Integration of Gas Chromatographs into Federal Highway Administration (FHWA)/Environmental Protection Agency Near Road MSAT Study in Las Vegas, NV

Extended Abstract 2009-932

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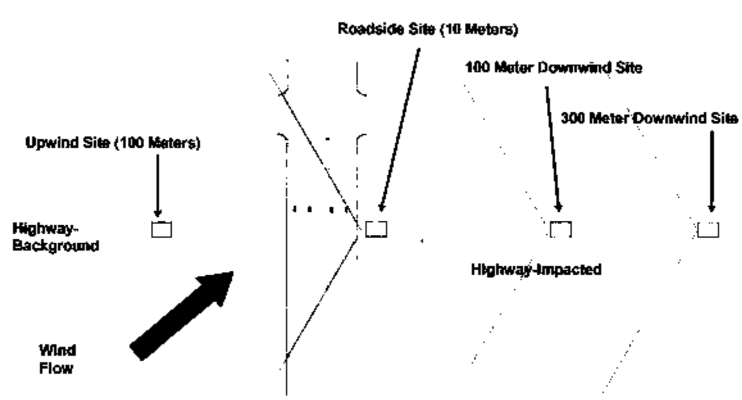
INTRODUCTION

Sierra Club challenged the Federal Highway Administration's (FHWA) and the Nevada Department of Transportation's (DOT) environmental assessment of the U.S. 95 expansion project in Las Vegas, NV regarding impacts of mobile source air toxics (MSATs; acetaldehyde, acrolein, benzene, 1,3-butadiene, formaldehyde) on air quality adjacent to the highway. A Settlement Agreement was reached between Nevada DOT and the Sierra Club which called for research studies to characterize the impact and behavior of particulate matter with aerodynamic diameter less than 2.5 microns ($PM_{2.5}$) and MSATs near highways[1]. The FHWA developed a detailed protocol outlining a uniform approach for conducting the studies to evaluate mobile source contributions of air toxics and $PM_{2.5}$, and their dispersion patterns adjacent to heavily traveled highways [annual average daily traffic (AADT) > 150,000][2]. The objective of the research study is to determine Mobile Source Air Toxics (MSAT) concentrations and variations in concentrations as a function of distance from the highway and to establish relationships between MSAT concentrations as related to highway traffic flows including traffic count, vehicle types and speeds; and meteorological conditions such as wind speed and wind direction. Air monitoring sites are configured as shown in Figure 1[3].

Figure 1. Las Vegas air monitoring station configuration.



This paper documents the technical evaluation of a semi-continuous gas chromatograph (GC) for the measurement of benzene and 1,3-butadiene in the near road environment. This paper will also consider the some of the non-technical implications associated with the operation of a GC outside the laboratory.

GC operation has been incorporated into ambient air monitoring networks for many years but most of these applications utilized relatively expensive GCs and required an excessive amount of knowledge and time to maintain data collection[4,5,6]. This evaluation will compare the performance of the GC to the criteria specified in the compendium protocol procedures. The decision to incorporate GC operation within the study was to be considered only after the operation of a single GC was evaluated. The near road measurement activities began with only one GC operating at the 10 meter site. The results of this evaluation will determine if the GC's performance is acceptable and also provide input into the decision to purchase additional GCs, resulting in near real time MSAT data at all four sites. Near real time MSAT data is desirable and the cost of four GCs has been estimated to be less than the project costs associated with one year of canister sampling and analysis.

Experimental Methods

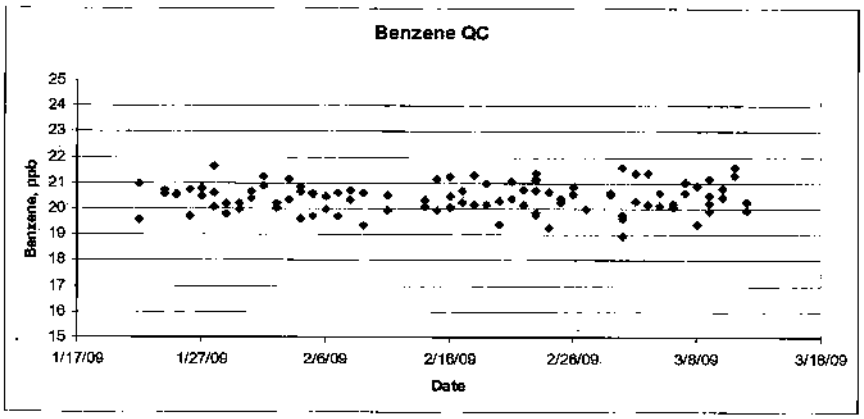
The procedures[7,8] guiding this project specify the use of canisters for 1,3-butadiene, benzene and acrolein. The optimized GC and Photo Ionization Detector (PID) technique was configured to measure 1,3-butadiene and benzene but not acrolein. The acrolein data would be obtained from the analysis of 2,4-dinitrophenyl hydrazine (DNPH)[9] or 5-dimethylaminonaphthalene-1-sulfonyl hydrazine (DNSH)[10] cartridges. Spanning one year of operation, the canister sampling procedure will provide 274 hourly averages. The GC will provide 17,500 half hour or 8760 hourly averages, providing a significantly enhanced data base, nearly thirty times more data than the canister procedure.

The GC chosen for this evaluation utilizes a 30 meter metallic column, a 6 port pneumatic valve, a PID, a thermally desorbed carbotrap and a reported detection limit of 10 parts per trillion (ppt). Contained within the GC is a permeation tube chamber, maintained at 35 deg C. A benzene permeation tube is used to standardize the response, verify retention time and to adjust for the baseline sensitivity of the detector. Each time the permeation tube is sampled, there are two measurements. The first response is compared to the previous three days of permeation tube response and the second response is used to determine a three day rolling average of instrument response. It is this response factor or base sensitivity that is used to calculate the concentrations of gases measured by the GC. Using this three day rolling average, the GC software calculates the response concentrations based upon a benzene response factor. The calculated concentrations are stored in folders containing data for each day. The base sensitivity, peak area and other operational data are also stored in these daily files. The base sensitivity is equivalent to the PID response of one nanogram (ng) of mass. The base sensitivity is monitored and recorded to account for the variations in lamp intensity. The analysis cycle is completed in 30 minutes, providing concentration data twice each hour. The ambient air sample enters the GC from a heated quartz manifold that is continuously purged at a rate of one cubic foot per minute. Ambient air within the manifold maintains sample representiveness with less than a one second response time. GC performance was also evaluated using a compressed gas cylinder containing benzene and 1,3-butadiene. The certified Spectra Gas, Branchburg, NJ, cylinder contained a nominal one part per million (ppm) concentration that was diluted to ppb concentrations using the on-site flow controller based dilution system.

Results and Discussion

With the exception of only a few days, the permeation tube response has been measured every day of operation. For the data represented in this paper, January 21 through March 13, 2009, a known concentration of 20 parts per billion (ppb) was measured by the GC every day. The average response was 20.6 ppb with a standard deviation of 0.6 ppb. Figure 1 provides a graphical representation of the benzene permeation tube responses.

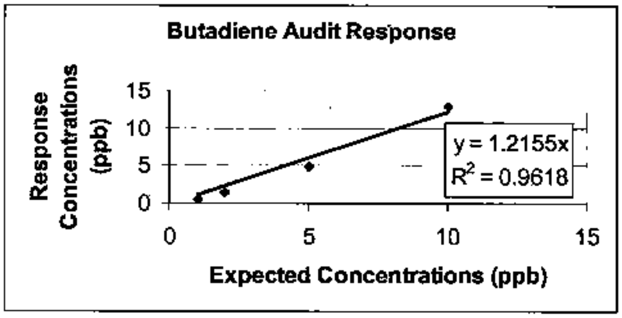
Figure 2. Permeation tube response.

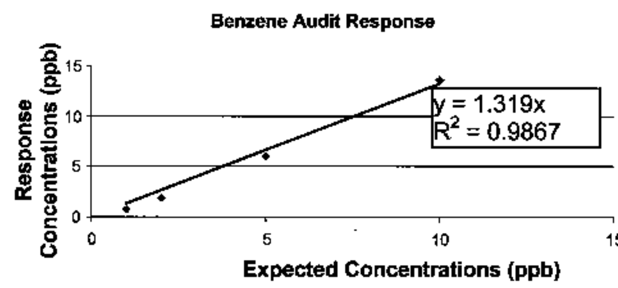


The GC was evaluated using a certified compressed gas cylinder, diluted from a nominal concentration of one ppm to the indicated ppb concentrations. The following table and graphs represent data collected on January 23, 2009.

Table 1. Compressed Gas Audit Response.

Diluted Compressed Gas Cylinder Concentration, ppb, 1/23/09	Number of points	1,3-Butadiene Average/Std Deviation	Benzene Average/Std Deviation
1.0	7	0.53/0.12	0.81/0.18
2.0	13	1.42/0.12	1.93/0.09
5.0	4	4.87/0.39	6.0/0.47
10.0	8	13.03/0.74	13.68/0.53





The referenced protocol method for canister analysis is the Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, Compendium Method TO-15. The performance of this GC was evaluated using the criteria outlined in this Compendium Method TO-15. Section 11 of Method TO-15 details the requirements for demonstrating acceptability for VOC analysis as; method detection limit of $\leq$0.5 ppb, replicate precision within 25 percent and audit accuracy within 30 percent for concentrations normally expected in ambient air.

At the writing of this paper, the majority of the 1,3-butadiene and benzene concentrations measured at the 10 meter site have been less than 2 ppb. Using the audit standard, the 1,3-butadiene and benzene accuracy responses are within 30 percent, based upon a linear regression analysis. Using the permeation tube response as an indication of precision, the results are within 6 percent. Using the audit standard responses at both 1 and 2 ppb, the method detection limit for 1,3-butadiene and benzene ranged from 0.28 to 0.57 ppb with an average method detection limit of 0.4 ppb.

SUMMARY

The data reported in this paper indicate that the GC has satisfied the compendium method and the reliability of the GC in the field would indicate that the GC should be used to enhance the MSAT data being collected. This data would also indicate that the three additional GCs should be purchased and operated in the near road air monitoring sites.

REFERENCES

1. U.S. FHWA. "The National Near Roadway MSAT Study." Accessed August 24, 2007, from http://www.fhwa.dot.gov/environment/airtoxicmsat/, 2007.

2. U.S. FHWA. Detailed Monitoring Protocol for U.S. 95 Settlement Agreement. Washington, DC http://www.fhwa.dot.gov/environment/airtoxicmsat/FinalDMPJune.pdf.2006.

3. Kimbrough, S., D. Vallero, et al. "Multi-criteria decision analysis for the selection of a near road ambient air monitoring site for the measurement of mobile source air toxics." Transportation Research Part D: Transport and Environment, 2008, 13(8): 505-515.

4. U.S. EPA, PAMS Implementation Manual (part-a), 1994.

5. U.S. EPA, PAMS Implementation Manual (part-b), 1994.

6. U.S. EPA, PAMS Implementation Manual (part-c), 1994.

7. U.S. EPA, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, Compendium Method TO-15 Determination Of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/Mass Spectrometry (GC/MS), Cincinnati, OH, 1999. EPA/625/R-96/010b.

8. U.S. EPA, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, Compendium Method TO-11A Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC) [Active Sampling Methodology], Cincinnati, OH, 1999. EPA/625/R-96/010b.

9. U.S. EPA, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, Compendium Method TO-14A Determination Of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/Mass Spectrometry (GC/MS), Cincinnati, OH, 1999. EPA/625/R-96/010b.

10. Herrington, J. S. and J. J. Zhang. "Development of a method for time-resolved measurement of airborne acrolein." Atmospheric Environment, 2008, 42(10): 2429-2436.