Comparison of Sampling and Analysis Methods for Measurement of Airborne Aromatic Hydrocarbons in Operating Petrochemical Plants

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Abstract

The concentration of aromatic compounds in air samples from operating petrochemical units is determined by three different gas chromatographic (GC) techniques. The data indicate that a portable GC provided data that is consistent with results obtained by charcoal tube adsorption and SUMMA canister sampling. The major limitation of the portable GC approach employed in this study is its higher detection limits compared with the other methods. A significant advantage of the portable GC is that it allows for significantly more samples to be obtained at a given site, thereby providing the opportunity to map out spatial and temporal distributions of aromatic compounds. Such information is used to develop strategies to limit worker exposure, identify possible emission sources, and trigger maintenance activities.

Introduction

The determination of aromatic compounds in air is required for a variety of health, safety, and environmental concerns. A number of different analytical approaches are currently available to address these concerns, although gas chromatographic (GC) (1,2) and infrared spectroscopic (3,4) techniques are most commonly employed. The choice of the best analytical methodology depends on a number of factors, including desired turnaround time, detection limit, number of components of interest, required analytical selectivity, precision, accuracy, and cost.

Direct analysis in the field provides several attractive features such as rapid turnaround and reduced overall costs. Several vendors currently market GC instrumentation well-suited for the determination of aromatics in air, including some hand-held capillary GC instruments (5). However, the performance of analyses in the field necessarily requires tradeoffs in some aspects of performance. These tradeoffs often take the form of resolution or detection limits sacrificed for ruggedness of the instrumentation and/or reduced analysis times.
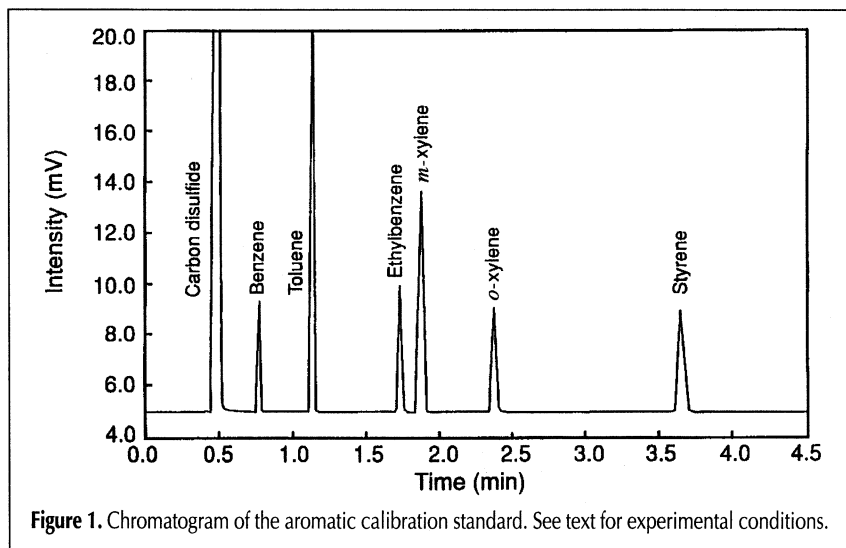
This report discusses three different GC approaches that were applied for the determination of aromatic compounds (benzene, toluene, ethylbenzene, xylene isomers, or BTEX). The sampling and field analyses were performed within operating units at three different petrochemical complexes. The first method was based on direct field analysis using a portable GC, the second was based on trapping organics on a charcoal tube adsorbent followed by GC analysis in the laboratory, and the third method was based on SUMMA canister sampling followed by GC–mass spectrometric (GC–MS) analysis in the laboratory. One goal of this study was to verify the accuracy and precision of portable GC analysis by comparing its performance directly against two other well-established techniques. A second objective was to identify unique advantages of portable GC analysis, such as its ability to define spatial and temporal variability of BTEX concentrations in ambient air.

Experimental

Portable GC analyses were performed on an HNU model 311 instrument (HNU Systems, Newton Highlands, MA) equipped with a gas sampling valve and a photoionization detector (PID). The separation was performed on a 5-ft × 1/8-in. stainless steel column packed with 20% OV-275 on 80/100 mesh Chromosorb PAW (Alltech Associates, Deerfield, IL). The column temperature was 100°C. Nitrogen was employed as the carrier gas at a flow rate of 25 mL/min. A 0.5-mL sample volume was injected. Air samples were initially drawn into a tedlar bag (1L, model 232-01, SKC, Eighty four, PA) and then injected into the instrument. Instrument performance was monitored by periodically analyzing a calibration check sample. The GC was recalibrated whenever the calibration check sample deviated by more than 15% from expected values. A certified gas blend containing 10 ppmv/component benzene, toluene, ethylbenzene, and xylenes was obtained from Scott Speciality Gases (Plumsteadville, PA). This blend was used for instrument calibration and as the calibration check sample. The portable GC instrument was not rated as intrinsically safe and was operated

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Figure 1. Chromatogram of the aromatic calibration standard. See text for experimental conditions.

at a site outside the battery limits of the unit. This was typically an instrument control room. Tedlar bag samples were transported immediately to the instrument, and the sample injection was typically performed within 5 min of sampling.

Charcoal tube sampling was performed by drawing 100 mL/min of air through an SKC charcoal tube (70 mm × 6-mm o.d., 50–100 mg charcoal) for a 30–45-min period. The sampling pumps were calibrated before and after daily sampling, and the calculated sample volumes were corrected for any drift in the pump sampling rate. Three charcoal tube sampling points were set up at each sampling site, which was typically a 100–300-m alley within a process unit. One tube was positioned at the center of the sampling site, and the other two were placed halfway between the midpoint and the end of the linear sampling path. These samples provided information on the spatial distribution of aromatics at the sampling site.

Charcoal tube samples were transported to the laboratory where the charcoal was transferred to a vial, desorbed with CS_2 (2 mL), and analyzed by GC for aromatics (benzene; toluene; ethylbenzene; and m-, p-, and o-xylene). The CS_2 extracts were analyzed on a Hewlett-Packard 5890 GC (Hewlett-Packard, Palo Alto, CA) equipped with a split–splitless injector and a flame-ionization detector (FID). The 15-m × 0.25-mm-i.d. column contained a 0.25-μm film of Supelco Wax (Supelco, Bellefonte, PA). The column temperature was 60°C isothermal, and the column head pressure was 15 psi. A 1-μL injection volume was employed. Total analysis time was less than 5 min. Figure 1 shows a typical chromatogram obtained on a calibration standard.

SUMMA canisters and Veriflow restrictors were obtained from Rasmussen Consulting (Hillsboro, OR). The canisters were certified to contain less than 1 ppbv total organics and were shipped to the field with a vacuum of 30 in. Hg. The Veriflow restrictors were connected to the evacuated canisters to form a static field sampler. The sample flow rate through the Veriflow restrictor was set at 70 mL/min. The canister air samples were collected by walking the static sampler assembly through a path along a line defined by the charcoal tube samplers. The sampling distance was approximately 50% beyond that of the charcoal tubes. These samples thus represented the

time-averaged concentration of aromatic compounds across a distance of 100–300 m. Canister samples were collected for 30–45 min, which corresponded to a sample volume of 2–3 L of air.

The canister samples were analyzed on an Entech 2000 concentrator (Entech Instruments, Simi Valley, CA) and a Hewlett-Packard GC–MS system. The latter comprised a 5890 GC coupled to a 5972 quadrupole MS. The Entech concentrator was operated in a three-stage "microscale purge and trap" mode, which was employed to concentrate organics and eliminate the water and carbon dioxide in the air sample prior to GC–MS analysis. The level of sample concentration gained in the "microscale purge and trap mode" allowed low ppb detection limits to be achieved for volatile organic compounds (VOCs) when quantitating with the MS in the scan mode. The concentrator glass bead trap was held at –185°C, the Tenax TA trap was at –5°C, and the megabore fused-silica tubing focusing trap was at –196°C. The focusing trap was rapidly heated to 100°C to transfer organics to the GC–MS for analysis. The GC column used for the general VOC analysis was a 30-m × 0.32-mm-i.d. (1.5-μm film thickness) DB-1 (J&W Scientific, Folsom, CA). The temperature program was 50°C for 4 min followed by an increase of 20°C/min to 220°C. m-Xylene and p-xylene coeluted on this column. A 30-m × 0.32-mm-i.d. (0.5-μm film thickness) DB-Wax column (J&W Scientific) was used to separate the xylene isomers with a temperature program starting at 50°C for 4 min increasing at 10°C/min to 200°C.

Results and Discussion

An HNU portable GC equipped with a PID (10.2 eV) was selected for this study. Although this instrument may be used with megabore capillary columns, a packed column was used for this study to achieve the separation of aromatic compounds from hydrocarbons of similar boiling points based primarily on stationary phase selectivity rather than column efficiency. The column selected for this study was a packed column containing a polar stationary phase (OV-275) that exhibits high selectivity for the separation of benzene from nonaromatic hydrocarbons of similar boiling points that are likely to be found in petrochemical process areas. The packed column is also more rugged and less prone to breakage in the small oven of the instrument than a fused-silica column. Figure 2 illustrates the separation of benzene in a sample of gasoline vapor. The concentration of benzene in the gasoline was approximately 0.6% (v/v).

Figure 3 shows a typical calibration curve obtained with the HNU portable GC for benzene over the range of 50–600 ppbv. Each point represents the average of three data points. The curve was linear but had a non-zero intercept. From these data, we estimated a detection limit (three times the standard devia-

tion of the blank) of approximately 100 ppbv for benzene. Similar detection limits were found for other aromatic compounds.

In Table I, the detection limits of the portable GC are compared with those of the two reference methods. Detection limits for charcoal tubes varied because of differences in sampling times. The highest detection limits were found for the portable GC. Detection limits for charcoal tubes were 2–5 times lower than those obtained by the portable GC. The lowest detection limits were obtained with the SUMMA canisters. These were approximately 100 times lower than those obtained by the portable GC.
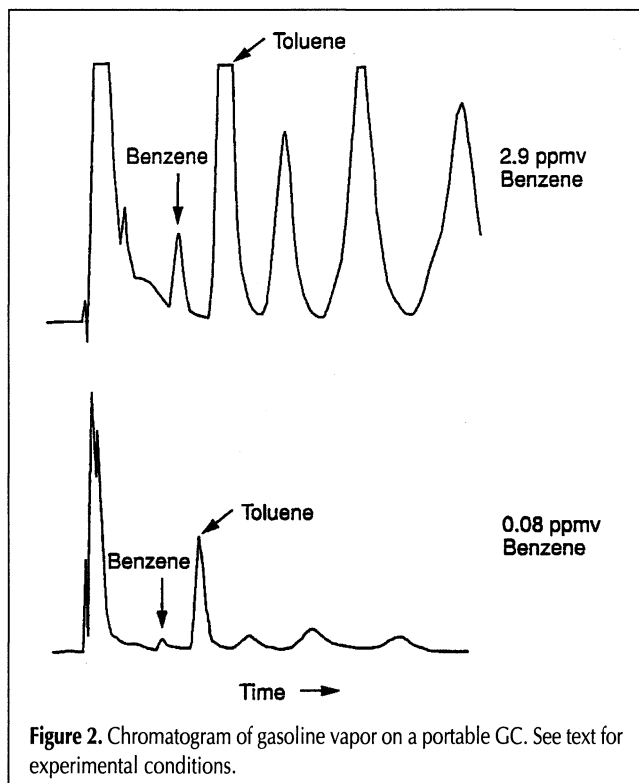

Figure 2. Chromatogram of gasoline vapor on a portable GC. See text for experimental conditions.
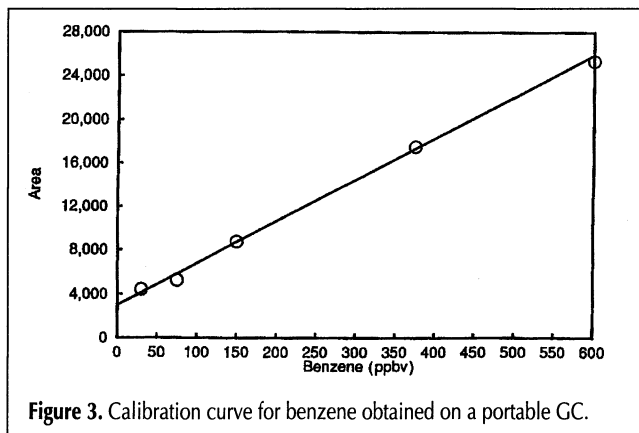

Figure 3. Calibration curve for benzene obtained on a portable GC.

Table I. Comparison of Technique Detection Limits for BTEX

Technique	BTEX detection limit (ppbv)
Portable GC (HNU 311 GC–PID)	100
Charcoal tube/GC–FID	20–80
SUMMA canister/GC–MS	1

Table II contains a summary of calibration check data for the portable GC. The instrument was calibrated at the start of each day, and the calibration was checked three to five times daily. In all cases, the initial calibration was found to be valid, and it was not necessary to recalibrate the instrument. For the 11 measurements performed over the three days of the study, the variability in component concentrations, as measured by the relative standard deviation, was consistent for all components and averaged 6.4%. Recoveries for all components averaged 96%. The recovery for toluene was somewhat lower than those for the other compounds.

Table III contains a summary of data from eight different sampling sites. In all cases, the portable GC results were compared to charcoal tube samples and a composite SUMMA canister sample. Results are reported for benzene; toluene; a sum of ethylbenzene, p-xylene, and m-xylene; and o-xylene. The ethylbenzene, p-xylene, and m-xylene components were summed because this group was not well-resolved by the portable GC analysis. In the table, the portable GC and charcoal tube results that are listed next to each other were obtained at adjacent locations. Individual portable GC analyses without a companion charcoal tube sample generally represent an unplanned analysis performed to investigate an odor or suspected localized fugitive emission.

The portable GC analyses provided point source measurements obtained over a short time period (1–2 min for filling the tedlar bag), thereby providing a "snapshot" of local conditions. The portable GC sampling locations were typically obtained at locations adjacent to the charcoal tube samplers or at specific suspected "hot spots" within the sampling area. Variations in portable GC analyses within a given sampling site indicated both temporal and spatial variations in the concentration of the aromatic compounds. Charcoal tube samples were time-averaged samples at discreet locations within the sampling site. Variations in charcoal tube samples within a given sampling site indicate spatial variations in aromatic concentrations over the time period of the sampling, typically 30–45 min. Differences between portable GC analyses and charcoal tube samples from the same location were indicative of temporal variations in aromatic concentrations. The SUMMA canister sample represented both a time- and spatially-averaged sample over a 30–45-min period, a time similar to that employed for the charcoal tube sampling. The aromatic concentrations measured by the SUMMA canister sampling technique were similar to a path-averaged concentration obtained with open-path infrared measurements.

At site 1, neither the portable GC nor the charcoal tubes were able to detect benzene or toluene. SUMMA canister results confirmed these concentrations were below the detection limits for these methods. However, detectable concentrations of C_8 aromatics (ethylbenzene, p-xylene, and m-xylene) were observed at site 1. The variation among the three charcoal tube samples and corresponding portable GC analyses indicated distinct spacial variations in C_8 aromatic concentrations. A single portable GC analysis at a suspected "hot spot" confirmed the presence of localized high concentrations and provided further evidence for the spacial distribution of ambient C_8 aromatic concentrations at this site. This sampling

Table II. Portable GC Calibration Check Sample Analyses

		Recovery (%)			
Day	Check no.	Benzene	Toluene	Ethylbenzene, m-xylene, & p-xylene	o-Xylene
1	1	86.0	79.0	85.0	80.0
1	2	100.0	88.0	100.0	90.0
2	1	106.5	99.1	104.7	97.1
2	2	99.2	92.8	99.1	95.2
2	3	94.9	84.2	95.3	95.2
2	4	92.8	87.4	93.8	90.5
3	1	107.6	97.0	106.2	103.8
3	2	101.3	92.8	101.9	98.1
3	3	102.3	94.9	102.8	100.0
3	4	97.0	90.6	95.0	95.2
3	5	96.0	89.6	97.5	96.2
Average recovery (%)		98.5	90.5	98.3	94.7
RSD (%)		6.3	6.4	6.1	6.6

Table III. Comparison of BTEX Data for Several Sampling Sites

Site	Benzene (ppbv) P*	C*	S*	Toluene (ppbv) P*	C*	S*	Ethylbenzene, m-xylene, & p-xylene (ppbv) P*	C*	S*	o-Xylene (ppbv) P*	C*	S*
1	< 100	< 45		< 100	< 45		< 100	< 45		< 100	< 45	
	†	< 45	16	†	< 45	40	†	100	410	†	< 50	120
	< 100	< 45		< 100	< 45		400	272		< 100	45	
	< 100			< 100			2400			500		
2	< 100	< 20		< 100	< 20		< 100	< 20		< 100	< 20	
	< 100	< 20	5	< 100	< 20	15	< 100	43	70	< 100	< 20	10
	†	< 20		†	< 20		†	89		†	22	
3	< 100	62		< 100	< 20		< 100	< 20		< 100	< 20	
	200	< 60	23	100	133	85	10200	3400	1150	2900	900	350
	< 100	< 60		< 100	83		2400	1700		300	500	
4	< 100	108		< 100	42		100	125		< 100	470	
	< 100	124	190	< 100	< 40	36	< 100	< 40	32	< 100	< 40	10
	200	113		< 100	43		2400‡	< 40		300‡	< 40	
5	400	364		< 100	45		< 100	< 35		< 100	< 35	
	400	435	240	< 100	43	100	< 100	< 35	49	< 100	< 35	15
	< 100	100		< 100	38		< 100	< 35		< 100	< 35	
6	100	200		< 100	48		< 100	< 45		< 100	< 45	
	400	236	120	< 100	< 45	58	< 100	< 45	49	< 100	< 45	10
	< 100	63		< 100	63		< 100	< 45		< 100	< 45	
	400			< 100			< 100			< 100		
7	300	450		< 100	150		< 100	150		< 100	50	
	200	230	150	< 100	38	80	< 100	38	60	< 100	< 30	20
	200	278		< 100	56		< 100	56		< 100	< 30	
8	< 100	118		< 100	182		< 100	45		< 100	< 40	
	100	67	135	100	800	130	< 100	67	80	< 100	< 40	25
	< 100	77		< 100	77		< 100	< 40		< 100	< 40	

* P = portable GC–PID, C = charcoal tube GC–FID, S = SUMMA canister GC–MS.
† Not sampled.
‡ Probable interference with portable GC measurement compared with charcoal tube GC analysis.

path passed directly through the operating unit and spanned a number of different types of process equipment. Thus spacial variations in aromatics were anticipated. Detailed information on the spacial distribution of aromatics within such units has proven useful to industrial hygiene and safety staff attempting to minimize exposure levels and improve work practices. The canister sample gave a time- and spatially-averaged value consistent with the higher charcoal tube sample.

Sample site 2 demonstrated extremely low levels of all aromatics. All three methods confirmed this result and were remarkably consistent. There was some evidence for a slight spatial distribution in the C_8 aromatics, but levels were extremely low. Benzene concentrations were 5 ppbv and could only be detected by canister sampling. This sampling site was located on the outer edge of the operating unit.

Sample site 3 was located in the areas of the operating unit expected to contain the highest concentrations of aromatics. As at the other sites, benzene and toluene levels were below or near detection limits for the portable GC and charcoal tube methods. Charcoal tube values for toluene averaged 113 ppbv with a standard deviation of 23 ppbv across the three sampling points at this site. Portable GC results also indicated toluene levels near 100 ppbv. Higher levels of C_8 aromatics were detected across this site. These were typically in the range of 1–2 ppmv but rose in one case to 10 ppmv. The large difference between the charcoal tube and portable GC results for the second set of samples was most likely indicative of temporal variations in C_8 aromatic concentrations over the 30-min sampling period. The canister value was lower than the portable GC and charcoal tube samples. This most likely arose because ambient concentrations at the extremes of the sampling path were lower that those near the charcoal tube samplers. Figure 4 shows a chromatogram obtained from a canister sample taken at sampling site 3.

The remaining five sample sites were all located within the same unit. Benzene was detected at all sampling points by charcoal tube analysis. However, the
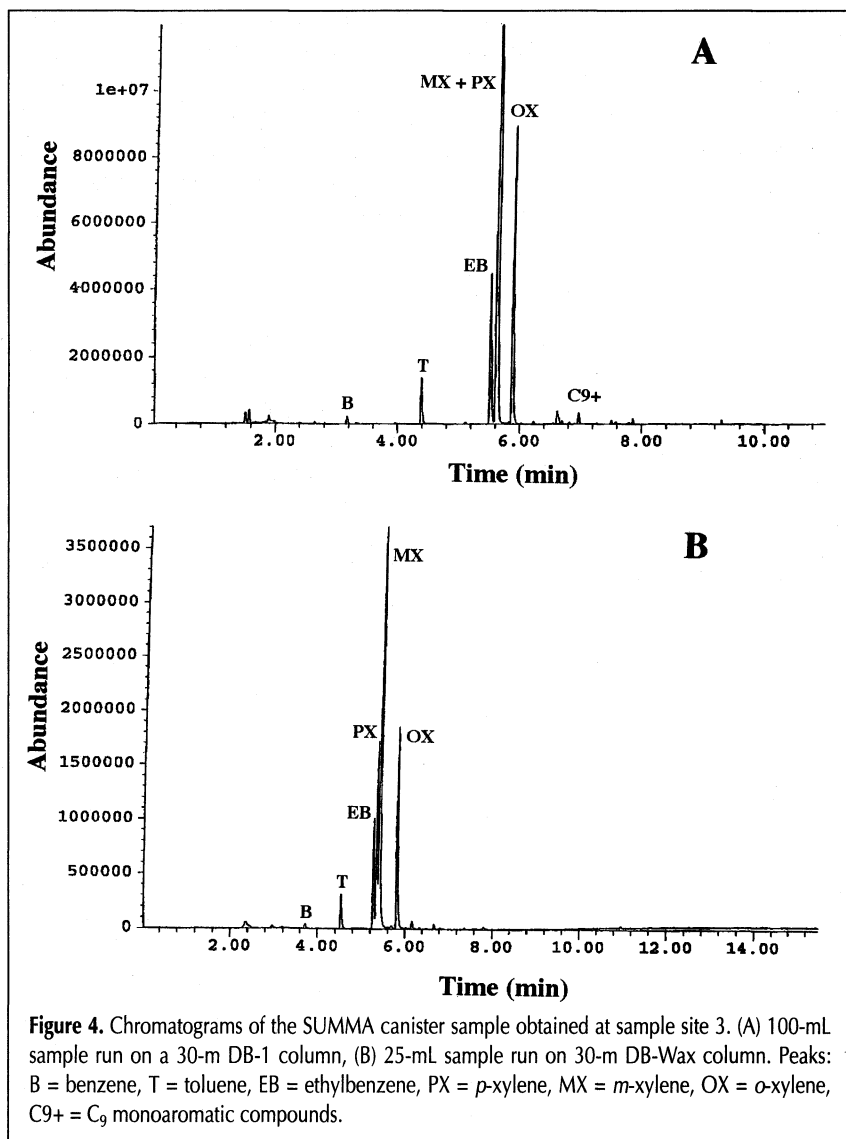
Figure 4. Chromatograms of the SUMMA canister sample obtained at sample site 3. (A) 100-mL sample run on a 30-m DB-1 column, (B) 25-mL sample run on 30-m DB-Wax column. Peaks: B = benzene, T = toluene, EB = ethylbenzene, PX = p-xylene, MX = m-xylene, OX = o-xylene, C9+ = C_9 monoaromatic compounds.

of the canister benzene results was 50 ppbv. Thus there was reasonable agreement between the benzene measurements, and furthermore, there was little variation in ambient benzene concentrations throughout this site. Concentrations of other aromatics were below the detection limits (less than 100 ppbv) of the portable GC at this unit. Canister results for toluene averaged 80 ppbv, ethylbenzene–p-xylene–m-xylene averaged 50 ppbv, and o-xylene averaged 15 ppbv.

Conclusion

Three different GC techniques were applied to determine the concentration of aromatic compounds in air within operating units at several petrochemical complexes. The data indicate that a portable GC provided data that was consistent with results obtained by charcoal tube adsorption and SUMMA canister sampling. The major limitation of the portable GC approach employed in this study was its higher detection limits compared with the other methods. A significant advantage of the portable GC is that it is possible to obtain significantly more samples at a given site, thereby providing the opportunity to map out spatial and temporal distributions of aromatic compounds. Such information may then be employed to develop strategies to limit worker exposure, identify possible emission sources, and trigger maintenance activities.

detected concentrations were extremely low (less than 1 ppmv). Once again there was some evidence for spatial distributions of benzene concentrations, but in general, benzene levels showed less variation across this unit compared with the C_8 aromatic concentrations at the other sites. The level measured by charcoal adsorption was often near to or below the detection limit of the portable GC. Agreement between these two analyses was generally excellent. At sampling site 7, for example, the average benzene concentration by portable GC was 230 ppbv, whereas that for the charcoal tubes was 320 ppbv. Given the low concentrations, these data indicated that the portable GC approach was able to provide results that showed little bias compared with the charcoal tube and canister approaches.

Charcoal tube analyses gave an average benzene concentration of 200 ppbv across the five sampling sites at this unit (sites 4–8) with a standard deviation of 130 ppbv. Canister results provided additional confirmation of the presence of benzene at concentrations below parts per million. Benzene concentrations ranged from 120 to 240 ppbv in the five canister samples taken at this unit with an average value of 170 ppbv. The 170 ppbv value compared well with the 200 ppbv value obtained from the charcoal tubes. The standard deviation

References

1. R.E. Berkley, M. Miller, J.C. Chang, et al. Evaluation of portable gas chromatographs. Proceedings of the *1993 U.S. EPA/A&WMA International Symposium on Field Screening Methods for Hazardous Wastes and Toxic Chemicals.* Las Vegas, NV, 1993, Air and Waste Management Association, Volume 2, VIP-33, 1993, p. 682.
2. P.A. David and R.E. Pauls. Applications of portable GC for air and water monitoring. *Process Control and Quality* 5: 151–58 (1993).
3. S.P. Levine and G.M. Russwurm. FTIR optical remote sensing for monitoring airborne gas and vapor contaminants. *Trends Anal. Chem.* 13(7): 258 (1994).
4. M.L. McKelvey, T.R. Britt, B.L. Davis, J.K. Gillie, L.A. Lentz, A. Leugers, R.A. Nyquist, and C.L. Putzig. Infrared spectroscopy. *Anal. Chem.* 68: 93R–160R (1996).
5. P.A. David and R.E. Pauls. Determination of BTX in air by handheld gas chromatography. Proceedings of the *1995 U.S. EPA/A&WMA International Symposium on Field Screening Methods for Hazardous Wastes and Toxic Chemicals.* Las Vegas, NV, 1995 Air and Waste Management Association,VIP-47, Volume 1, 1995, p. 221.