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Improving the Accuracy and Precision of Broadband Optical Cavity Measurements

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Abstract: Most extinction measurements require a stable light source to attain high precision and accuracy. Here, we present a convenient approach to normalize light source intensity in broadband optical cavity measurements. In the absence of sample extinction, we show that the in-band signal – the high finesse spectral region of the optical cavity in which sample extinction is measured with high sensitivity – is strongly correlated with the out-of-band signal. The out-of-band signal is insensitive to sample extinction and can act as a proxy for light source intensity. This normalization approach strongly suppressed in-band intensity changes in two incoherent broadband cavity-enhanced absorption spectroscopy (IBBCEAS) instruments with dissimilar light sources and optical cavity properties. Intensity fluctuations in an arc lamp system were suppressed by a factor of 7 to 16 and in the LED spectrometer by a factor of 10. This approach therefore improves the accuracy and precision of extinction measurements where either property is limited by the light source stability.

KEYWORDS:

normalization; broadband optical cavity; atmospheric; UV/visible; aerosol; gases

1. Introduction

Highly sensitive and stable measurements of sample extinction are required for many laboratory and field applications. An important example is in atmospheric monitoring of aerosols – here measurements cover extensive time periods and sample extinction (i.e., the sum of absorption and scattering) can be small. Under such circumstances, a spectroscopic system must combine high sensitivity and long-term intensity stability for measurements to achieve the necessary precision and accuracy. At the same time, aerosol samples have broad extinction spectra characterized by a power law (Angstrom exponent). Broad spectral measurements are needed to characterize this dependence and to distinguish

between black carbon and brown carbon based on the onset of brown carbon absorption at short visible and ultraviolet wavelengths[1–3].

Optical cavities have become an essential tool for sensitive measurements of sample extinction[4,5]. The long effective photon pathlength (or, equivalently, the long photon lifetime) through a sample in the cavity is the main reason for the sensitivity of this approach. Several spectroscopic methods are based upon these attributes of optical cavities, most notably laser-based methods like cavity ring-down spectroscopy (CRDS) and cavity-enhanced absorption spectroscopy (CEAS). CRDS measures the time rate of decay of photons in the cavity and is insensitive to fluctuations in the intensity of the light source. In comparison, CEAS measures the time-integrated intensity transmitted through an optical cavity. As a result, the light source stability often limits the attainable sensitivity and accuracy in a CEAS system.

For extinction measurements across relatively broad spectral windows (e.g., > 10 nm), broadband CEAS methods play an important role. Fiedler et al. first described incoherent broadband cavity-enhanced absorption spectroscopy (IBBCEAS)[6], and many spectroscopic systems based on a similar optical configuration have since been developed (sometimes termed BBCEAS[7], CE-DOAS [8], or BBCES[9,10]). IBBCEAS and related methods have been used for trace gas quantification in laboratory, chamber, and field studies [7,11–13], for studies of ambient particles and their optical properties [9,14,15], for sensitive liquid analysis [16,17], and measurement of absorption cross sections[10,18–20]. IBBCEAS can also be combined with a nephelometer into an albedometer, allowing concurrent measurements of extinction, scattering, and (by subtraction) absorption on the same sample[21]. IBBCEAS has proved accurate for both trace gases and aerosol in comparisons against instruments based on different measurement principles [20–22].

For aerosol samples, drifts in the light source intensity of CEAS and IBBCEAS instruments are difficult to distinguish from the broad and unstructured spectra of aerosols and some gases. Sensitive aerosol extinction measurements therefore require rigorous stabilization of the light source intensity, regular reference measurements (e.g., of a clean gas stream), or normalization of intensity changes. The latter strategy must compensate for both short term-intensity fluctuations and longer term drifts in light output. Various approaches have been used. Over the short term, the intensity can be predicted from its temporal trend in the absence of a sample[19]. However, this approach is only satisfactory for short-term measurements. A more robust approach is external normalization [13,25]. Alternatively, the stable absorption bands of sample gases can be used to normalize the system response. Varma et al. demonstrated this approach using the O_2 B-band at red wavelengths [26], and Thalman and Volkamer used a similar

method on the absorption of H_2O and O_4 lines [24]. However, this approach is not always feasible because it depends on a fortuitous and stable absorption in the spectral range of interest. Other normalization strategies are desirable.

For broadband optical cavity systems, differences in the spectral transmission characteristics at different wavelengths can be exploited to compensate for fluctuations in the light source intensity. In IBBCEAS systems, the cavity acts as a band-rejection filter over wavelengths where the cavity mirror reflectivity is high. The transmitted intensity in this spectral region is extremely sensitive to changes in the sample extinction owing to the long effective photon pathlength through the sample. We term this the in-band region — it is the region in which sample extinction is measured. In contrast, out-of-band wavelengths (that is, those falling outside the high reflectivity region of the cavity) are efficiently transmitted through the optical system. The effective photon pathlength in the cavity is short at these wavelengths and the effect of sample extinction is negligible. This spectral difference in the optical properties of the cavity implies that out-of-band intensities could serve as a proxy for the overall intensity of the light source as long as relative intensity changes are comparable in both spectral regions. This approach is convenient because out-of-band wavelengths are already measured in most broadband optical cavity instruments, either directly or as a baseline signal arising from the finite background light suppression of spectrographs (typically around 10^{-4}). No modification of the experimental system is necessary to implement the approach.

Our purpose in this work is to describe intensity normalization of the in-band intensity in a broadband optical cavity spectrometer based on out-of-band intensities. We show that there is a strong linear relationship between in-band and out-of-band intensities in the absence of sample extinction. This correlation can be used to improve the accuracy of the extinction measurement where this is primarily limited by light source fluctuations. We discuss the assumptions underpinning the method and consider its applicability to other broadband cavity instrument systems. The approach is conveniently implemented in broadband spectrometers and leads to improved long- and short-term signal stability and accuracy without increasing instrument complexity.

2. Experimental

To demonstrate the normalization approach, two IBBCEAS instruments with different performance characteristics were used in this study. One instrument was based on an LED light source and had a relatively high finesse optical cavity; the other, lower finesse cavity had a much broader spectral window and used a Xe arc lamp as a light source. The optical cavity signal was attenuated in a different manner for each instrument.

The optical system of the LED IBBCEAS instrument comprised a near-UV LED, optical cavity, and fiber spectrometer, along with aspheric lenses and filters (Fig. S1). The LED was mounted on a metal core PCB board and its temperature was held at 20 ± 0.1 °C. The LED had an optical output of 470 mW and its emission spectrum was nominally centred at 375 nm. LED light was focused and coupled into an optical resonator composed of two high reflectivity mirrors separated by 98 cm. The maximum mirror reflectivity was above 0.9995 and the high reflectivity region extended from 360 to 390 nm. Light transmitted through the optical cavity was measured with a Ocean Optics QE65 Pro spectrometer. The sample stream (5 L min^{-1}) was filtered to prevent particle extinction from affecting the signal; cavity mirrors were purged with nitrogen at (0.1 L min^{-1}) to protect the mirrors from particle deposition. The instrument was heated to 40 ± 0.5 °C to thermally stabilize the cavity and prevent water condensation inside the instrument. The spectrometer resolution was 0.4 nm FWHM at 334 nm. Mirror reflectivity was calibrated from Rayleigh scattering of CO_2 and N_2 and checked against O_4 dimer absorption.

The second IBBCEAS instrument was similar to previously reported instruments in our group [16,26]. The main differences compared to the LED system were the light source, a Cermax 175 W xenon arc lamp, and the optical cavity. The arc lamp system required more stringent filtering than the LED system. A BK7 window reduced deep-UV output and ozone production, and other filters (Asahi XUS0450 shortpass filter, Thorlabs FM04 UV cold mirror, and KG3 coloured glass bandpass filter) restricted the spectral transmission mainly to the high reflectivity region of the optical cavity. Even so, some out-of-band light was transmitted through the system, especially from 700 nm upwards. The mirrors of the optical cavity were separated by 98 cm. Cavity mirrors had a nominal reflectivity of 99.6% across a wide spectral range (300 to 450 nm). The intensity spectrum of light transmitted through the optical system and cavity was measured with a Shamrock 163 spectrograph and Andor iDUS CCD camera. The wavelength scale and resolution were calibrated using a mercury penray lamp. For the results reported in this work, the spectral window extended from 214 to 474 nm and the instrument resolution was approximately 1.6 nm. Metal tubing was used for the sample stream to avoid particle losses arising from electrostatic charging on nonconductive tubing. The sample stream flowed (3 L min^{-1}) into the cavity from both sides and exited from the centre. The 10 cm nearest each mirror was purged with a slow flow of clean air (0.3 L min^{-1}). The acquisition time for each spectrum was 12.6 s.

3. Results

3.1 LED IBBCEAS instrument

Figure 1a shows the transmitted intensity spectrum of the LED based instrument with the typical peak output of the LED occurring at 367 nm. The cavity mirrors in this instrument are highly reflective from 360 to 395 nm. A small, secondary peak is apparent at 334 nm. This peak arises because the weak, shortest wavelength output of the LED overlaps with a sharp increase in cavity transmission at short wavelengths. As the LED has no output below 330 nm, any intensity measured at these shorter, nominal wavelengths is essentially a measurement of background light arising from longer wavelengths.

To explore the relationship between in-band and out-of-band intensities, light intensity variations of the LED instrument were simulated by placing different neutral density filters between the LED and the cavity (Fig. 2a). The broad spectral coverage of the filters reduces light intensity across a wide spectral range. A corresponding reduction of the measured intensity is evident across the entire spectrum (Fig. 1a), both at in-band (>354 nm) and at background wavelengths (< 354 nm). The relationship between the 334 nm intensity peak and the intensity maximum at 368 nm is shown in Fig. 3a. The two intensity measurements were highly correlated, suggesting that the measured background intensity at 334 nm was a useful proxy for the in-band intensity and thus suitable for normalizing the in-band wavelength.

The normalized signal, I_N, at each time t was calculated according to:

$$I_N(t) = (I(t) - I_B(t)) \left[\frac{I_R(t_R) - I_B(t_R)}{I_R(t) - I_B(t)}\right] \quad \text{(Eq. 1)}$$

where I is the measured intensity at some in-band wavelength, I_R is the intensity at the reference wavelength, and $I_B(t)$ is the baseline intensity, that is, the measured intensity with the light blocked. The reference time for normalization purposes is denoted t_R. Intensities are wavelength dependent except for the reference wavelength, which is fixed at some out-of-band wavelength (or range of wavelengths). For this instrument, the intensity of the 334 nm intensity peak after subtracting the baseline was used as the reference wavelength for normalization. We emphasise that while the results presented above are based on normalization at the 334 nm peak, similar results were found using the baseline intensity, as we show below with the arc lamp system.

Figure 2a shows the time profile of the peak intensity with three stepwise decreases in the system transmission. The system response was stable after each step, but the instrument precision (1σ = 0.76%) was shot-noise limited. Compared to the original signal, the intensity was reduced by 24% by the last step. Normalization based on Eq. (1) markedly improved the long-term intensity stability. Close inspection of Fig. 2a reveals a marginal decrease of 2.3% in the normalized signal from the start to the end of the experiment, a factor of 10 improvement. This decrease arose from the weak spectral dependence of the attenuation filter. Linear extrapolation of the measured wavelength dependent

attenuation between the reference and signal wavelengths was estimated to account a change of 2.1%, fully accounting for the observed decrease. The improvement in long-term intensity stability by a factor of 10 is therefore likely an underestimate. In summary, the normalization approach showed excellent performance in stabilizing the LED instrument response against changes in the light intensity entering the optical cavity.

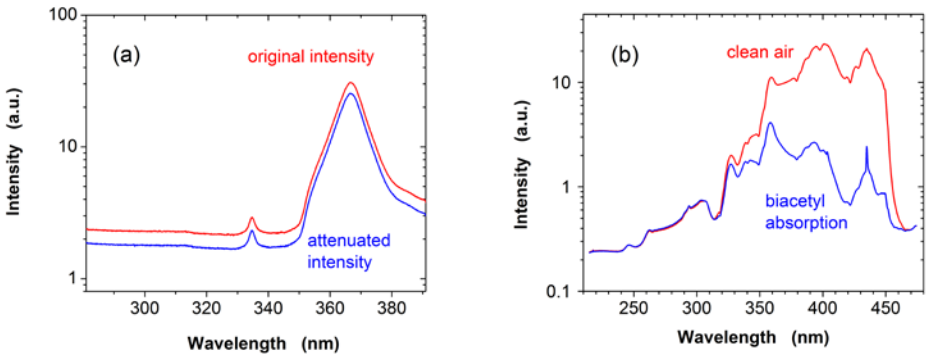


Fig. 1. Transmitted intensity spectra of the two IBBCEAS systems at full power (red) and attenuated intensity (blue). (a) LED IBBCEAS system in which most LED output falls in the in-band (high reflectivity) region above 354 nm; a small out-of-band peak is visible at 334 nm. The reduced intensity of about 20% (blue) was produced by filtering the light source. (b) Xe arc lamp system showing broad spectral coverage from 320 to 460 nm. The reduced intensity spectrum (blue) arose from biacetyl absorption in the cavity. Both instruments exhibit significant intensity in the out-of-band regions (below 330 nm for the LED instrument and below 250 nm for the arc lamp system).

Because the short-term performance of the LED system is shot-noise limited, the uncertainty in the intensity at 334 nm ($1\sigma = 0.57\%$) reduces the precision of the normalized signal ($1\sigma = 1.0\%$), consistent with adding the uncertainties of the original signal and the reference intensity in quadrature.

3.2 Xe arc lamp system

The transmitted intensity spectrum of the Xe arc lamp IBBCEAS instrument is shown in Fig. 1b. To achieve high reflectivity over a broad spectral region, the optical cavity mirrors of this spectrometer had appreciable spectral variations in the mirror reflectivity. This gave rise to the broader features in the transmission spectrum. Sharper structures in the transmission spectrum may have arisen from some deterioration of the mirror coatings.

The light intensity output of the Xe arc lamp has appreciable intensity fluctuations over time. In this system, the lamp intensity was normalized based on the background signal at short (<250 nm) wavelengths. In-band light transmission was varied by injecting liquid biacetyl into the sample inlet stream of the instrument.[28] Biacetyl absorption was seen as a strong decrease in the in-band intensity between 330 and 450 nm (Fig. 1b), especially at its maximum

absorption cross section above 400 nm[29]. In contrast, out-of-band intensities (< 320 nm and > 460 nm) were unaffected by sample absorption.

The time profile of the intensity at 400 nm is shown in Fig. 2b. Biacetyl produced a sharp initial drop in transmitted light, followed by a gradual recovery in transmission as this sticky compound was flushed from the system. Three additions of biacetyl in the instrument are shown over the course of the experiment. Aside from the sample absorption, relatively large changes in the light output of the lamp also occurred occasionally. This behavior is typical of arc lamps.

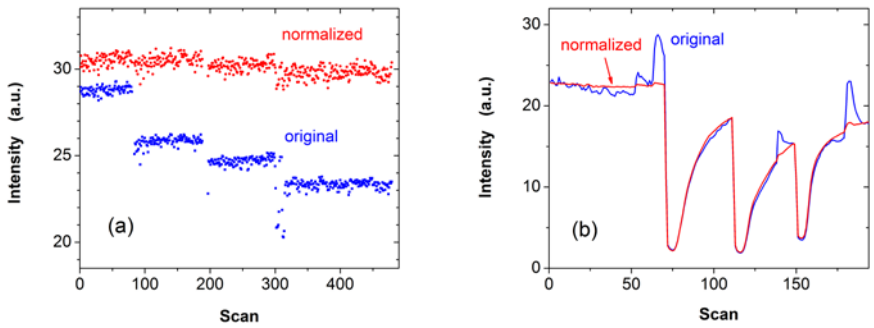


Fig. 2. (a) Time series of the LED IBBCEAS system during successive attenuation of the LED beam with different neutral density filters. The original intensity (blue) at the maximum (after subtracting the baseline) is shows three stepwise decreases in intensity. The normalized data is shown in red. The small (maximum of 2%) decrease in the normalized signal arises from the spectral dependence of the attenuation filters. (b) Time series of the transmitted intensity at 400 nm in the Xe arc lamp IBBCEAS system. Cavity transmission was attenuated with three injections of liquid biacetyl into the inlet stream. Blue and red traces respectively show the original and normalized intensities.

Applying Eq. (1) as in the LED spectrum, the intensity at 400 nm was normalized based on the background light intensity at a nominal wavelength of 215 nm. Other out-of-band wavelengths (including at the longest wavelengths, >470 nm) were also found to be suitable for normalization. Figure 3b shows the correlation between the intensity at 400 nm and the normalization signal at 215 nm. Again, both intensities were highly correlated when the sample was non-absorbing, demonstrating the strong relationship between the background signal and the lamp intensity. In contrast, absorption reduced the in-band intensity at 400 nm without affecting the background intensity, as seen in the vertical line in Fig. 3b.

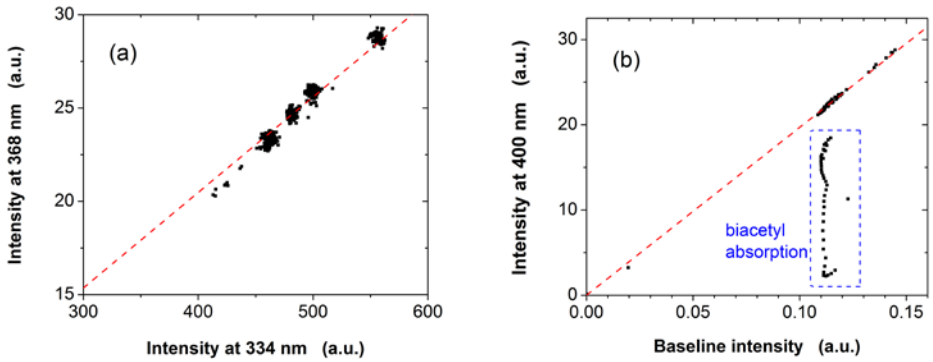


Fig. 3. (a) Correlation between the mean intensity of the 334 nm peak and that around the 368 nm maximum in the LED IBBCEAS instrument. The dashed red line shows the linear fit to the data where the fit intercept was constrained to the origin. (b) Correlation between the baseline intensity and the intensity at 400 nm in the Xe arc lamp IBBCEAS instrument. The contribution of one biacetyl absorption event is highlighted. The dashed red line shows the linear fit to the data excluding the absorption event. The fit intercept was constrained to the origin.

Normalizing the original spectrum based on this relationship markedly improved both the long and the short-term stability of the instrument (Fig. 2b). Large fluctuations in the light intensity were strongly suppressed, by between 7 to 16 times. Small residual features in the normalized time profile probably arise partly from changes in the CCD detector response and temperature control when there are large, sudden changes in the incident energy on the detector. An example of this influence is seen in the gentle, positive slope of a few points at the maximum biacetyl absorption in Fig. 3b. This small detector effect is not relevant for smaller or slower changes in extinction. We conclude that normalizing the in-band signal greatly improved the overall stability of the instrument by compensating for broad changes in light source intensity, without being altered by changes in the in-band intensity resulting from sample extinction.

4. Discussion

Signal normalization based on out-of-band light markedly improved the stability of broadband optical cavity systems against changes in light intensity. This method was demonstrated using two IBBCEAS spectrometers with dissimilar optical characteristics. One spectrometer had a high finesse optical cavity and LED emission over ca. 50 nm; in contrast, the arc lamp spectrometer featured a lower finesse cavity (with a much broader high reflectivity region) and lamp output over ca. 2000 nm. The normalization strategy developed in this work was shown to strongly suppress intensity changes that did not arise from sample extinction. As the vertical line arising from absorption in Fig. 3b indicates, the method is not strongly influenced by the sample extinction. This approach therefore improves the accuracy of extinction measurements where this is

limited by the stability of the light source or of the optical system (excluding the optical cavity). The approach would not compensate for intensity variations stemming from changes in the optical cavity alignment. This is because cavity alignment affects the effective photon pathlength at in-band wavelengths and alters the retrieved sample extinction. Where this situation occurs, regular calibration of the effective pathlength is necessary.

This normalization approach assumes that the relative optical output of the light source has a weak spectral dependence – that is, fractional changes in source intensity are similar across the wavelengths of interest. When this assumption holds, as with arc-lamps [13], relative changes in light intensity at one wavelength are a reliable proxy for relative intensity changes at another wavelength. For the purposes of normalization, the measured intensity at the selected out-of-band wavelength must correlate strongly with the intensity of wavelengths in the high finesse region of the optical cavity. Out-of-band wavelengths are suitable for normalization because the effective photon pathlength is short and sample extinction negligibly affects the transmitted intensity.

The assumption of weak spectral dependence does not apply for all light sources. In particular, LED emission spectra may be temperature dependent, so sufficient temperature control is required to apply this normalization approach to an LED-based instrument, as we showed above with our LED spectrometer.

Two approaches were applied to normalize the signal. In the arc lamp system, the reference intensity was based on the baseline at short wavelengths. This signal arises from background light because the spectrograph cannot completely suppress all light entering it. In the LED spectrometer, we instead selected a small peak arising from the overlap of the cavity mirror pass band and the short wavelength emission of the LED. This is a direct measure of part of the light source spectrum. The latter approach is noteworthy because it could be deliberated incorporated into the design of LED broadband spectrometers. For example, a strong normalization signal could be produced by careful section of LED and cavity mirror spectra to allow more out-of-band spillover at relatively weak intensities of the light source. The out-of-band intensity would appear amplified owing to the high transmission efficiency of the optical cavity and would be a useful proxy for the light source intensity. This approach is similar in some respects to typical normalization procedures, for instance, that used by Washenfelder and co-workers where out-of-band light was picked off and separately coupled into the spectrograph [13].

Practical application of out-of-band wavelengths for normalization must meet some conditions. The first is that sufficient out-of-band intensity is required to avoid worsening the precision of the normalized measurement. In the shot-noise limited case of the LED IBBCEAS spectrometer, the precision of the normalized

in-band intensity is slightly lower than that of the initial measurement. The precision could be improved by averaging over more reference wavelengths or by careful optical system design, as described above. We also note the importance of shielding the spectrograph from ambient light, which would compromise the relationship between the measured baseline and the in-band signal.

The normalization approach developed in this work is particularly valuable for measuring aerosol extinction spectra over an extended period. This is because fluctuations in light source intensity are indistinguishable from changes in sample extinction. Intensity normalization is less critical for quantifying trace gases with narrow absorption features because the absorption magnitude of such structured absorption is quantified relative to the baseline extinction, regardless of whether this arises from the sample or from optical instabilities in the light source.

The approach is also valuable where a reference blank spectrum cannot be easily measured, such as in open-path systems in the field [30] or across atmospheric simulation chambers. The approach is most beneficial for less stable light sources like arc lamps, which may be used for their other attractive features like high near-UV radiance and their broad emission spectra. The approach also has potential for liquid broadband CEAS measurements.[16,17] Liquid measurements are similar to those of aerosols in the sense that broad spectra are measured and that mirror reflectivities are not particularly high owing to strong light scattering in liquids.

Finally, we note that these results were achieved without any changes to the experimental configuration of our system and could be used with pre-existing data. The approach is thus a convenient way of improving the quality of measurements and is particularly valuable in dealing with longer-term drifts in lamp output.

5. Conclusions

We have demonstrated a normalization approach that is broadly applicable to many broadband optical cavity spectrometers. We showed that out-of-band light is strongly correlated with the in-band signal and can be used to correct for changes in the light source output over time. The approach was demonstrated with both relatively stable and unstable light sources, and with higher and lower finesse optical cavities.

The out-of-band signal could be taken from background light levels in the detector or from direct measurement of the light source spectrum if it spills over into the out-of-band region. This approach could be built into the design of new spectrometers so as to provide a strong signal for normalization.

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Supplemental material:

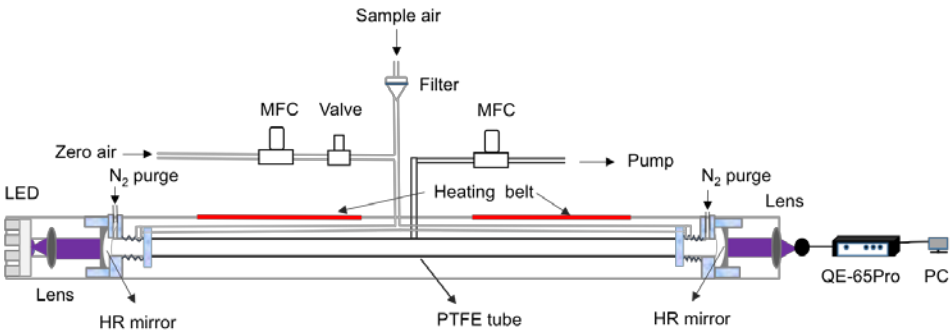


Fig. S1. Optical and sample handling configuration of the LED IBBCEAS instrument.