Using Spectral Averaging and Signal Processing to Leverage Existing Short-term Fence Line UV Spectroscopic Data to Retrieve Accurate, Long-term Gas Concentrations to Meet New Monitoring Goals

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What is UV DOAS

• Spectrographic technique for measuring atmospheric components in situ.

Active vs. Passive



Principles of DOAS

The Beer-lambert law

$$OD_i = \sigma_i \overline{c}_i I$$

 OD_i = optical density, σ_i = absorption cross-section, c_i = concentration, *I* = pathlength (for species *i*)

Advantages of DOAS

- Overlapping absorption structures due to different species can be separated
- Species not anticipated can be measured later.
- Spectral fingerprint Presence of Gases verified
- Warning against unexpected absorbers (residual)
- Mostly Immune against continuous (broad band) extinction due to e.g. aerosol or molecules
- High sensitivity, since many trace gas lines (bands) are used.
- No analytic cost associated with the sample (no lab) And Low maintenance costs

Disadvantages

- Atmospheric turbulence induce intensity variations in the spectra.
- Upfront costs considerable 40 200k
- Only a limited number of molecules have suitable absorptions in UV and visible region.
- Rain, snow, fog and clouds make measurements impossible due to the strong attenuation in the UV-Visible region.
- Path Average concentration vs. Peak concentration



A concentrated cloud of 50 ppm, 10m in diameter, in a background of 0 ppm also gives a reading of 500ppmm.



When the 500 ppmm is divided by 50m the result is a value of 10 ppm, which is the 'path averaged' concentration.

Some Gases/features



Can detect a wide range of UV absorbing chemical compounds

Nitric oxide Acrolein Nitrogen dioxide Acetaldehyde Ozone Ammonia Phenol Benzene m-, o-, p-xylene 1,3-Butadiene Styrene **Carbon disulfide** Sulfur dioxide Formaldehyde Toluene Hydrogen sulfideand more

Some Example Spectra



Hardware



Data Trail

- Raw Spectra Background Sample
- Absorbtion
- Concentration vs Time

Deuterium Source Raw Spectrum



Xenon Source Raw Spectrum



Raw Data - Xenon Source

Background Spectrum

<u>Collect a data spectrum in the atmosphere when the target gas is not present.</u> <u>Define this as the background spectrum.</u>



Single Beam Raw Spectrum - Background

Sample Spectrum

<u>Collect a data spectrum in the atmosphere when the target gas is</u> <u>present. Define this as the Sample spectrum</u>.



Single Beam Raw Spectrum – Sample Spectrum

Absorbance Spectrum

Subtract the logarithms of the two spectra. This resulting spectrum is defined as an absorbance spectrum.



Absorbance Spectrum

Concentration time series



Limits of Detection

- How do you know you have a detection?
- Spectral Feature of Gas larger than the noise
- 2x to 6x depending on false positive vs. false negatives level of caution
- Absorbance spectrum correlation to ref spec.

Current Use UV DOAS

- Fence-line
- 5 min time resolution
- 5 bbp Benzene LOD
- Detect Peaks and Leaks
- Use with Wind data to pinpoint sources



Absorbance Spectra Various concentrations Benzene, 5 min

New Monitoring Goals

- Longer term exposures
- Lower Levels of detection Required
- Fine Time resolution not needed
- EPA Refinery Rule 1 ppb Benzene -2 week sample time



Absorbance Spectra Various concentrations Benzene, 40 min

Requirements

- UV system has to save spectra for each small time frame
- Signal Strength changes need to be accounted for
- Changes in Pressure cause differential Oxygen absorption which need to be accounted for

Theory vs. Reality

- Limit of detection improvement 1/sqrt N
- 100 times sample time implies 1/10 L.O.D

Theory vs Data



Why not as good as Theory

- Signal strength fluctuation
- O2 Absorption Atmos Pressure change
- Missing /bad data
- Advanced algorithms can get closer to Theory

Next Generation Argos UV

- More thermally stable spectrometer/better detector array

- 5 min Detection limits for benzene in the partsper-trillion (Based on EPA's ETV methodology for determining detection limits)

- Detection limits generated using field data
- Final independent validation study completed in Summer 2015

New Spectrometer



Conclusions

- Existing UV fence-line monitors can meet or exceed new requirements
- Better Time resolution 1 ppb LOD Benzene much less than 14 day time resolution.
- Several Compounds can be measured
- Can average spectra from a subset of wind directions much better source apportionment.
- New Spectrometer promises to deliver 1 ppb L.O.D with 5 min scans