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

\[ OD_i = \sigma_i c_i l \]

\( OD_i = \) optical density, \( \sigma_i = \) absorption cross-section, \( c_i = \) concentration, \( l = \) 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

- Acrolein
- Acetaldehyde
- Ammonia
- Benzene
- 1,3-Butadiene
- Carbon disulfide
- Formaldehyde
- Hydrogen sulfide
- Nitric oxide
- Nitrogen dioxide
- Ozone
- Phenol
- m-, o-, p-xylene
- Styrene
- Sulfur dioxide
- Toluene
- .....and more
Some Example Spectra
Hardware
Data Trail

• Raw Spectra  -  Background  -  Sample
• Absorbtion
• Concentration vs Time
Deuterium Source Raw Spectrum

Raw Data - Deuterium Source

Counts

Nanometers

H2S
1-3 BuT
NH3
SO2
O3
NO
NO2
Acrolein
H2S
Benzene
Toluene
Xylenes
SO2
Formaldehyde
CS2
ClO2

single beam
Xenon Source Raw Spectrum
Collect a data spectrum in the atmosphere when the target gas is not present. Define this as the background spectrum.
Collect a data spectrum in the atmosphere when the target gas is present. Define this as the Sample spectrum.
Absorbance Spectrum

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

Chalmette Air Monitoring (SO2)

[Graph showing concentration levels over time with various limits marked]

- Ambient SO2
- 10 Min Limit
- 24 Hour limit
- Annual Limit
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

Absorbance

Nanometers

-0.004
-0.003
-0.002
-0.001
0
0.001
0.002
0.003

252 253 254 255 256 257 258 259 260

Nanometers

5 min 0 ppb
5 min .6 ppb
5 min 1 ppb
5 min 1.8 ppb
5 min 6 ppb
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
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 parts-per-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

New Spectrometer 2015

- 1 ppb Benzene
- 5 min Noise
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