

## Techniques

- Differential Optical Absorption Spectroscopy

## Keywords

- UV/VIS Absorbance
- Near-Infrared Spectroscopy
- Continuous Emissions Monitoring
- Environmental Monitoring
- Air Pollution, Clean Air Act
- Field Spectroscopy

## Introduction

Since the 1950s, it has been widely known that coal-burning power plants emit dangerous levels of particulate and gaseous pollutants into the atmosphere, including ash, soot, SO<sub>2</sub>, NO<sub>2</sub>, and NO. Over the ensuing 70-years, there has been much progress on reducing emissions to ensure cleaner air, particularly in the United States and Europe. For example, the United States passed the Clean Air Act (CAA) in 1963, giving the Environmental Protection Agency (EPA) the authority to take action to improve air quality and promote public health. But, even though the CAA has been modified several times (1970, 1977, 1982, and 1990) to expand the EPA's power, according to a 2013 study conducted at the Massachusetts Institute of Technology (MIT), air pollution is still responsible for roughly 200,000 deaths each year in the United States alone [1]. As the developing world has continued to industrialize in its transition into modernity, the demand for energy is skyrocketing, particularly in places like China and India. While cleaner technologies are meeting some of the worldwide markets, roughly 40% of the electricity generated around the world is from coal-burning power plants; in countries such as China and India, this is as high as 70 to 75% [2]. As a result, environmental monitoring systems are just as relevant today as they have ever been.



## Continuous Emission Monitoring Systems

From the early days of the CAA, engineers have been developing ways to purify smoke stack exhaust with technologies such as electrostatic precipitators [3,4]. But, real-



*Air pollution monitoring station*

time monitoring of gaseous pollutants has historically been far more of a challenge. Fortunately, with the advances in optical sensing technologies over the past 20 years, engineers are now capable of developing a continuous emission monitoring system (CEMS), using absorption spectroscopy. Like any other covalently bound molecule, gasses have absorption bands in both the infrared (vibronic) and UV/Vis (electronic) regions of the spectrum. There are pros and cons to operating in both of these regimes.

Standoff infrared absorption techniques both in the near-infrared (NIR) and mid-

infrared (MIR), require the use of tunable laser sources such as distributed Bragg reflectors (DBRs) and quantum cascade lasers (QCLs) used in conjunction with InGaAs and HgCdTe photodetectors. Through processes like tunable diode laser absorption spectroscopy (TLDA) and differential absorption lidar (DIAL), NIR and MIR absorption spectroscopy can provide highly accurate quantization of molecular species. But the major downside of this approach is that in most cases, each species of interest will require a different excitation laser, further compounding the already

expensive component cost. By contrast, using a methodology called differential optical absorption spectroscopy (DOAS), UV/Vis absorption can be used to measure a wide range of molecular species with a sin-

gle broadband light source. Not only does DOAS decrease the cost of multi-species detection, but it is also often far less expensive for single species detection as well because of its use of inexpensive CCD spec-

trometers and a constant current D2 emission lamp. In many cases, DOAS can even be performed using sunlight, although this is typically not advisable for CEMS due to the inherent fluctuations of sunlight levels.

## Differential Optical Absorption Spectroscopy

The earliest reported use of DOAS for atmospheric measurements was in 1973, for the monitoring of NO<sub>2</sub> concentrations by monitoring absorption bands between 430 nm and 450nm [5]. But, as stated above, it wasn't until the advent of modern CCD based spectrometers that the technique gained commercial viability. Today, DOAS is performed by recording two absorption spectra, one a reference scan through a column of atmosphere devoid of analyte (ideally) and one through an identical pathlength containing the analyte. A detailed mathematical treatment of DOAS is beyond the scope of this application note. Still, it is essential to point out that by taking the difference of these two spectra and applying the Beer-Lambert Law, the resultant differential spectrum is now



Vehicles on a congested highway

dependent solely on the absorption cross-section of the species in the analyte and the

difference between the column densities of the species and reference spectrum [6]. Furthermore, since the cross-section can be represented as the sum of a slowly varying and rapidly verifying function, the differential spectrum allows for the separation of these two components. Since both Rayleigh and Mie scattering are slowly varying functions, the differential spectrum in conjunction with mathematical tools such as a Fourier Transform filter eliminates both attenuations and scattering from the data [7].

Figure 1 shows the absorption bands of a wide range of common atmospheric pollutants, including the SO<sub>2</sub>, NO, and NO<sub>2</sub> mentioned above. From this chart, it is clear that the vast majority of molecular species, with the notable exceptions of CO and CO<sub>2</sub>, can be detected from 200nm to 460 nm. As a result, it is possible to use a single compact fixed grating spectrometer in a DOAS based CEMS. It is important to note that whenever choosing a spectrometer to measure in the UV region of the spectrum, it is critical to use an ultra-low stray light

configuration to minimize stray light in the

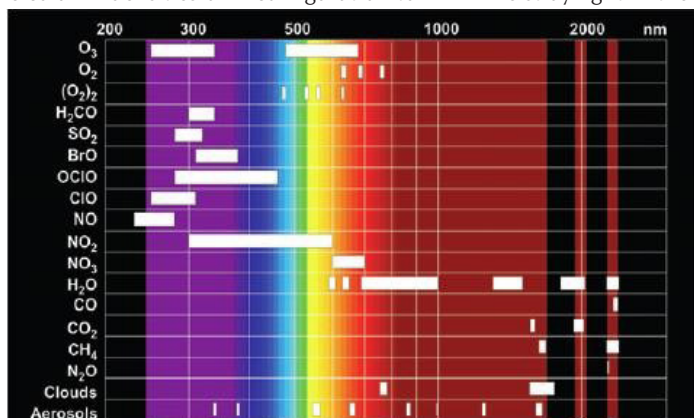


Figure 1: Absorption bands of common atmospheric species

system. Cross Czerny-Turner spectrograph designs, while compact tend to have inherently higher stray light than transitional Czerny-Turner spectrographs. Examples of ultra-low stray light spectrometers include the AvaSpec-ULS2048XL-EVO and AvaSpec-ULS2048X64-EVO from Avantes. Both of these instruments from Avantes feature their ultra-low stray light design and back-thinned CCD detectors for superior UV sensitivity and signal to noise. Figure 2 shows a typical CEMS setup for DOAS where a concave mirror is used to collimate a broadband light source (typically a D2 lamp) across the monitoring path, where a second concave mirror is then used to couple the transmitted light into a fiber optic cable which directs it into the spectrometer.

## Additional DOAS Applications

In addition to CEMS, sunlight based DOAS is also widely used for general environmental monitoring. For example, a team of Greek scientists presented data at the 2015 conference Advances in Atmospheric Science and Applications, where they used a mini multi-axis (MAX) DOAS system to measure tropospheric column densities of NO<sub>2</sub>, SO<sub>2</sub>, and HCHO in urban, rural, and suburban loca-

tions around Thessaloniki, Greece [8]. The mini-MAX-DOAS system utilized an AvaSpec-ULS-TEC spectrometer from Avantes configured from 300nm to 450 nm. Of the three systems deployed, one used a 25-micron entrance slit with a ~0.25 nm resolution, and the other two utilized a 50-micron entrance slit with ~ 0.38 nm resolution. A second group at the Max Planck Institute

in Germany also used a similar mini MAX-DOAS system based upon an Avantes spectrometer to collect similar measurements Romania and Germany [9].

## Instrument Selection

As societies around the world continue to grow, so too will the need for clean technologies, including the monitoring of environmental pollutants both in the form of CEMS and field-based DOAS systems. In both cases, these applications require sensitive, stable, high resolution, low stray light spectrometers; to ensure accurate and reliable DOAS measurements with low detection limits and high signal-to-noise ratios. The Avaspec-ULS optical bench offers the highest degree of stability and smallest stray light of any miniature spectrometer on the market, and the option of either CMOS or back-thinned CCD detector options provides the flexibility to manage cost and sensitivity tradeoffs.

Among the most highly-recommended back-thinned instruments, the Avantes ULS2048 series spectrometers offer incredible performance. The AvaSpec-ULS2048XL-EVO features extra-large 14x500 micron pixels that delivers exceptional efficiency in the UV range (200-400nm) and the NIR (950-1160nm). The internal shutter allows in-line dark capture integration times as low as 2 microseconds. The uncooled AvaSpec-ULS2048x64-EVO is another instrument with a proven track record for DOAS applications due to its high UV response,

0.9mm detector height, and fast integration times.

All of the AvaSpec-ULS series spectrometers discussed above are also available as OEM modules. They can be integrated into turn-key industrial or field sensing devices, in addition to function as an add-on to existing laboratory equipment set ups. These instruments can communicate via USB, Ethernet, and the native digital & analog input/output capabilities of the Avantes AS7010 electronics board, which provides for a superior interface with other devices. Additionally, the Avantes AvaSpec DLL software development package, with sample programs in Delphi, Visual Basic, C#, C++, LabView, MatLab, and other programming environments, enables users to develop code for their own applications.

For more information about the full range of laboratory and OEM spectrometer options available from Avantes,

please feel free to visit the website at [www.avantesusa.com](http://www.avantesusa.com) or give us a call at +1 (303)-410-8668 where our knowledgeable applications specialists are standing by to help.

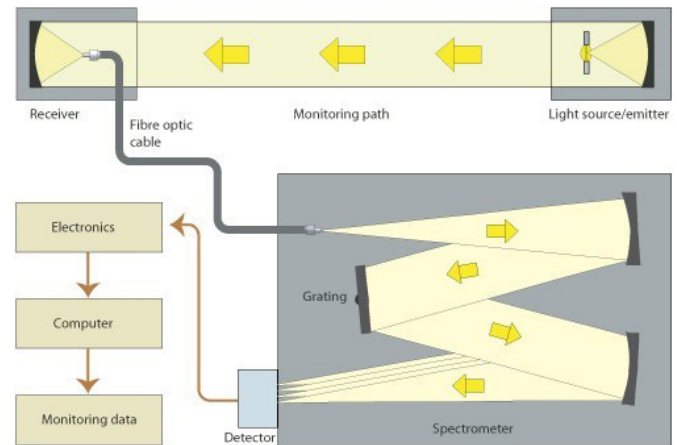


Fig 2. Typical CEMS setup, using DOAS

### References

- [1] Caiazzo, Fabio, et al. "Air pollution and early deaths in the United States. Part I: Quantifying the impact of major sectors in 2005." *Atmospheric Environment* 79 (2013): 198-208.
- [2] G, Karen. "What Are Smoke Stacks?" *sciencing.com*, <https://sciencing.com/info-8068108-smoke-stacks.html>. 23 March 2020.
- [3] Marks, Alvin M. "Smokestack aerosol gas purifier." U.S. Patent No. 3,520,662. 14 Jul. 1970.
- [4] Kirchhoff, Franz-Josef, and Joachim Brandt. "Electrostatic precipitator." U.S. Patent No. 4,097,252. 27 Jun. 1978.
- [5] Brewer, A. W., C. T. McElroy, and J. B. Kerr. "Nitrogen dioxide concentrations in the atmosphere." *Nature* 246.5429 (1973): 129-133.
- [6] U. Platt (1994), "Differential optical absorption spectroscopy (DOAS)," in *Air Monitoring by Spectroscopic Techniques*, M. W. Sigrist, ed., Chemical Analysis Series, vol. 127, pp. 27-84.
- [7] Haiming, Zheng. "Experiment study of continuous emission monitoring system based on differential optical absorption spectroscopy." 2008 International Workshop on Education Technology and Training & 2008 International Workshop on Geoscience and Remote Sensing. Vol. 1. IEEE, 2008.
- [8] Drosoglou, Theano, et al. "Retrieval of tropospheric columns from ground-based MAX-DOAS measurements performed in the greater area of Thessaloniki and comparison with satellite products." *Experimental Biology* 49.3 (1969): 669-677.
- [9] Riffel, Katharina, et al. "NOx emissions of various sources in Romania and the Rhein-Main region in Germany based on mobile MAX-DOAS measurements of NO2." *EGU General Assembly Conference Abstracts*. Vol. 18. 2016.
- Riddle, Sharla. "How Bees See and Why it Matters." *Bee Culture: The Magazine of American Beekeeping*. (May 20, 2016).