a 694 Pa decrease in pressure inside the vacuum cell (assuming nitrogen). Also puzzling is the fact that the cell and seal is obviously intact, because no gas appears to have entered/exited the cell throughout the campaign of Fig. 4(b). (Moreover, the cell produces reliable measurements for the refractive index of all gases, which will be proven in the next section.) Further, cycling the cell by 1 K showed a fractional change in pathlength  $9 \times 10^{-9}$ /K: while interpretation of this test is coupled  $\left(\frac{\mathrm{d}n}{\mathrm{d}T}\right)_p$ with а temperature-dependence of the interferometer, it does place a fairly reliable constraint on how much gas could possibly be inside the cell; for example, if it is air inside the cell, its pressure could be no larger than 108 Pa. Finally, a large change in  $\phi_i$  is possible if a beam were to slowly walk off a photodetector, but such an effect would most likely also cause change in the amplitude of the heterodyne signal: there was no change. In any event, conjuring this effect for the cell setup, while the etalon showed no evidence of it, is also not easy to explain, because both used the same photo/phasedetection configuration in the same bench setup: the beginning of Fig. 4(b) is eleven days after the end of Fig. 4(a). So neither dimensional instability, a compromised vacuum cell, or beam

walk/clipping seem credible in explaining Fig. 4(b)—user-error is as viable as any other explanation. Again, as with etalon drift, what is observed here for one specific device should not categorically dismiss the cell concept.

For the cavity, its  $\sigma$  ratio Ar: He is closest to what is expected. The small difference between the Ar: He ratio of  $\sigma$  versus ratio of polarizability can be attributed to the well-established problem of helium permeation into titania-silicate glass [12,27]. Instability in cavity length caused by helium permeation is clearly evident in the vacuum zero data of Fig. 4(a). A synopsis is that helium permeation into the cavity material causes its length to increase over time; to correct for this effect, the data are reduced to constant density and fit with a diffusion-model [27]  $\beta\sqrt{t}$  to deduce the measurement of helium refractivity immediately after the fill (i.e., at time t = 0). In principle, this fitting and extrapolation can be done at the level of  $10^{-6} \cdot (n-1)$  in a system designed with rapid thermal response. However, the large volume system reported on here (Fig. 2) is designed for side-by-side refractometer comparison, and not optimized for thermal response: in helium, the thermal time constant is 1100 s, and the increase in temperature caused by pV-work is 35 mK for a 60 kPa fill. Under these suboptimal conditions, constant density data near t = 0 are unreliable, consequently extrapolation to t = 0 is prone to variability. Nevertheless, the helium  $\sigma$  in Table 2 corresponds to 4.2  $\times$  $10^{-6} \cdot (n-1)$ , which is not bad performance. After the helium tests, the vacuum zero of Fig. 4(a) returns to monotonic/predictable shrinking of cavity length in argon and nitrogen. In summary, for the cavity, the helium  $\sigma$  in Table 2 is larger than expected because of helium permeation.

Finally, a few words about plausibility of the deduced parameters in Table 2. For the etalon gas pathlength  $L_{e}$ , the gas-calibrated value can be compared to what was measured dimensionally with calipers. The estimate of dimensional etalon length was 26 µm shorter than what was deduced by gas calibration. For the etalon distortion coefficient  $\frac{\kappa_e}{3}$ , the gas-calibrated value is 1.9 % lower than  $\frac{1}{3K}$ , using the material datasheet for bulk modulus K. This difference is small, but it can be mentioned that the etalon is not friction-free to deform, and by manufacturer design is pinched at its ends by setscrews mounted in an aluminum frame. While no attempt has been made to estimate what effect point-contact friction in an aluminum frame might have on the deformation of a glass-ceramic optic, it would intuitively seem to decrease compressibility, because the frame is 19 % less compressible than the etalon. For the cell gas pathlength  $L_c$ , the gas-calibrated value is 12 µm longer than the dimensional estimate. For the cell distortion coefficient  $\frac{\varepsilon_w}{L}$ , the gas-calibrated value is 8.7 % lower than what is predicted by the model for window pathlength error, which is calculated based on finite-element analysis in App. B. While this difference between model and experiment is large, it is expected and can be explained. The dominant contributor to  $\varepsilon_w$  is mirror bending, and the model assumes the beam is centered on the mirror where deformation is largest. To first-order, treating the deformed mirror as triangular, the deformation slope is 7.3 (fm/Pa)/mm, so an offcentering of one beam by only 1 mm would reduce  $\varepsilon_w$  by 13 %. Overall, the agreement between the calculated and measured (deduced) values for  $\varepsilon_w$  support recent claims [14,15] that window pathlength error in cell-based refractometers is understood.

## 4. Further testing and results

After the two-gas calibration, a series of tests were performed to validate the approach. First was a consistency test with nitrogen, a third reference gas of known n(p, T). Transitioning from "dry" gases, the effect that water vapor can have on these various refractometer topologies was investigated. The testing finished with a comparison of all three refractometers to the Edlen equation, which has historically been the reference for the refractive index of air in dimensional metrology. The tests reported in this section are critically influential on subsequent uncertainty estimates for each refractometer. To keep the argument



**Fig. 6.** Tests in water vapor. (a) Data from the cavity used to determine the molar polarizability of water vapor. (b) Error in the refractive index reading from the two calibrated trackers relative to the calculated value.

concise, all uncertainty discussion and budgets are disposed to Appendix D.

## 4.1. Consistency tests in nitrogen

The main interest for testing in nitrogen is that it is also a reference gas of well-known n(p, T) [14]. In this consistency test, the deduced parameters of the etalon and cell have been fixed by the two-gas calibration (helium and argon). Consequently, any deviation between the measured and calculated refractive index of nitrogen is a sign of trouble.

The nitrogen measurements are summarized in Fig. 5, which shows disagreement in the measured and calculated refractive indexes. The measured refractive index is defined by (2) or (3), in which the two unknown tracker parameters have been deduced by the two-gas calibration above. The calculated refractive index is obtained via (5), together with knowledge of gas pressure and temperature. The shaded area in Fig. 5 indicates standard uncertainty on the calculated value of *n* (*p*, *T*), corresponding to about  $16 \times 10^{-6} \cdot (n - 1)$ , as described in Ref. [14].

The FP cavity has two sets of data, because it was common to both tests: the first side-by-side with the etalon labeled "e", and the second side-by-side with the cell labeled "c". The two nitrogen datasets are separated in time by 48 d. The cavity shows agreement within  $10^{-9} \cdot n$ 

compared to the calculated refractive index. An alternative interpretation of the cavity data in Fig. 5 is that the molar polarizability reported in Ref. [14] has been validated at the same level of uncertainty (i.e., limited by how accurately the thermodynamic pascal can presently be realized). The cavity reproducibility in the tests "e" and "c" of Fig. 5 is within  $(2.4 \pm 2.6) \times 10^{-6} \cdot (n-1)$ , or  $6.5 \times 10^{-10} \cdot n$  for ambient nitrogen. While impressive, this is not state-of-the-art [17], and can be explained by the suboptimal thermal design of Fig. 2: reproducibility of  $6.5 \times 10^{-10} \cdot n$  for ambient nitrogen corresponds to reproducibility of 0.7 mK in gas temperature. This shortcoming could be circumvented by (i) enclosing the cavity mode inside a bore through a copper block, with the block mounted such that it does not touch the glass, and (ii) inserting the thermometers inside the copper block, very close to the mode bore. Simulations show that such an arrangement can reduce thermal settling times by about a factor of twenty.

For the trackers, agreement between the measured and calculated values of nitrogen refractive index is equivalent to what is observed with the cavity, but the tracker data display much larger standard deviation. For the etalon, the mean offset from the calculated refractive index of nitrogen is  $0.3 \times 10^{-9}$ , with standard deviation  $7.3 \times 10^{-9}$ . The cell has a mean offset of  $0.6 \times 10^{-9}$  and standard deviation  $7.0 \times 10^{-9}$ . These performances are remarkably good—the calibrated trackers perform within best-knowledge of gas properties, and performance is arguably two orders-of-magnitude more accurate than what is realistic with an uncalibrated tracker. The performance of Fig. 5 is approximately the uncertainty a calibrated tracker might be expected to demonstrate in the measurement of any dry gas. An in-depth uncertainty discussion is given in App. D.

These consistency tests in nitrogen are extremely encouraging. However, since the ultimate interest is in the refractive index of moist air, the performance of a calibrated tracker in dry gas may lead to false confidence. Consequently, attention must be devoted to the effect of water vapor, as described next.

## 4.2. Tests with water vapor

Tests with water vapor can be analyzed two ways. First, is to interpret the cavity measurement as absolute and accurate, and thereby report a reference value for the molar polarizability of water vapor. As Schödel et al. [28] discussed, past measurements of water vapor refractivity are rare and of low-accuracy—Schödel et al. made comparisons with "recent" data from 1914, 1939, and 1949, showing discrepancies at the level of  $\pm 1.5$  %. Clearly, an independent determination of the refractivity of water vapor testing is to see how much the trackers deviate from the reference value for the refractivity of water vapor.

#### 4.2.1. Molar polarizability of water vapor

A sample of distilled and degassed water was connected to the gas inlet of the apparatus in Fig. 2. When the chamber was at high-vacuum, opening the valve to the water sample evaporated the water into the chamber. At 20 °C, the saturation pressure of water is  $p_{\rm ws} =$  2.339 kPa [21], and relative humidity  $\varphi = \frac{p_{w}}{p_{ws}} \times 100$  is determined by the pressure of water vapor  $p_w$ . All tests were carried out  $p_w < 2$  kPa. To determine the molar polarizability of water vapor using the FP cavity, the two important pieces of information are required: (i) an independent method to determine the effect of water vapor on the reflection phase-shift of the cavity mirrors, and (ii) a pressure transducer calibrated below 2 kPa. The first requirement is taken care of in App. C. The second requirement is accomplished in an ancillary step, by running the cavity in argon at known temperature, and realizing the optical pressure scale [29]  $p_{\text{ops}} = \frac{2RT}{3A_n}(n-1) + \cdots$  using the reference properties [19] for argon gas established [14] relative to helium. A calibration lookup table was produced by comparing the calculated  $p_{ops}$  to the transducer reading.



**Fig. 7.** Comparison of the cavity and etalon refractometers to updated versions [43,44] of the Edlen equation. Subplots (a) to (d) show the environmental conditions of lab air during the comparison. (e) Air refractivity measured by the FP cavity-based refractometer. (f) Disagreement of all estimates of the refractive index of air, relative to the cavity. All data sampled with 30 s averaging.

Molar polarizability is found by reducing the Lorentz–Lorentz quotient  $\frac{n^2-1}{(n^2+2)\rho}$  to the zero-density limit; thereby deducing  $A_R = \frac{4\pi}{3}N_A\alpha$ , with Avogadro's constant  $N_A$  [30], and electronic polarizability  $\alpha$ . Molar density  $\rho = \frac{p}{ZRT}$  is calculated from the measured pressure p and temperature T, together with the gas constant R [30]. For the compressibility factor Z, the reference property calculator CoolProp [21] was used, which implements the thermodynamic formulation of the International Association for the Properties of Water and Steam (IAPWS) of 1995 [31]. (For reference, at p = 1 kPa and  $T_{90} = 293.15$  K, CoolProp outputs Z = 0.9994385 for water.)

Reduced data are shown in Fig. 6(a), and at  $\rho \rightarrow 0$  the result for molar polarizability is  $A_R = 3.746(8) \text{ cm}^3/\text{mol}$ . This value produces  $n - 1 = 2.305(5) \times 10^{-6}$  at p = 1 kPa,  $t_{90} = 20$  °C, and  $\lambda = 632.9908$  nm. The present result is in good agreement with Schödel et al. [28], who reported  $n - 1 = 2.301(3) \times 10^{-6}$  at the same conditions. Disagreement in the two measured refractivities is 0.18 %. The present measurement is at least a factor of two less accurate than Schödel et al.; uncertainty is completely dominated by the effect of moisture on the reflection phase-shift in the cavity mirrors. Further details about measurement uncertainty are given in App. D. It is pointed out that deviation from



**Fig. 8.** Comparison of the cavity and cell refractometers to updated versions of the Edlen equation. The cell has been drift-corrected with 0.85 ×  $10^{-9}$ /h. All data sampled with 30 s averaging.

constant molar refraction evident in Fig. 6(a) is most likely due to apparatus error (the moisture effect on the mirrors). At these low densities, nonlinear effects in density—the contribution of refractivity virial coefficients and/or residual error in the density virial coefficients in the equation of state—nonlinear effects in density are at least  $10^3$  times smaller than the trend in Fig. 6(a).

Despite the agreement of the present results with Schödel et al. [28], the reference data situation for water vapor refractivity is less than satisfactory. This fact was commented upon by Schödel et al. for older experimental data; more recently, the lack of reliable experimental benchmarks has frustrated theoretical work [32]. Other aspects are also worth noting. For example, the present result is 2.0 % lower than the IAPWS formulation [33] of water refractivity, which has n - 1 = 2.357 $\times \ 10^{-6}$  at the same conditions. On the other hand, the results of Achtermann et al. [34] at higher temperatures and pressures show a strong (non-monotonic) temperature dependence of about 5.827  $\times$   $10^{-4}$  $(cm^3/mol)/K$  in the range (373 < T < 498) K, and extrapolate to  $A_R =$ 3.686 cm<sup>3</sup>/mol at 20 °C; the present result is 1.4 % higher than Achtermann et al., and the difference between the two results is a factor of 3 larger than statistical variability in the Achtermann et al. dataset. However, in contrast to these  $\pm 2$  % disagreements among past experiments, comparison to recent theory is more encouraging: Lao et al. [32]



**Fig. 9.** Testing the effect of water vapor on a mirror coating. (a.) Plumbing setup to monitor the phase profile of the mirror as a function of water vapor pressure. (b.) Phase profile across the mirror, showing the thinfilm coating as the central island, and the substrate as the annular island. (c.) Step-height between the two islands—mirror stack and surrounding substrate—was monitored as the pressure of water vapor was varied. Errorbars represent standard deviation in the Fizeau estimate of step height, which was the average of 10 measurements (about 30 s) repeated 70 times. (d.) The mirror consisted of a masked thinfilm coating on a glass substrate.

calculated a static value of vibrationally-averaged electronic polarizability  $A_{\varepsilon}^{\text{total}}(0) = 3.675 \text{ cm}^3/\text{mol}$  for the water molecule. This static value can be adjusted to optical frequency using Cauchy moments based on the dipole oscillator strength distributions of Zeiss and Meath [35]. At 633 nm the result is  $A_{\varepsilon}(\omega) = 3.744 \text{ cm}^3/\text{mol}$ ; this theoretical value is 0.04 % lower than the present experimental work.

#### 4.2.2. Tracker error in water vapor

The refractive index readings of the trackers were compared to the reference value of water vapor, established above. Deviation between the measurement and calculation is shown in Fig. 6(b). The nitrogen test of Fig. 5 proved that the calibrated trackers were accurate within  $6 \times 10^{-9}$  for the refractive index of a dry gas; Fig. 6(b) reveals that errors in the measurement of a moist gas are at least 20 times larger. On the one hand, this result is not surprising, because it has been observed before [12], without clear explanation; on the other hand, the explanation now offered may be considered surprising.

It is well-known that a thinfilm coating is sensitive to humidity [36, 37]. The canonical model [36] describes the deposited layer as having (preferential) columnar structure with a large internal surface area, which is filled up with water (by adsorption and capillary condensation); water adsorption effectively increases the refractive index of the thinfilm. For a dielectric stack mirror, this increase in refractive index shifts the peak reflectance (center wavelength) to higher wavelength [38,39], and the shift can be as large as 10 %, depending on deposition technology and substrate preparation. While not much information appears in literature about the effect of moisture on the reflection delay, an inference can be made from what is known about the center wavelength. A simple quarterwave stack mirror model [40] was setup with 6-pairs  $SiO_2/Ta_2O_5$ . The model assumes each layer of the coating adsorbs

identical volume of water. To explain a 7 % increase in center wavelength [38,39], the mirror model requires a increase in the refractive index of the Ta<sub>2</sub>O<sub>5</sub> by 5.9 % and increase of the SiO<sub>2</sub> by 8.4 %. These changes in refractive index correspond to about 10 % liquid volume of water adsorbed into each layer. The result on the mirror phase response  $\alpha = \frac{d\phi_{\rm B}}{d\nu}$  is an increase in  $\alpha$  of  $3 \times 10^{-15}$  rad/Hz, corresponding to the reflecting surface of the mirror moving "further away" by some  $\delta \alpha \frac{c}{4\pi} = 70$  nm: a surprising result. (It should be added that the 9.2 % shift in center wavelength reported in Ref. [38] was for electron-beam deposition onto a room-temperature substrate. A heated substrate reduced the center wavelength shift to 2.4 %. Ion bombardment during deposition reduced the shift to 0.2 %.)

The preceding remarks, based on an inference from literature [38], are merely a qualitative warning about the potential size of the moisture effect in a thinfilm (mirror) for interferometry. Quantitatively assigning how much the refractive index of each layer increases in response to water vapor exposure is beyond the scope of this work. The present interest is to characterize the net effect on optical pathlength in a refractometer. This was done by assuming the water vapor data measured by each system had an end-effect shift in pathlength, and fitting

$$\varepsilon_{\varphi} = \gamma \exp\left[-a\left(\ln\frac{100}{\varphi}\right)^2\right].$$
 (8)

The physical motivation behind the fit is the Dubinin-Radushkevich equation [41], which describes gas adsorption as a function of the ratio of saturation pressure to equilibrium pressure. The fit parameter  $\gamma$  is related to the micropore volume, and  $a = \left(\frac{RT}{E}\right)^2$  is given by the gas constant *R*, temperature *T*, and the characteristic energy of adsorption *E*. In this work, a fixed value a = 0.14 was assumed, which was based on the fit to the denser data of Fig. 9(c) in App. C. From Fig. 6(b), the end-effect corrections are  $\gamma = -9.95$  nm for the two-mirror etalon, and  $\gamma = -9.28$  nm for the one-mirror cell; from the separate test of on cavity mirror in Fig. 9(c),  $\gamma = -6.96$  nm for the two-mirror cavity.

These results for  $\gamma$  are somewhat surprising. First, the cavity has ionbeam sputtered coatings. It is established [38] that ion bombardment increases the packing density of a thinfilm, and reduces the dependence of the center wavelength on moisture by more than an order of magnitude. However, the cavity only exhibits a factor 3 reduction in the (reflection delay) end-effect compared to the cell. On the other hand, the etalon topology should have nominally zero sensitivity to moisture, because the reference and measurement pathlengths both reflect from coatings exposed to the same level of humidity; reflections are from different mirrors, but the coating recipe ought to be similar so that there is common-mode cancellation. However, the etalon  $\gamma$  is 31 % larger than the cavity, and only 2 times smaller than the cell. Any interpretation of these  $\gamma$  results are suspect, because details about the coating technology used in the etalon and cell mirrors are unknown. Nevertheless, the following two speculations are offered. (i) The etalon mirrors must be electron-beam deposited, so each mirror will have the  $\sim$  70 nm shift in optical position estimated above, and the observed  $\gamma=-9.95$  nm is residual error after imperfect cancellation (imperfect because the mirrored surfaces have dissimilar packing densities caused, for example, by dissimilar substrate temperature, masking, deposition angle, etc). (ii) The cell mirror must be coated ion-assisted (or magnetron sputter), which is more sensitive to water adsorption than the ion-beam sputter coating of the cavity mirrors; a hard/dense coating technology such as ion-assisted electron-beam would be desirable in the cell because the invar tubes are bonded directly to the coated substrate. These conjectures welcome correction.

## 4.2.3. Necessity of a three-gas calibration

The two preceding subsections have revealed two important facts: (i) the molar refractivity of water vapor is well-known, and (ii) all three

refractometers studied, which employ thinfilm reflective coatings, have a debilitating humidity-related error, as large as  $10^{-7} \cdot n$  in the refractive index of air. The logical conclusion is to add a correction to the refractometer working equations for an end-effect caused by moisture. This correction would be determined as the difference between the measurement of water vapor refractivity and its reference value, as plotted in Fig. 6(b). In short, extend the two-gas calibration to a three-gas calibration. The working equations then include an end-effect parameter. Taking the etalon as example, (2) becomes

$$n-1 = \frac{\Delta \Phi \cdot \lambda + 8\pi L_{\rm e} \frac{\kappa_{\rm e}}{3} p}{8\pi L_{\rm e} \left(1 - \frac{\kappa_{\rm e}}{3} p\right)} + \frac{\varepsilon_{\varphi}}{L_{\rm e}},\tag{9}$$

with the correction  $\varepsilon_{\varphi}$  given by (8) with the fit parameter  $\gamma$ , and being proportional to relative humidity  $\varphi$  to which the trackers are exposed.

To extend the two-gas calibration to a three-gas calibration, reference properties for water vapor are provided in the framework of (5) and Table 1. For H<sub>2</sub>O:  $c_1 = 6.7496 \times 10^{-7}$  (K/Pa),  $c_2 = 1104 \times 10^{-13}$  (K/Pa)<sup>2</sup>, and  $c_3 = 88040 \times 10^{-18}$  (K/Pa)<sup>3</sup>. For all practical (room temperature) purposes of tracker calibration, it is only the linear term that is relevant, and  $c_1$  is based on the weighted average of the present measurements and those of Schödel et al. [28]. The nonlinear terms are not known based on high-accuracy refractometry; rather, they have been computed via (6), using refractivity virial coefficients from Ref. [42], and density virial coefficients from the reference equation of state [21, 31].

For the comparisons in air, described next, the trackers will have their humidty corrections applied. That is, the trackers have undergone a three-gas calibration to achieve the levels of performance now reported.

#### 4.3. Comparison with an Edlen equation

The refractive index of air can be calculated using Edlen-style equations  $n(p, t_{90}, \varphi, x_{CO_2})$ , with knowledge of air pressure p, temperature  $t_{90}$ , relative humidity  $\varphi$ , and concentration of carbon dioxide  $x_{CO_2}$ . This calculation can be considered no better than a few parts in 10<sup>8</sup> because the original input data [45] was no more accurate than this. Further, owing to historical problems in window pathlength error and issues with the molar refractivity of water vapor, revisions to the original formulation can be considered no better than a few parts in 10<sup>8</sup>. Consequently, the nitrogen and water vapor tests reported in the previous sections are of paramount importance, because the reference refractivity to which the systems are compared is an order of magnitude more accurate than what is known about air refractivity in an Edlen equation. So, having noted their secondary importance, comparisons of the calibrated trackers in air to an Edlen equation are now described.

Comparisons to Edlen were carried out in the same setup of Fig. 2, with a few minor changes. The vacuum plumbing was removed so that the interior of the chamber was in ambient air. Thermal stabilization (aluminum envelopes and insulating foam) was still maintained. Consequently, the 1.5 L chamber volume communicated with the lab air via a 16 mm inner diameter tube. Such a setup has been known to lead to humidity gradients [46] in stagnant conditions, and this was observed at the  $\pm 4 \times 10^{-8} \cdot n$  level. Therefore, flow of lab air at a rate of 12 mL/s through the chamber was induced by pumping the gas inlet through a needle valve. Measurement of air pressure and temperature used equipment described above, at the same levels of uncertainty: 1.6 Pa and 1 mK, respectively. Relative humidity was estimated with a chilled-mirror hygrometer; the dew-point response was calibrated within 0.1 °C (0.4 %RH) by comparison to a humidity generator. Concentration of carbon dioxide was monitored within 25  $\mu$ mol/mol with a meter based on infrared absorption; the meter response was calibrated

in pure nitrogen and a binary mixture of N<sub>2</sub>: CO<sub>2</sub> at 500(25) µmol/mol concentration. The uncertainty contribution of these environmental monitoring equipment to the Edlen calculation corresponded to  $6 \times 10^{-9} \cdot n_{air}$  chiefly limited by the hygrometer.

Results of the comparison are shown in Fig. 7 for the cavity and etalon test, and shown in Fig. 8 for the cavity and cell test. The comparisons used two revised versions of the Edlen equation: one due to Birch and Downs [43] and the other due to Bönsch and Potulski [44]. These two formulations are what is most often encountered in precision length metrology at 633 nm. The results are encouraging, strongly supporting the concept of a three-gas calibration for the trackers. It must be repeated that the etalon and cell have had humidity corrections of  $6.7 \times 10^{-8} \cdot n$  and  $11.9 \times 10^{-8} \cdot n$  applied to their respective working equations. The justification for these humidity corrections-a three gas calibration-was described in the previous section. (It should also be mentioned that the time constant associated with adsorption is on the order of 60 s, and has no effect on Figs. 7 and 8, in which relative humidity fluctuates slowly.) Additionally, in Fig. 8, the deduced refractive index from the cell has been corrected for drift at the rate  $0.85 \times 10^{-9}$ /h; the magnitude of this correction is justified by the change in vacuum zero of Fig. 4(b).

The results show excellent agreement, all within mutual standard uncertainty, but it is emphasized that the FP cavity measurement is the master refractometer and arbiter, to which other estimates of the refractive index of air are compared. The cavity has the lowest uncertainty, which is described in detail in App. D. Its accuracy and errors have crossvalidations and constraints in several disparate aspects, some of which have been mentioned in this work (polarizability of pure gases [14], refractivity of water vapor [28,32]), and some of which are implicit (dispersion of neon [14,47,48], compressibility of silicon [49]) and have not been mentioned. Consequently, Figs. 7 and 8 can be interpreted as more than a single-wavelength validation of the Edlen equation: insofar as the revisions of Birch and Downs [43] and Bönsch and Potulski [44] contain later-revealed errors (window pathlength error, water vapor, etc.), they are in fortuitous agreement with one of the most accurate measurements of air refractivity to date. Indeed, the formulation of Bönsch and Potulski is remarkably accurate: within 0.2 imes $10^{-8} \cdot n_{air}$  of the actual value of room air at 633 nm. Bönsch and Potulski is a formidable achievement: after a generation, it remains best-practice.

## 5. Conclusion

This article has described a gas calibration procedure that enables a commercial wavelength/refractive-index tracker to measure the refractive index of a gas absolutely. The procedure consists of measuring two pure gases of known n(p, T), and then deducing the two unknown tracker parameters: gas pathlength and the distortion error. In dry gas, the calibrated trackers demonstrate performance at the level of  $4 \times 10^{-9} \cdot n$ . Moisture adversely affects performance, causing error on the order of  $10^{-7} \cdot n_{\rm air}$  in the refractive index of air. Nevertheless, if the trackers are calibrated with a third gas—water vapor—the moisture-related end-effect can also be corrected. After calibration with three gases—helium, argon, and water vapor—the trackers demonstrated agreement within  $3 \times 10^{-8} \cdot n_{\rm air}$  for the absolute refractive index of lab air. Validation comparisons were made between the calibrated trackers, an Edlen-style equation, and a master FP cavity refractometer (which was the arbiter).

To conclude with what was admitted from the beginning, this article has described measurement systems that are more than three decades old, and hardly qualifies as novel or groundbreaking. Rather, the intent was to highlight an application in precision engineering that can clearly benefit from recent advancements in gas reference properties [19]. The gas-based calibration procedure described, together with the quantitative detail provided by the suite of tests and the uncertainty analyses, suggest avenues for new developments in these "old" measurement systems. The insights offered range from the trifling (increasing the length of the tracker improves accuracy), to the trying (thinfilm technology is a barrier to sub-nanometer interferometry in air); from the encouraging (one formulation of the Edlen equation is almost exact at 633 nm), to the enabling (high-accuracy dimensional metrology need not be restricted to vacuum).

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

## the work reported in this paper.

## Acknowledgments

This work was conceived in May 2020 after an interaction with my colleague John Kramar, concerning what level of accuracy would be feasible if a linescale interferometer were to operate in air and use commercial metrology. My colleague Allan Harvey provided valuable insight into the refractivity of water vapor, shared the experimental data of Ref. [34], and pointed out the recent calculation of static dipole polarizability in Ref. [32].

## Appendix A Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.precisioneng.2022.04.011. The supplementary material is an archive file of research data which includes:

- a Python script which implements the calibration procedure of Section 3, together with the respective input experimental data for helium and argon gases. The script is generalized enough that any user supplying p,  $t_{90}$ ,  $\phi_i$ , and  $\phi_f$  from a specific tracker setup can perform the calibration and establish absolute performance.
- experimental data for nitrogen gas, together with a Python script which reproduces Fig. 5.
- experimental data for water vapor, together with a Python script which deduces molar polarizability. This data and analysis are the basis for the reference value stated for  $A_R$  of water vapor and Fig. 6.
- experimental data for the refractive index of air. These data are the basis for the Edlen comparisons of Figs. 7 and 8. The datafiles also contain environmental records of p,  $t_{90}$ ,  $t_{dp}$ , and  $x_{CO_2}$ .

The supplementary material is also available at the NIST public data repository: https://doi.org/10.18434/mds2-2568.

## B Additional details on $\varepsilon_{\rm w}$

The cell-based tracker sketched in Fig. 1(b) is formed by a window, vacuum-tubes, and a mirror. In this scenario, pressure-induced distortions arise from two mechanisms: nonuniform changes in window pathlength and mirror bending.

For a measurement and reference beam passing once through one window, window pathlength error has the form  $\Delta[(n_{w1} - 1)L_{w1}] - \Delta[(n_{w2} - 1)L_{w2}] + (n_{gas} - 1)(L_{w2} - L_{w1})$ . Here,  $L_{w1}$  and  $n_{w1}$  refer to the thickness and refractive index of the window with gas on both sides, while  $L_{w2}$  and  $n_{w2}$  refer to the window which has vacuum on one side. Shelton described a procedure to calculate the error analytically [13] using the approximation  $\Delta[(n_w - 1)L_w] \approx \Delta n_w L_w + (n_w - 1)\Delta L_w$ . Recent implementations [14,15] build on Shelton's approach by incorporating finite-element methods to estimate change in window thickness  $\Delta L_w$ , and the change in refractive index of the glass  $\Delta n_w$  can be obtained by the induced stress output of the finite-element analysis together with the stress-optic coefficients [50].

Here is simply stated the relevant outputs of the calculation procedure [14] for this geometry and pressure-loading configuration. For one pass through one window, the window with gas on both sides has  $\Delta n_{w1}L_{w1} = 87.5$  fm/Pa and  $(n_{w1} - 1)\Delta L_{w1} = -39.0$  fm/Pa; the window with vacuum on one side has  $\Delta n_{w2}L_{w2} = 75.2$  fm/Pa and  $(n_{w2} - 1)\Delta L_{w2} = -21.0$  fm/Pa; the difference in window pathlength between measurement and reference beams is 5.9 fm/Pa. The magnitude of this error is a factor 4 smaller than Ref. [14], and a factor 2 smaller than Ref. [15]. The sign is emphasized: both portions of the window have an increase in pathlength, but the part of the window with vacuum on the inside has a larger increase in pathlength. To correct a refractivity measurement, the measurement pathlength needs 5.9 fm/Pa added to it, relative to the reference pathlength in vacuum. This sign is same as Refs. [14,15], but there are differences in the pressure-loading configuration. In Ref. [15] and the present case, the pressure-loading configuration has the reference pathlength inside a cell permanently at vacuum, and the measurement pathlength is in gas outside the cell: that is, all exterior surfaces of the cell and window are pressurized during a refractivity measurement. In this case, the change in window pathlength is dominated by change in the refractive index of the glass  $\Delta n_w L_w$ , rather than change in geometric thickness ( $n_w - 1$ ) $\Delta L_w$ . In contrast, the pressure-loading configuration of Ref. [14] pressurized the inside of the glass cell, and all other surfaces remained at vacuum; in that case, ( $n_w - 1$ ) $\Delta L_w$  was dominant.

Next, the contribution of mirror bending to  $\varepsilon_w$  manifests as the difference in displacements between two portions of the mirror: one portion remains at vacuum, while the other portion is pressurized together with all other external surfaces. For this geometry, the difference in mirror bending is -40.9 fm/Pa, with pathlength between the vacuum portion of the mirror and window becoming shorter than pathlength between the gas portion of the mirror and the window. Again, sign is emphasized: it is opposite to the window pathlength error above. As pressure increases, the vacuum portion of the mirror is effectively pushed into the vacuum tube, which relative to the measurement beam in gas appears as a net increase in pathlength.

Finally, a measurement and reference beam completing a "roundtrip" through the cell experience two passes through a compressed window, together with one reflection from a deformed mirror. Consequently, the net change in pathlength is (5.9 - 40.9 + 5.9) = -29.1 fm/Pa, arising from the two pressure-induced distortion mechanisms. Since the differential interferometer implements the doublepass (two roundtrips),  $\varepsilon_w = -58.2$  fm/Pa. Again, sign is emphasized: net  $\varepsilon_w$  for the present cell has opposite sign to Refs. [14,15], and this is because the present cell has a mirror on one end, rather than two windows with an external stationary/isobaric mirror. For the present cell, mirror bending, which shortens the reference (vacuum) pathlength, is the dominant effect explaining sign of  $\varepsilon_w$ .

[Note that the mismatch in thermal expansion between the fused silica window/mirror and invar vacuum tubes creates a very small temperature-induced distortion error. This has a window pathlength component of -0.02 nm/K, and a mirror-bending component of 0.12 nm/K. The combined

effect is a net increase in doublepass pathlength of 0.17 nm/K, which is more than an order of magnitude smaller than typical thermal drift in a commercial heterodyne interferometer. This result assumes thermal expansions 0.4  $(\mu m/m)/K$  and 0.6  $(\mu m/m)/K$  for fused silica and invar, respectively.]

## C Change in mirror coating step-height

The sensitivity of a mirror coating to change in humidity [36,38,39] can be tested using a Fizeau interferometer. The basic requirement is that the mirror stack (coated area) does not cover the entire substrate. The Fizeau measurement is performed as a step-height analysis: the interferogram is masked into two regions—dielectric coating and glass substrate—and the analysis tracks changes in the height of the coating relative to the substrate as relative humidity is varied. The fact that a stack height is typically less than 10 µm, together with the close lateral proximity of the stack and substrate, mean that the many disturbing influences are greatly reduced, and the measurement can approach 0.2 nm levels of precision and temporal stability.

The scheme and results are shown in Fig. 9. The mirror was placed in a vacuum chamber which could be turbopumped. The phase profile across the mirror was monitored as a function of water vapor pressure, covering the range high-vacuum to 2 kPa. The measurand was change in step-height between the mirror coating and surrounding substrate. The overall result is the change in step-height as a function of water vapor pressure, shown in Fig. 9(c). The fit function shown is physically motivated by a model for adsorption on a microporous surface, as explained in the main text. For the measured data of Fig. 9(c),  $\gamma = -3.48$  nm and a = 0.14. The parameter  $\gamma$  has been used in the main text to compensate the end-effect error in the FP cavity, together with knowledge of relative humidity, via the correction term  $\varepsilon_{\varphi}$  and (8). Note that the  $\gamma$  of Fig. 9(c) is for one mirror only, and not a two-mirror FP cavity system. It should also be mentioned that the change in step height in response to water vapor exposure is rapid. The measurement of Fig. 9 sampled the step height about twice per minute, and this was too slow to make a quantitative estimate of the time constant. Qualitatively, two aspects can be mentioned: the time constant for adsorption into the coating is on the order of 60 s, whereas the time constant for release of water from the coating is about three times slower.

Finally, the mirror tested and shown in Fig. 9(d) is an ion-beam sputtered  $Nb_2O_5/SiO_2$  stack with high-reflectivity at 633 nm and 1542 nm (that is, the mirror is not a quarterwave stack). The present estimate for a moisture-dependent change in reflection phase-shift is about 11 % smaller than the inference of Ref. [12], but both exhibit the same sign: the apparent position of the mirror shifts into the stack when exposed to water vapor. In Ref. [12], the moisture-dependence of reflection phase-shift was inferred as an end-effect equal in two cavities of different lengths, but made with mirrors from the same coating run. The measurement concept of Ref. [12], when performed in water vapor, is arguably stronger than the Fizeau approach above, though the former requires some effort. The FP cavities of Ref. [12] were made with ion-beam sputtered mirrors having a quarterwave Ta<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> stack. The assembly differences between the cavities of Ref. [12] and the present work are noted: the present work has mirrors stood-up and silicate-bonded to a glass bar (Fig. 2), while Ref. [12] had mirror faces optically-contacted to the ends of a large glass block.

## D Uncertainty analyses

Section 3 described a procedure to enable a etalon/cell-based tracker to operate absolutely, and Section 4 performed a variety of tests validating their performance. Here, those sections are built upon, and an analysis of uncertainty for each refractometer provided, with a focus on measurement of the absolute refractive index of air  $n_{air}$ . Tabulated uncertainty budgets are discussed. Throughout this Appendix, the notation u(x) is used to denote the standard uncertainty of the quantity x. Unless otherwise stated, all uncertainties in this work are one standard uncertainty, corresponding to a 68 % confidence level.

## D.1 $u(n_{air})$ : etalon-based refractometer

The first two entries in Table 3 are gas pathlength of the etalon and the pressure-induced distortion. These two unknown parameters were deduced via the two-gas calibration procedure of Section 3. The stated uncertainties are statistical assessments, provided by the diagonal elements of  $(\chi_{\nu}^2 \cdot \mathcal{I}^{-1})^{1/2}$ , with  $\chi_{\nu}^2$  being the reduced chi-square statistic (i.e., the residual sum of squares result from (7) divided by the degrees of freedom), and  $\mathcal{I}$  is the information matrix (i.e., the negative-Hessian evaluated at the final-iteration least squares estimate) [51]. Stability and reproducibility of these parameters need further study. For example, the optical length of the etalon  $L_e$  will depend on setup and ancillary optics (e.g., the differential interferometer), and the effective compressibility  $\kappa_e$  will be influenced by fixturing of the optic in its metal frame. Consequently, it must be stipulated that  $u(L_e)$  is only valid so long as the etalon and interferometer setup remains undisturbed from point of the two-gas calibration. It is also noted that this statistical assessment of  $u(L_e)$  is about five times smaller than the errorbars in the nitrogen test of Fig. 5. Those large errorbars are covered by the dimensional instability entry below.

In addition to statistical uncertainty in  $L_e$  and  $\frac{\kappa_e}{3}$ , there is the systematic uncertainty arising from the need to accurately measure the pressure and temperature of the calibrating gases, helium and argon. Furthermore, there is systematic uncertainty in the proportionality coefficients of Table 1, excepting helium because its coefficients are known from calculation [20] within  $3 \times 10^{-11} \cdot n$  at ambient conditions. Concisely, both contributions to  $n(p,T)_{calc}$ —proportionality coefficients and measured  $\frac{p}{T}$ —are dominated by uncertainty in pressure, at about 1.6 Pa at 100 kPa. At ambient conditions, this corresponds to a  $3 \times 10^{-9} \cdot n$  uncertainty in the reference value of argon [14], and a further  $3 \times 10^{-9} \cdot n$  from the present argon pressure measurement. The entry  $n(p,T)_{calc}$  in Table 3 is added in quadrature. The entry is surely overestimated: first, because pressure measurement dominates both the past reference values and the present calibration procedure, while uncertainty in both cases originates from a measurement of helium refractivity at known pressure in the same absolute refractometer [14]; second, because the statistical entries  $L_e$  and  $\frac{\kappa_e}{3}$  already cover some irreproducibility in the  $\frac{p}{T}$  measurement.

 Table 3

 Standard uncertainty for the calibrated 127 mm etalon measuring the absolute refractive index of air.

Component	$u(n_{\rm air})  imes 10^{-9}$
<i>L</i> <sub>e</sub> , 1.0 μm	2.1
$\frac{\kappa_{\mathrm{e}}}{3}$ , 1.4 $ imes$ 10 <sup>-14</sup> /Pa	1.4
$n(p,T)_{calc}, 4.3 \times 10^{-9}$	4.3
$\Delta \Phi$ , 4.6 mrad	0.9
λ, 1 pm	0.4
$L_{\rm e}(T) \& \phi_{\rm i}(T), 6.7 \text{ nm/K}$	5.2
$\varepsilon_{\varphi}$ , 1.9 nm	15.0
periodic nonlinearity, 2.0 nm	15.8
dimensional instability, 0.8 nm	5.9
hysteresis etc., 140 pm	1.1
combined $k = 1$	23.8

The estimate  $u(\Delta\Phi)$  is treated as having two components: (i) uncertainty in making a measurement of change in phase difference, and (ii) interferometer "noise"/instability. The first is governed by phasemeter performance. Several diagnostic tests were performed on the phasemeter. When selfreferenced with the signal from a synthesizer, the phasemeter demonstrated total deviation less than 0.1 mrad for analysis intervals up to  $10^5$  s. When fed with phaselocked signals differing by 1 Hz, periodic error in the phase readout was less than  $\pm 0.05$  mrad. So phasemeter error is order-of 0.1 mrad and negligible. However, as noted in the main text, the use of a high-end lock-in amplifier as phasemeter is not standard-operating procedure, and in the real-world a tracker system may have  $u(\Delta\Phi)$  much larger than Table 3. For example, "entry-model" electronics are specified to resolve  $\frac{\lambda}{512}$  (or 24 mrad). This performance of entry-model electronics should be placed in context of the resolving capability of the interferometer, which is the second and dominant component in the assessment of  $u(\Delta\Phi)$ . Here, resolving capability is taken as the total deviation [23] on an analysis interval of 3600 s, using the steady-state vacuum data of Fig. 3(a). By this metric, the resolving capability of the etalon-based system is 4.6 mrad, and  $\delta n = \frac{\delta\phi A}{\delta r L}$ .

The vacuum-wavelength of the Zeeman-split, polarization-stabilized laser was assumed without comparison to a molecular reference (e.g., an iodine-stabilized laser). Uncertainty on the recommended wavelength of a HeNe laser [11] only contributes  $4 \times 10^{-10} \cdot n$  error.

Various mechanisms cause temperature-induced error in the etalon system. At vacuum, temperature-induced changes in  $L_e$  and  $\phi_i$  are intrinsically tied together, and so decoupling temperature effects in the etalon from temperature effects in the interferometer is open to interpretation. As a baseline test, the entire envelope of Fig. 2 was cycled between ( $293 < T_{90} < 294$ ) K with the etalon in place, and revealed a change in interferometer phase 450 mrad/K, equivalent to change in pathlength 6.7 nm/K. Interpreting this result as a thermal expansion coefficient for the etalon yields  $5.2 \times 10^{-8}$ /K, a number somewhat high for a low thermal expansion glass-ceramic. This interpretation suggests that some of the 6.7 nm/K pathlength change observed must be attributed to temperature sensitivity of some other pathlength apart from etalon length, such as the differential interferometer. For the differential interferometer, the manufacturer's specification is 80 nm/K; clearly the etalon and interferometer system is operating well-within specification. The entry " $L_e(T) & \phi(T)$ " assumes that air temperature fluctuates by 0.1 °C, and that no compensation has been applied for thermal expansion of the etalon or a sensitivity of pathlength difference to operating temperature.

The entry  $\varepsilon_{\varphi}$  covers moisture-induced instability in the reflection phase-shift from the thinfilm coatings that form the etalon. This entry is the combined effect of contributions from a fit and from experimental observations. The sign and magnitude of the correction  $\varepsilon_{\varphi}$  was determined by fitting an adsorption model for a microporous thinfilm to the error between the measured and calculated values for the refractive index of water vapor, across a range of relative humidity. Error data are shown in Fig. 6(b). The uncertainty of the fit coefficient  $\gamma = -9.95(45)$  nm based on the square-root of the covariance matrix is felt to be too optimistic. Added to this is a factor to cover the increased variability in the vacuum zero observed in Fig. 4(a), which had standard deviation in  $\phi_i$  of 72 mrad; in terms of total pathlength this additional factor is 1.81 nm. It is likely that the  $\varepsilon_{\varphi}$  entry in Table 3 is overestimated, because the uncertainty in the fit term and observed instability have the same origin, and it is also likely that some of the observed instability is duplicated in the entry for dimensional instability below. However, without more study, the evaluation proceeds conservatively.

The entry for periodic nonlinearity is based on manufacturer specification for the differential interferometer.

Dimensional instabilities are most likely due to instability in the etalon (and not in the interferometer). While Fig. 4(a) shows a large and somewhat unpredictable  $10^{-7}$  variation in  $L_e$  over 50 days, most of the drift (i.e., initial) can be attributed to a thermal cycle (bakeout) [24,52]. Further, the larger instabilities evident in water vapor are already covered by  $u(\varepsilon_{\varphi})$  above. Therefore, the evaluation of dimensional instability is based on observations about dry gas and temporal drift. For the nitrogen tests in Fig. 4(a), the etalon exhibits standard deviation in the vacuum zero of 27.3 mrad, or  $5.4 \times 10^{-9} \cdot n$ . After thermal relaxation, the linear trend on the etalon in Fig. 4(a) is about  $7.3 \times 10^{-10}$ /d. While the observation period is short, this value linear extrapolates to  $2.7 \times 10^{-7}$  per year. (Although there is some variation in literature values for fractional length changes in glass-ceramic [8, 12,53], it is reasonable to assume a value  $10^{-14}$ /s, or a few parts in  $10^7$  per year.) The entry for dimensional instability in Table 3 uses the quadrature sum of a  $5.4 \times 10^{-9}$  random fluctuation together with a  $7.3 \times 10^{-10}$ /d drift which can only be corrected within 10 % over 30 d.

Finally, Table 3 has the entry "hysteresis etc." In principle, this entry is already covered by  $u(L_e)$ , but there is possibly a (undetected) systematic in the characterization, arising from either compressibility hysteresis and/or helium permeation. Glass-ceramics are well-known to have expansivity hysteresis (e.g., Ref. [52] and references therein), in which a specimen of known length, when cycled in temperature, will not return to its original length. However, it also has compressibility hysteresis, in which cycling a specimen in pressure changes its length. A past estimate [12] of this effect is about  $(1.1 \pm 1.1) \times 10^{-14}$ /Pa, which suggests the length of the etalon  $L_e$  has irreproducibility at the level of 140 pm —below the detection limit of the Michelson interferometer. Likewise, helium permeation is another possible systematic. Unlike the case of cavity (which is made from titania-silicate glass), in which helium permeation is a significant effect, there was no evidence that helium exposure affected the etalon (which is made from glass-ceramic) characterization. This is no surprise: helium diffusion in glass-ceramic [54] is known to be more than an order-of-magnitude smaller

than titania-silicate glass. On the other hand, the etalon does not have high enough resolution to see effects at the 100 pm level. Nevertheless, based on past experience [12] with an FP cavity made in glass-ceramic, one can be confident that helium permeation has no significant effect on the etalon characterization; that is, any hidden systematic caused by helium permeation is no larger than the compressibility hysteresis  $1.1 \times 10^{-14}$ /Pa, which is below the pathlength detection limit.

## D.2 u(nair): cell-based refractometer

Several uncertainty components for the cell share the same origin and magnitude as that of the etalon. Consequently, the entries  $L_c$ ,  $\varepsilon_w$ ,  $n(p,T)_{calc}$ ,

 $\Delta\Phi$ ,  $\lambda$ ,  $\varepsilon_{\varphi}$ , and periodic nonlinearity in Table 4 will not be discussed, but the approach to their evaluation is described in the previous subsection. Temperature effects in a cell are different than an etalon. For example, for changes in operating temperature at vacuum, any observed change in pathlength is predominantly due to temperature sensitivity of the differential interferometer. Regarding cell length, consider that mismatch in thermal expansion coefficients between the vacuum tubes and windows causes a thermal-induced distortion of about 0.17 nm/K; more details in App. B. Experimentally, a change in the operating temperature of the cell and interferometer caused a pathlength change of 266 mrad/K, or 6.7 nm/K equivalent. This sensitivity is two orders of magnitude larger than the distortion effect of material mismatch in the cell. The manufacturer specification for thermal sensitivity of the differential interferometer is 10 nm/K, so present performance is within specification. The entry  $u[\phi_i(T)]$  in Table 4 assumes that air temperature fluctuates 0.1 °C, and no compensation is applied for drift in interferometer phase.

#### Table 4

Standard uncertainty for the calibrated 70 mm cell measuring the absolute refractive index of air.

component	$u(n_{\rm air})  imes 10^{-9}$
L <sub>c</sub> , 0.61 μm	2.4
$\varepsilon_{\rm w}$ , 1.1 fm/Pa	1.1
$n(p,T)_{\rm calc}, 4.3 \times 10^{-9}$	4.3
$\Delta \Phi$ , 3.9 mrad	1.3
λ, 1 p.m.	0.4
$\phi_i(T)$ , 266 mrad/K	8.9
<i>L</i> ( <i>T</i> ), 4.2 nm/K	6.0
$\varepsilon_{\varphi}$ , 3.6 nm	51.4
periodic nonlinearity, 2 nm	26.7
dimensional instability, 2.3 nm/d	94.2
combined $k = 1$	111.3

Regarding the other temperature effect, thermal expansion, while the cell is largely immune to changes in cell temperature during a refractivity measurement, the working equation (3) demands that  $L_c$  is precisely known either at vacuum or in gas. The consequence is operation away from the 20 °C must compensate the gas-calibrated value of  $L_c$  for the thermal expansion of Invar. An assumed thermal expansion coefficient for Invar of 0.6 × 10<sup>-6</sup>/K is based on literature measurement [55]. The entry L(T) in Table 4 assumes that air temperature fluctuates by 0.1 K and that no correction is applied for changes in cell length.

In principle, dimensional stability for the cell depends only on pathlength stability of the interferometer. This is because dimensional instability in cell length affects n - 1 and not n. An assumed dimensional stability of Invar  $2 \times 10^{-6}$  per year is based on literature [26]: if cell length remains uncorrected over 30 d, the error in  $n_{air}$  would be less than  $5 \times 10^{-11}$ . However, as noted in the main text and in Fig. 3, there is a large and unexpected drift in the cell-based system, which is nominally linear in time at a rate of 90 mrad/d. The entry in Table 4 assumes that drift in the cell-based system can be corrected within 10 % over 30 d. This single entry completely dominates  $u(n_{air})$  for the cell, but evidence in Fig. 3(b), and to a lesser extent Fig. 8 (e), suggest that the estimate is pessimistic. It is repeated that no explanation for the preponderance of this effect can be presently offered, and user-error is as likely as any other.

## D.3 u(nair): FP cavity-based refractometer

From (4), the change in resonant frequency  $\Delta f$  has two components: offset and proportional. At pressures below 1 kPa, correcting  $\Delta f$  for the frequency dependence of the reflection phase-shift can be a dominant uncertainty; however, for the atmospheric conditions that interest this article, the effect is negligible. The proportional error in  $\Delta f$  concerns cavity length. The length of the FP cavity  $L_{fp} = \frac{c}{2\Delta\nu_{fsr}}/(1 + \epsilon_a)$  is inferred by measurement of a free-spectral range  $\Delta\nu_{fsr}$ . Free-spectral range  $\Delta\nu_{fsr}$  was measured within 0.3 kHz, by careful attention to minimize electronic offsets and residual amplitude modulation. However, to avoid error deducing  $L_{fp}$  in a two mirror cavity, the frequency-dependence of the reflection phase-shift must also be taken into account, via the term  $\epsilon_a = \frac{ac}{2\pi L}$ . Uncertainty in  $\epsilon_a$  depends on the term  $\alpha = \frac{d\phi_R}{d\nu}$ , which is how much the reflection phase-shift changes as a function of laser (resonant) frequency, and is characteristic of a mirror coating. Exact details on the mirror stack are known from the manufacturer, and one can have confidence in determining  $\alpha$  within 10 % by calculation [40]. In the estimate of  $u(L_{fp})$ , the  $u(\epsilon_{\alpha})$  is dominant by a factor of 2, and it is therefore treatment of phase-shift on reflection that is the dominant contributor to  $u(\Delta f)$ . [Note that uncertainty in an actual frequency measurement is governed by the timebase error of the frequency counter, and is on the order of  $10^{-16}$  for the refractive index of atmospheric air.]

Pressure-induced distortion  $\frac{\kappa_{fp}}{3}$  is deduced as the value that minimizes error between a measurement of helium refractivity at known pressure and temperature, versus what n(p, T) is calculated *ab initio* [20]—the cavity has a one-gas calibration. As such, the measurement of  $\frac{\Delta f}{\nu_t}$  for helium contributes uncertainty. However, in practice, uncertainty in  $\frac{\kappa_{fp}}{s}$  is dominated by two effects unrelated to frequency measurement: helium permeation and

pressure measurement [i.e., the input for calculating n(p, T)]. For the latter, the pressure transducer was calibrated within 16 µPa/Pa by measurement of helium refractivity at known temperature in a primary refractometer [14]. (The meaning of "primary" is that pressure-induced distortion in the primary refractometer was corrected independent of exact knowledge of pressure, thereby avoiding the circuitous problem of traceability.) The 16 µPa/Pa uncertainty in the measure of helium pressure limits knowledge of  $\frac{K_{IP}}{3}$  to about 0.01 %. The effect of helium permeation on the correction has a long history [12,17], and was synopsized in the main text. Based on multiple tests with this cavity/apparatus and other independent cavities/apparatuses [12,17], one can be confident that the effect of helium permeation can be corrected so that it does not contribute more than 0.01 % error in  $\frac{K_{IP}}{2}$ .

Frequency can be measured with arbitrary precision. In measuring absolute resonance frequency  $\nu_{\rm f}$ , an iodine-stabilized laser is used as the frequency reference, and the entry in Table 5 is a negligible contributor to  $u(n_{\rm air})$ .

 Table 5

 Standard uncertainty for the 150 mm FP cavity measuring the absolute refractive index of air

component	$u(n_{ m air})  imes 10^{-9}$	
Δ <i>f</i> , 36 kHz	0.2	
$rac{\kappa_{ m fp}}{3},1.5 imes10^{-15}$ /Pa	0.2	
ν, 5 kHz	< 0.1	
<i>L</i> ( <i>T</i> ), 0.9 nm/K	0.6	
$\varepsilon_{\varphi}$ , 0.7 nm	4.7	
dimensional instability, 19 pm/d	0.3	
combined $k = 1$	4.7	

The coefficient of thermal expansion for the cavity was measured by recording the change in resonance frequency at vacuum as a function of temperature [56]. The result for instantaneous thermal expansion  $\frac{dL}{L} \frac{1}{dT} = 6.2 \times 10^{-9}$  /K is based on the limited temperature range (293 <  $T_{90}$  < 294) K. The entry L(T) in Table 5 assumes that, in compensating for  $n_{air}$ , the temperature of air fluctuates by 0.1 K, and that no correction is applied for thermal expansion of the cavity.

Instability of the phase-shift on reflection in the presence of water vapor has been evaluated by two independent means. One approach, described in App. C, measured the effect directly using a Fizeau interferometer, for a mirror identical to those which form the cavity. The second method, implicit in Section 4, deduced the effect as error between the reference value for the refractivity of water vapor [28], and what was measured with the cavity. Consistency between the two methods—within 0.5 nm per mirror at relative humidity of 40 %—give confidence that this error is understood. Nevertheless, the effect is by far the dominant entry in Table 5, and warrants further investigation, given how little attention the effect has received in the literature. The present levels of confidence are a 10-year development, after first encountering the error in Ref. [12].

The dimensional instability of the cavity was evaluated on week-long timescales. If extrapolated to short timescales, the drift rate is consistent with the  $3.9 \times 10^{-16}$ /s previously observed [12], and comparable with the  $1 \times 10^{-16}$ /s to  $2 \times 10^{-16}$ /s instabilities in titania-silicate glass cavities observed by others [57] operating at state-of-the-art. For the cavity, the problem of dimensional instability is that an assumption on the resonance frequency at vacuum  $\nu_i$  in (4) develops error over time. The entry for dimensional instability in Table 5 refers to expected performance over the duration of 30 days, immediately after  $\nu_i$  has been determined, and assumes drift in  $\nu_i$  can be corrected within 10%.

## D.4 $u_r(A_R)$ : water vapor

The water vapor test of Sec. 4 can be interpreted to deduce the molar polarizability  $A_R = 3.746(8) \text{ cm}^3/\text{mol}$  from measurements of n(p, T) in the FP cavity. As such, many of the refractive index components of Table 5 contribute to relative standard uncertainty  $u_r(A_R)$ . Since these components have already been described, together with the fact that  $u_r(A_R)$  is dominated by only one component, mean that not every entry in Table 6 will be discussed; instead the discussion is restricted to the three largest contributors.

## Table 6

Relative standard uncertainty determining the molar polarizabilty of water vapor at  $T_{90} = 293.15$  K and 633 nm.

component	$u_r(A_R)  imes 10^{-4}$
fractional frequency $\frac{\Delta f}{\nu}$	< 0.1
distortion $\frac{\kappa_{fp}}{3}$	< 0.1
phase-shift instability $\varepsilon_{\varphi}$ , 0.7 nm	20.2
dimensional instability, 19 pm/d	0.4
pressure p, 0.1 Pa	1.0
temperature $T_{90}$ , 1 mK	< 0.1
regression	3.1
combined $k = 1$	20.9

The dominant contributor to  $u_r(A_R)$  is correction and instability in the reflection phase-shift caused by moisture. The effect has already been described in the previous section and Table 5, in the context of the refractive index of air. Here, all that is added is that the reflection phase-shift changes cavity length the equivalent of 3.1(5) nm per mirror at 40 %RH, whereas the optical signal  $\Delta nL$  is only 345 nm at 1 kPa of water vapor. Consequently, a "small" error in the refractive index of atmospheric air becomes a large relative error in the refractive index of water vapor.

In deducing  $A_R$  from the zero-density limit of the Lorentz-Lorenz quotient, measurements of water vapor pressure and temperature come into play in the determination of molar density. At the low pressures of room-temperature water vapor, of the two, it is only pressure that is of concern. As described in the main text, the pressure transducer was calibrated *in situ* using measurements of argon refractivity at known temperature. Uncertainty in the realization of the optical pressure scale  $u(p_{ops})$  for argon [14] is more than an order of magnitude smaller than the entry in Table 6. After calibration, subsequent pressure measurements of water vapor are dominated by statistical irreproducibility in the transducer.

Finally, regressing molar refraction to the zero-density limit has a statistical uncertainty in the fit coefficients. The data and fit are shown in Fig. 6 (a). The entry in Table 6 is based on the square-root of the diagonal elements in the covariance matrix.

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