

# Testing of Cerex Open-Path Ultraviolet Differential Optical Absorption Spectroscopy Systems for Fenceline Monitoring Applications

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## INTRODUCTION

Industrial facilities, energy production, and refining operations can be significant sources of gas-phase air pollutants.<sup>1-4</sup> Some industrial emissions originate from fugitive sources (leaks) or process malfunctions and can be mitigated if identified.<sup>5</sup> In recent amendments to the National Emission Standards for Hazardous Air Pollutants from Petroleum Refineries, the U.S. Environmental Protection Agency (EPA) is for the first time requiring fenceline measurements for benzene as a surrogate for facility fugitive emissions using time-integrated passive samplers with potential use of time-resolved measurements as alternate or supporting information.<sup>6,7</sup> Time-integrated passive sampling can establish average concentrations around a facility and point to potential problem areas, but the information provided is not real-time and reflects integrated source contributions in the local air shed.<sup>8</sup> Time-resolved measurements that combine pollutant concentration and wind data can be used to support passive sampling strategies by helping to decipher the origin of emissions and provide time-stamped information on fenceline concentrations.<sup>9-11</sup>

Ground-based optical remote sensing (ORS) is a class of time-resolved techniques that can be used for fenceline monitoring and to assist in quantification of emissions from fugitive and area sources.<sup>12-17</sup> ORS systems employ open-path optical beams to spectroscopically speciate and quantify path-averaged pollutant concentrations in an advected plume. The long optical paths used to help capture spatially variable emissions from the nearby sources. Open-path ultraviolet differential optical absorption spectroscopy (UV-DOAS) is a sub-class of ORS that is particularly useful for measurement of benzene and related aromatic compounds.<sup>18-20</sup> Although UV-DOAS has been commercially available for over a decade, method development questions remain regarding expected performance characteristics and standardized data analysis approaches. In recent years, significant advances in sensor performance and analytical approaches have improved both minimum detection capability and automation of analysis.

In this extended abstract, we investigate the performance of two mid-cost UV-DOAS systems produced by Cerex Monitoring Solutions (CMS) for measurement of benzene. We define and compare the benzene method detection limits (MDLs) using field data from an older generation system, set up for general measurement of a range of compounds, with calibration cell test data

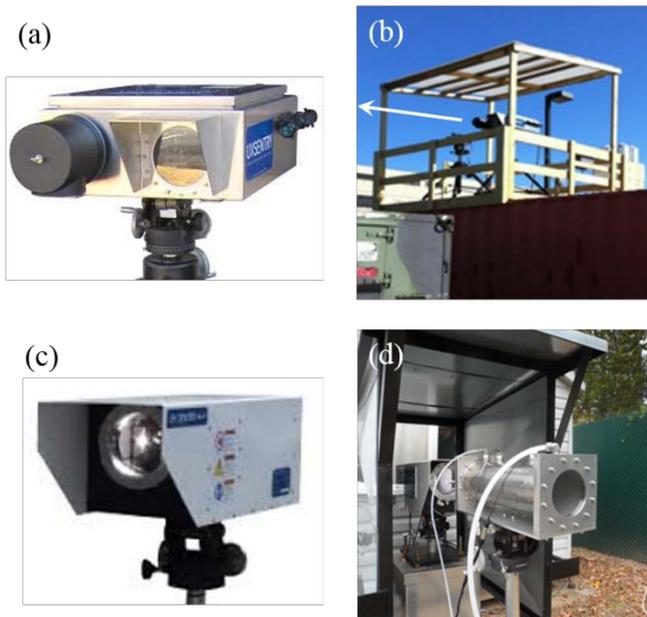
from a newer system optimized for fenceline applications. For the presentation, calibration test cell data for the field-deployed system is expected to be available for comparison.

## EQUIPMENT AND METHODS

Both UV DOAS instruments were variations of the Cerex UV Sentry (CMS, Atlanta GA, USA). Both instruments were monostatic in configuration with an integrated UV light source, a launch/receive telescope, spectrometer, and analysis computer at one end of the optical path and retroreflecting mirrors at the other end. The total (double pass) optical path lengths for both deployments were similar at 323 m and 326 m for the field and test range units, respectively. Both units were operated with five-minute time resolution where spectral scans (typically greater > 1500) were automatically acquired and integrated producing a single field spectrum used to determine the average benzene concentration along the optical path, also called path-averaged concentration (PAC). The benzene spectral analysis for both units was performed in the 253 nm range. The two systems used different internal hardware and versions/configurations of the Cerex control and analysis software, reflecting both differences in applications (general use vs. fenceline-optimized) and technical advancements over time.

The field UV DOAS [Figures 1(a) and 1(b)] was deployed by the City of Philadelphia, Department of Public Health, Air Measurements Services (AMS) as part of a 2011 EPA Community-Scale Air Toxics Monitoring Grant. This system was set up for simultaneous measurement of multiple compounds including: acetaldehyde, ammonia, 1,3-butadiene, formaldehyde, nitrogen oxide, sulfur dioxide, styrene, trimethylbenzene, benzene, ethylbenzene, toluene, *m*-xylene, *o*-xylene, and *p*-xylene, with the last six compounds collectively referred to as BTEX. The measurement performance for these compounds varies and is not described here (other than benzene). In addition to a configuration for measurement of multiple compounds, this general-use UV DOAS employed a deuterium lamp as a UV source and was produced with subsystems and software used by Cerex in model year 2012. This unit is here after referred to as GD12. The midpoint of the GD12 optical path was located  $\approx$  430 m due east of a refinery in South Philadelphia with further information on the deployment contained elsewhere.<sup>9,11</sup> The GD12 was deployed in January 2014, will be upgraded in December 2015, and will continue deployment into 2016. The example field data described here were acquired during a two week period in November 2014 where benzene events were detected.<sup>11</sup> In-field optical cell calibration data for GD12, similar to the described below, may be available for presentation at the conference.

**Figure 1. Cerex UV Sentry, (a,b) GD12 unit deployed on elevated platform in South Philadelphia, and (c,d) FX15 unit deployed at EPA test range, projecting through 0.5 m optical cell.**



The other Cerex UV Sentry [Figure 1(c)] was tested in November, 2015, at EPA's open-path optical test range in Durham, NC, using a 0.5 m length calibration cell [Figure 1(d)]. This UV DOAS system was optimized for fenceline measurement of BTEX and was produced with subsystems and software currently in development by Cerex (model year 2015). With a high-output xenon light source, this fenceline unit, referred to here as FX15, is capable of optical path lengths in excess of 1 km with proper on-site infrastructure. The specific FX15 configuration tested here is designed for high performance measurement of BTEX but cannot measure the GD12 range of compounds without reconfiguration. To test the performance of the FX15, the in-beam optical cell was filled with mixtures of ultrahigh purity zero air and test gases at 5.5 Lpm using a calibrated Environics Series 2000 Computerized Multi-Component Gas Mixer (Environics Inc., Tolland, CT, USA). The test gas cylinders were a nominal 10 ppm benzene in air and a BTEX mix with 10 ppm of each component in air. A variety of cell fill points ranging from 0.05 ppm to 10 ppm were used, producing a simulated PAC of 0.15 ppbv to > 40.0 ppbv of benzene. For accuracy tests, the optical cell was filled/flushed ~10 times between each test point with partial fills excluded from the analysis. Accuracy and linearity will be described in the presentation with current treatment focusing on MDL definition, so measurements acquired during the cell fills (partial fills) are included as they provide value.

The analyses of the GD12 and FX15 data differ in this treatment. For both, the Cerex software calculates an absorbance spectrum from the field spectra and a mathematically produced synthetic background that includes instrument-specific noise information. Additional filtering and spectral alignment steps are performed followed by a multi-component classic least squares (CLS) fitting operation and comparison to a scaled benzene (or other) reference to determine the PAC. Interfering compounds, [e.g., oxygen (O<sub>2</sub>) and ozone (O<sub>3</sub>)] are accounted for by the CLS routine. For the FX15 data, an additional step is employed where a benzene-free field spectrum that was acquired close in time to the analyzed field spectrum is used. This second field spectrum carries information on time-specific instrument performance and atmospheric conditions, especially O<sub>2</sub> and O<sub>3</sub> levels that change throughout the day. Employing specially-selected analyte-free background spectra to improve CLS performance, whether as part of a standard absorbance calculation, or to augment a synthetic background procedure, is called use of a dynamic background. Ideally, the dynamic background can change throughout the day to track changing conditions. Alternatively, it can be a selected background applied for a fixed period of time (e.g., a day or week). Both approaches have utility although robust automatic selection of dynamic backgrounds has yet to be routinely demonstrated and is investigated in this project.

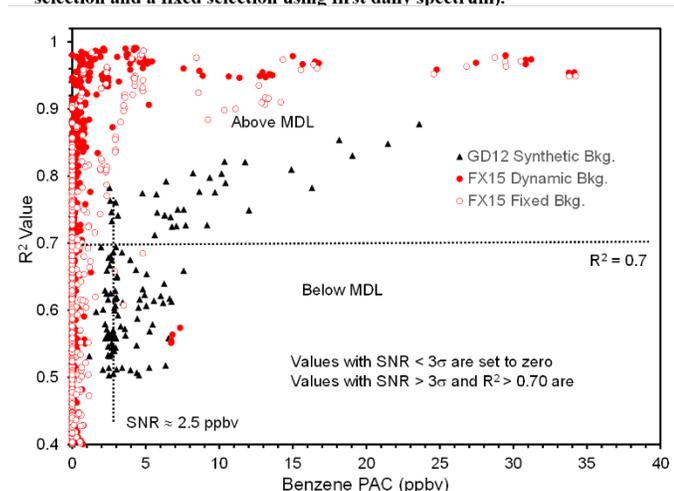
For most fenceline applications with relatively low benzene PACs (< 100 ppbv) and with accurate, properly scaled spectral references, the performance of the benzene determination depends on: (1) the amount of benzene in the field spectrum, (2) the amount of benzene in the selected background (if employed), (3) the effective system signal to noise ratio (SNR), and (4) the quality of interference cancellation. The first two factors refer to the degree to which the analyte is present, with the latter producing negative accuracy bias. The SNR is related to UV light intensity throughput and the inherent noise/stability of the system, particularly the spectrometer. Here, we define SNR through a comparison of the CLS-determined benzene PAC (the signal) to the standard deviation ( $\sigma$ ) in a 275 nm to 276 nm window of the absorbance file, with  $\text{SNR} > 3\sigma$  defined as above the detection threshold. The software also calculates the Pearson correlation coefficient ( $R^2$ ) between the scaled reference spectrum and the CLS-determined benzene spectrum with values > 0.70 defined as the above detection threshold. As the

amount of benzene increases in the field spectrum, the  $R^2$  values increase, approaching  $\sim 0.95$ . The quality of the interference cancellation (for benzene) refers to the ability of analysis to account for primarily  $O_2$  and  $O_3$ . Some approaches report CLS analysis residuals as a data quality indicator (DQI) but this is not done by the Cerex software at this time. Interference cancellation affects both the SNR and  $R^2$  DQIs and plays a major role in determination of the MDL for the system. For the purpose of this analysis, we define the MDL as an  $SNR > 3\sigma$ , and  $R^2 > 0.70$ .

## RESULTS

In Figure 2, we compare a measure of MDL performance of the GD12 and FX15 systems by plotting the benzene PAC as a function of the  $R^2$  DQI. The GD12 data are from a two week period of the Philadelphia AMS field deployment showing 34 values above MDL ( $< 1\%$  acquired data). The  $SNR > 3\sigma$  value for the GD12 was  $\sim 2.5$  ppbv for most days during this period, and the  $R^2$  values did not exceed 0.9, even at relatively high PAC observed during a benzene event that was corroborated with other measures.<sup>11</sup> The FX15 with a synthetic dynamic background selection produces a much lower noise floor (typically  $< 0.1$  ppbv) and  $R^2$  values  $> 0.9$  at the  $\sim 1$  ppbv signal level. The use of the same synthetic background procedure but with a non-optimal choice of supporting background

Figure 2. Benzene PAC vs  $R^2$  with MDL for GD12 field data using synthetic bkg. and FX15 test cell data using augmented synthetic bkg. (dynamic selection and a fixed selection using first daily spectrum).



spectra (the first spectrum acquired during the test day at midnight), produces the FX15 open circle data. Not only does the MDL for this fixed background case increase compared to the dynamic case but an accuracy bias is evident (further discussed in presentation). Of course, the objective of the augmented synthetic background procedure is to improve both system noise and spectral interference cancellation and the use of spectra acquired at night does little to improve the latter, as test cell data runs were executed in the daytime under higher  $O_3$  levels.

It is evident that benzene MDL for a well-tuned FX15, optimized for fenceline BTEX applications, can be significantly better than the multi-species GD12, with its slightly older hardware and analysis approach. However, the robustness and potential biases associated with the newly developed dynamic synthetic background technique need further review. At the time of writing, additional optical cell tests for the FX15 are in process. More information on measurement accuracy and possible negative performance factors associated with the new approach will be discussed in the presentation, likely in addition to similar tests with an upgraded version of the GD12 in the AMS Philadelphia deployment.

## SUMMARY

Development of cost-effective, time-resolved fenceline measurement methods that facilitate improved emissions mitigation strategies is of growing interest to both industry and regulators. UV-DOAS systems are particularly useful for benzene measurements and significant advances in sensor performance and automated analytical approaches are improving both MDLs and analysis automation. This extended abstract discussed two Cerex UV DOAS systems and provides an

initial analysis of improvements in MDL performance for the compound benzene, with further information available in presentation.

## ACKNOWLEDGMENTS

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