AVANTES
MEMBER OF THE NYNOMIC GROUP

APPLICATION NOTE

THE OPTIMAL SPECTROSCOPY CONFIGURATIONS FOR DOAS

INTRO

BACKGROUND INFORMATION

The environmental impact of carbon emissions from fossil fuels, the most widely recognized and well-known air pollutant, is undeniable. However, CO2 is far from the only pollutant contributing to poor air quality. Among the many other byproducts generated from coal and petroleum processing, sulfur oxides (SOx) and nitrogen oxides (NOx) are particularly interesting due to their impact on human health. These emissions lead to acid rain and are a leading cause of respiratory illness and ozone layer depletion. In 2020, we published an application note, "Differential Optical Absorption Spectroscopy," outlining how differential optical absorption spectroscopy (DOAS) is used in continuous emission monitoring systems (CEMS) for quantitating SOx and NOx emissions. Over the past several years, interest in the technique has grown exponentially through increased government funding and industry attention, with emissions monitoring now factoring into environmental, social, and governance (ESG) ratings. Therefore, we thought revisiting the subject from a slightly different perspective would be interesting.

Our original application note on DOAS provided a general overview of the topic, discussing the advantages and disadvantages of UV/Vis vs near-infrared (NIR). We demonstrated that UV/Vis absorbance spectroscopy in the 200 - 500 nm region was ideal for monitoring nearly every atmospheric pollutant of interest, with the notable exception of carbon oxides (COx), which is typically measured in the near-infrared or mid-infrared. In this new application note, we will briefly revisit the DOAS technique but then focus on the practical considerations regarding optimal spectrometer configurations. We encourage readers interested in a more detailed overview of the technique to refer to our previous DOAS application note.

BASICS OF DOAS

Differential absorption spectroscopy can take many different forms, yet, on a fundamental level, it relies on normalizing the spectra to a region without absorption from the analyte of interest. For example, NO2 has a strong absorption band centered at 403 nm, whereas NO has a peak absorbance at 226 nm. While both bands are relatively broad, there is a "dead zone" between the two at around 300 nm. Therefore, by looking at the difference in atmospheric absorption between 300 nm and 403 nm or 300 nm and 226 nm, one can accurately quantify the level of NO and NO2 present. Using this differential methodology eliminates any ambiguity associated with pressure, temperature, or other fluctuations in the ambient environment. Figure 1 shows a typical schematic configuration of a DOAS-CEMS system where a broadband UV/Vis light source (D2, Hg, or Xe typically) is collimated using a parabolic mirror directing the light path through the atmosphere to a receiver, which then focuses that light into a fiber-optic cable directing it to the spectrometer.

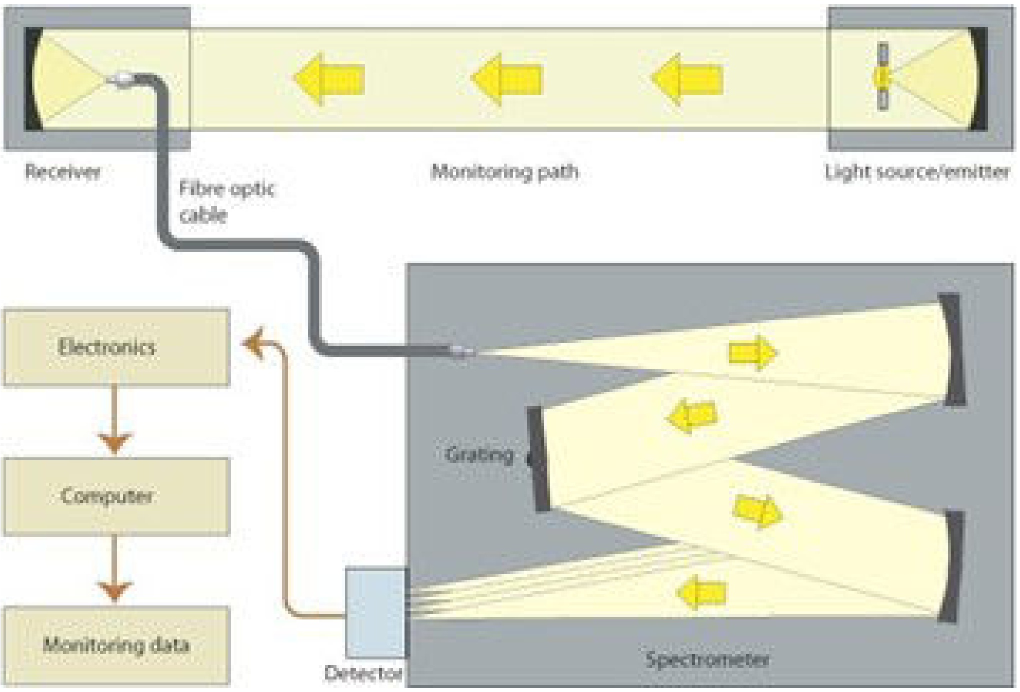

FIGURE 1: Typical CEMS setup using DOAS.

According to the National Institute for Occupational Safety and Health, NO2 levels in the atmosphere should be limited to less than one ppm, corresponding to a concentration of 0.0001%. Achieving this extremely low detection level with traditional miniature spectrometers requires extremely large molecular density. Early DOAS systems relied on measurements over vast distances (meters to kilometers) to increase the number of molecules probed by the collimated light. While effective, this requires large permanently mounted instrumentation, which impedes wide-scale industrial implementation. Multi-pass reflectance cells can be utilized in conjunction with vacuum pressure cells to increase sensitivity, but these approaches are still always restricted by size, weight, and power (SWaP) requirements. Therefore, ensuring that the spectrometer is simultaneously compact, low noise, and high sensitivity with a wide dynamic range is essential.

CONSIDERATIONS FOR SPECTROMETER REQUIREMENTS

In the previous DOAS application note, we commented on the importance of minimizing stray light whenever working in the UV region of the spectrum. We highlighted the fact that, unlike other miniature spectrometer manufacturers who use crossed Czerny-Turner spectrometers, Avantes exclusively uses the more traditional “unfolded” Czerny-Turner design. Not only does this eliminate stray light due to beam path crossover, but it also facilitates the implementation of additional baffling, further improving the stray light rejection. Additionally, Czerny-Turner spectrometers facilitate higher f-number optical designs, which reduce off-axis aberrations such as coma and increase spectral resolution.

While noise reduction is essential, so is improving the signal strength and dynamic range. Most modern miniature spectrometers relied upon either front-illuminated complementary metal-oxide-semiconductor (CMOS) linear array detectors or charge-coupled device (CCD) front-illuminated detectors. CMOS detectors are low cost and reliable with fast read-out time, but below 400 nm, their quantum efficiency (ratio of incoming photon to output electrons) is extremely poor. This is mainly due to the low penetration depth of UV photons. One common workaround is to coat the detector with a thin fluorescent coating, which up-converts the UV photons into the visible, increasing the quantum efficiency to ~10% below 400 nm. Front-illuminated CCD detectors have largely been phased out by major manufacturers making CMOS the only commercially viable option for most spectrometers today.

An alternative approach is a back-thinned (BT) back-illuminated charge-coupled device (CCD) array detector. The charge coupling effect allows the signal to be transferred from pixel to pixel and read through a common point along each row or column. Therefore, since there is no need for electronic patterning across the back of the detector, it can be etched down to a thickness of 10 to 15 microns, significantly increasing both the UV absorption and decreasing the probability of electron ”re-absorption.” This allows BT-CCDs to have quantum efficiency greater than 60% in the UV region while simultaneously reducing the effects of stray light (no need for upconversion). Furthermore, reducing the overall volume of pixels decreases the availability of thermally generated electron-hole pairs, reducing the dark current. Figure 2 compares the typical quantum efficiency of a BT-CCD detector compared to the relative sensitivity of a CMOS detector. It is important to note when looking at the figure that the relative intensity of the CMOS detector is normalized to the peak of the quantum efficiency curve. As a rule of thumb, typical CMOS detectors have a maximum quantum efficiency between 40-60%, which aligns with the previous statement of ~10% quantum efficiency in the 200 – 400 nm range.

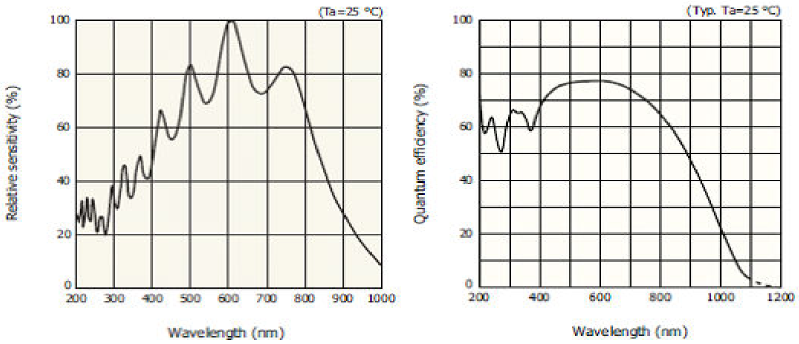

FIGURE 2: Quantum efficiency curves for a traditional CMOS detector (left) compared to a Back-thinned CCD detector (right).

AVANTES SPECTROMETERS FOR DOAS APPLICATIONS

Avantes offers several spectrometers equipped with BT-CCD detectors, but of particular interest for portable DOAS applications is the AvaSpec-ULS2048XL-EVO (see Figure 3). By combining Avantes' ultra-low stray light spectrometer (<0.5%) with a 2048-pixel (14x500 microns per) BT-CCD detector, the AvaSpec-ULS2048XL-EVO can provide high sensitivity (460,000 counts/µW per ms) and high signal-to-noise ratio (525:1) without thermoelectric cooling (TEC). Since the AvaSpec-ULS2048XL-EVO does not need a TEC, it can be powered via a standard USB port, requiring less than 5W of total power consumption. Combining the high sensitivity and low power consumption with its lightweight (1.18 kg) compact form factor (175 x 127 x 44.5 mm3¬), the AvaSpec-ULS2048XL-EVO is the ideal solution for DOAS factoring both SWaP and performance.

FIGURE 3: Spectrometer with integrated BT-CCD

For DOAS applications requiring even lower detection limits, Avantes also offers a TE-cooled version, the AvaSpec-ULS2048x64TEC-EVO (see Figure 4). This system also utilizes a BT-CCD, but now it can be cooled to -30 °C below ambient, greatly reducing the thermally induced dark current and allowing for integration times up to 120 s. While it should be noted that integrating a TEC does slightly increase the SWaP – 18W, 185 x 145 x 185 mm3, 3.5 kg – the 6x increase in integration time often outweighs any disadvantages associated with SWaP.

FIGURE 3: AvaSpec-ULS2048x64TEC-EVO Spectrometer with integrated TE-cooled BT-CCD

FINAL THOUGHTS

What we will continue to witness is a persistent rise in the demand for field-deployable CEMS based on DOAS. This surge is propelled by governments advocating for stricter emissions standards, while global industries are concurrently investing in a cleaner, greener future. In response to this growing demand, Avantes' distinctive spectrometer offerings are well-positioned to contribute to the expansion of this crucial field. They provide the necessary sensitivity, stability, resolution, and stray light rejection essential for DOAS. In particular, the Avaspec-ULS optical bench offers the highest degree of stability and lowest stray light (<0.5%) of any miniature spectrometer on the market, and the availability of cooled and uncooled BT-CCDs options provides the flexibility to manage SWaP and sensitivity tradeoffs. Additionally, for CO2 DOAS measurements, Avantes NIRLine instruments such as the AvaSpec-NIR256-2.5-HSC-EVO have been demonstrated to be capable of supporting the DOAS application.

It is also important to note that while all the components discussed were standalone modules, they are also available as OEM modules or can be integrated into multichannel rack mount systems. These units can communicate via USB, Ethernet, and the native digital & analog input/output capabilities of the Avantes AS7010 electronics board provides for a superior interface with other devices. Additionally, the Avantes AvaSpec DLL package, with sample programs in Delphi, Visual Basic, C#, C++, LabView, MatLab, Python and many other programming environments, enables users to develop their own code.

For more information about the full range of spectrometer options available from Avantes for NIR spectroscopy, please feel free to visit the website at www.avantes.com, email at info@avantes.com or give us a call at +1 (303)-410-8668 where our knowledgeable applications specialists are standing by to help.

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