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ON-SITE SCREENING FOR BENZENE IN COMPLEX ENVIRONMENTS

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A technique is described for on-site screening of workplace atmospheres for benzene in the presence of many potentially interfering substances. The technique allows benzene monitoring with reasonable specificity at the part per million (ppm) level in confined spaces. A commercially available portable gas chromatograph (GC), shown in the laboratory to be capable of resolving benzene from a complex mixture of hydrocarbons, was compared in the field with other portable GCs, sorbent tube samples, and detector tubes. During three field evaluations samples were collected in Tedlar© bags, which allowed replicate, on-site analyses by up to three portable gas chromatographs and three types of detector tubes. Additionally, replicate samples were collected from each bag onto charcoal tubes for subsequent laboratory analysis by capillary column flame ionization gas chromatography and by gas chromatography/mass spectrometry. The portable GCs resolved samples to the extent that an integratable response with the retention time of benzene was seen. In some samples this response was not due solely to the presence of benzene, but such instances would overestimate the concentration and provide a more conservative result. The portable GCs had a total analysis time of less than 10 minutes and detected concentrations of benzene below the Occupational Safety and Health Administration's permissible exposure limit of 1 ppm (in most samples, below 0.1 ppm, although the limit of quantitation was matrix dependent). While benzene concentration measurements using detector tubes were less precise, they agreed in almost every instance with the other techniques regarding whether the space was within the 1 ppm "safe for entry" concentration.

Workers in shipyard and maritime employment, covered by Occupational Safety and Health Administration (OSHA) standards 29 CFR Parts 1910,(1) 1915,(2) and 1917,(3) potentially are exposed to a variety of hazards, including benzene, during cleaning and repair of confined spaces that had contained hazardous substances. To prevent this exposure, these workplaces must be certified as safe by an industrial hygienist or marine chemist.(4) Since both the current general industry(5) and proposed maritime(6) OSHA permissible exposure limit (PEL) for benzene are 1 ppm by volume for a time-weighted average and 5 ppm for a 15 minute short-term exposure limit, the ability to detect benzene with reasonable specificity at this concentration is necessary for such certification. (The National Institute for Occupational Safety and Health [NIOSH] recommended exposure limit [REL] is 0.1 ppm, and the American Conference of Governmental Industrial Hygienists has proposed a change of their threshold limit value© [TLV] to 0.1 ppm.(7,8)) Currently, the most common technique selected for monitoring benzene in these conditions uses detector tubes. Depending on the type of tube selected, however, this technique may lack either the sensitivity to detect benzene at the required concentration (particularly with respect to the REL or TLV criteria), or the specificity to isolate benzene in a complex mixture of hydrocarbons, or both.

For these reasons, an investigation of available techniques for estimating benzene concentrations in marine vessels was initiated. Prior work by NIOSH investigators with benzene analysis by portable gas chromatography (GC) using a photoionization detector (PID) resulted in Method 3700 in the NIOSH *Manual of Analytical Methods* (NMAM).(9) This method was evaluated down to 1 ppm with an estimated limit of detection of 0.05 ppm. The technique provides a quick response, and instrumentation is commercially available. But while Method 3700 indicates that the technique has the sensitivity required for the purposes described, that method also states:

> A limitation in the use of this type of portable GC (e.g., packed column, room temperature

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Mention of company names or products does not constitute endorsement by the Centers for Disease Control and Prevention. This project was funded in part by the U. S. Coast Guard (MIPR No. Z51100-2-E00528).

> isothermal) is the limited ability to separate the analyte from any interferences present. . . . Its ability to separate the benzene peak from other contaminants was not evaluated. However, the use of this or any other packed column operated at room temperature to separate complex mixtures is severely limited. Therefore, the application of this method should be confined to relatively uncomplicated atmospheres.

However, the environments in the confined spaces of marine vessels are not "uncomplicated atmospheres." Conversely, an accurate measurement of benzene concentration for these purposes is not necessary in the strictest sense because an estimation of the benzene level in air is acceptable as long as the true concentration is not underestimated. Underestimation could allow workers to enter areas where benzene was, in fact, above the permissible level. Therefore, it was determined that a screening procedure for benzene offering specificity, speed, and few false negatives was acceptable.

A screening procedure is a compromise among confidence in the absolute measurement, speed of the analysis, and simplicity of apparatus. When the proposed chromatographic screen is used, the absence of an instrument response at the retention time for benzene indicates the absence of benzene, assuming all contaminants that would produce a negative interference are absent. The presence of a response may indicate the presence of either benzene or a compound with a similar retention time. While such a response, in some cases, overestimates the level of benzene, thereby compromising the validity of the absolute measurement, it is an error on the side of worker safety.

One goal of this project was to eliminate the interferences from the most common environmental co-contaminants (toluene and xylene), thereby developing a screening procedure that would produce a minimum number of false positives for the detection of benzene. (The potential for negative interference is minimal, since the gases capable of causing this phenomenon elute unretained by the chromatographic columns used in this study.) A second goal was the ability to measure accurately below 1 ppm (the OSHA PEL) and below 0.1 ppm (the NIOSH REL). This was thought to be achievable based on laboratory investigations.

Prior to the field work described in this article, this method was evaluated in the laboratory using a Photovac 10S GC. The information obtained there constitutes the background data for the revision of the NMAM analytical method(10) and is compiled in a separate report on this work.(11) In the laboratory it was shown that the GC could detect benzene concentrations in clean air to 0.02 ppm; could separate benzene from toluene and xylenes over a temperature range from 1 to 42°C using an ambient temperature instrument; produced peak area and retention times (at constant temperature) with variations of 4.7% and 0.5%, respectively; could integrate peaks with the retention time of benzene in samples of gasoline and crude and diesel oil vapors; and could achieve analysis times of less than 10 minutes. The laboratory work also indicated that samples collected in Tedlar© bags showed a decrease in benzene concentration of up to 35% after 24 hours for some samples, although for the short periods of use required by this study (< 2 hours) this was acceptable.

This article describes three field tests conducted using the equipment and methodology tested in the laboratory. Since diversity of samples was an important consideration, two field tests were conducted on the Gulf Coast and one on the West Coast to maximize the variety of cargoes and types of vessels encountered. In addition to the GC used in the laboratory study, two additional chromatographic units were tested. Also, detector tubes were used to analyze field samples for comparison with other measurements because this is the most commonly selected technique for this determination. Finally, charcoal sorbent tube samples were collected for all field samples for subsequent laboratory analysis to provide an additional measurement of benzene for comparison.

EXPERIMENTAL DESIGN AND MATERIALS

Field tests were conducted in conjunction with routine inspections of marine vessels to facilitate collection of samples that would be typical of real-world conditions. The NIOSH investigators accompanied certified marine chemists (CMCs) who conducted the monitoring on these vessels in the normal course of their work and obtained bag samples from compartments that the CMC would ordinarily test for benzene. In some instances the CMC or someone on site made measurements of lower explosive limit (LEL) or total hydrocarbons, and these data are included as comments (see Table I) without editing. No determination of personal exposures to benzene or other toxins was conducted.

During all three field studies, samples were collected by pumping air at approximately 4 L/min into a 40 L Tedlar bag. (This large sample volume was not required for the GC analysis, but was needed to accommodate the additional testing being done in this study.) When barges were sampled, the sample was drawn through a length of tubing lowered to approximately 2 m (6 ft) above the bottom of the hold of the barge. When ships were sampled, the pump and bag were taken into the hold of the tanker and the sample was collected from an easily accessible location at least halfway down in the hold. Measurements were made of ambient temperature, relative humidity, and wind speed and direction. Information on cleaning and ventilating procedures and previous cargoes was collected. Following collection, bag samples were taken from the vessel to a nearby location where GCs and other equipment were arranged to facilitate quick analysis. All analyses and collection of charcoal tube samples were usually completed within 2 hours of collection of bag sample.

While the development of a screening procedure in the laboratory centered around a portable GC/PID, the opportunity arose to evaluate other portable GCs in the field. Instruments investigated were as follows.

(1) The Photovac 10S series portable gas chromatograph (Photovac International, Inc., Deer Park, N.Y.) with a photoionization detector. This unit was configured with the capillary column option, listed by the manufacturer as CPSil 5 CB (length unspecified), and operated at 30°C

TABLE I. Description of Samples Collected During Field Studies, Grouped by Last Cargo(s) of the Vessel from which They were Taken

Sample	*Location*	*Vessel*	*Last Cargo(s)*	*Comments*
D1	Gulf Coast	barge	diesel	
D2	Gulf Coast	barge	diesel	tank shoveled previous night
D3	Gulf Coast	barge	diesel	tank dry, vented overnight
D4	West Coast	barge	diesel, gasoline	2–3% LEL in tank
D5	West Coast	barge	diesel, gasoline	3–4% LEL in tank
D6	West Coast	barge	diesel, gasoline	
D7	West Coast	barge	diesel, gasoline	<1% LEL in tank
D8	West Coast	barge	diesel, gasoline	after tank cleaning
D9	West Coast	barge	diesel, gasoline	strong ventilation flow
D10	Gulf Coast	barge	diesel	1–2% LEL
C1	West Coast	oil tanker	cargo washings	after much cleaning
C2	West Coast	oil tanker	Alaskan crude	after much cleaning
C3	West Coast	oil tanker	gas oil, Hondo crude	tank vented
C4	West Coast	oil tanker	slop tank	tank dry
C5	Gulf Coast	barge	light crude	0–1% LEL
S1	Gulf Coast	barge	#6 oil/quench oil	after tank wash, no ventilation
S2	Gulf Coast	barge	#6 oil/quench oil	late in cleaning cycle
S3	Gulf Coast	barge	#6 oil	<1% LEL, being ventilated
S4	Gulf Coast	barge	#6 oil	1–2% LEL
S5	Gulf Coast	barge	#6 oil	1% LEL
J1	West Coast	aircraft carrier	JP-5	100 ppm total hydrocarbons
J2	West Coast	aircraft carrier	JP-5	50–75 ppm total hydrocarbons
J3	West Coast	aircraft carrier	JP-5	40–50 ppm total hydrocarbons
H1	Gulf Coast	barge	unknown	
H2	Gulf Coast	barge	unknown	tank almost ready for entry
H3	Gulf Coast	barge	unknown	tank hand washed previous night
H4	Gulf Coast	barge	unknown	late in cleaning cycle
H5	Gulf Coast	barge	neutral oil	had been hot water washed
H6	Gulf Coast	barge	raformate	had been hot water washed
H7	Gulf Coast	barge	aromatic solvents	
H8	Gulf Coast	barge	versol	
G1	Gulf Coast	barge	gasoline/gasoline/diesel	<1% LEL
G2	Gulf Coast	barge	gasoline	1–2% LEL, unvented overnight
X1	Gulf Coast	barge	benzene	had been steam cleaned
X2	Gulf Coast	barge	cumene	

with a carrier gas (air) flow rate of 15 mL/min. This column option became available subsequent to the laboratory studies and provided a more stable retention time than the ambient system evaluated there. It had the short analysis time and the separation capabilities required. These units weighed approximately 12 kg (26 lb), were 46 cm (18 inches) wide by 16 cm (6 inches) high by 34 cm (13 inches) deep, and contained internal rechargeable batteries for power. Air carrier gas was from an internal cylinder. These GCs accepted either packed or isothermal macrobore capillary columns leading to a photoionization detector with a 10.6 eV lamp. Instrument operation and data output were through a dedicated microprocessor.

(2) The Scentoscreen portable gas chromatograph with an argon ionization detector (AID) manufactured by Sentex Systems (Ridgefield, N.J.). This unit weighed approximately 11.8 kg (26 lb), was 34 cm (13.5 inches) wide by 16.5 cm (6.5 inches) high by 49.5 cm (19.5 inches) deep, and contained internal rechargeable batteries for power. It used argon carrier gas from either an internal or external cylinder at 26 psi (flow rate was not measured). Sample intake was via an internal pump onto a thermally desorbed preconcentrator. It contained a 0.32 cm (1/8 inch) by 1.8 m (6 ft) isothermal packed column in front of the argon ionization detector, both operating at 50°C. Instrument operation and data output were through a laptop computer. Like the PID unit, the AID was commercially available in the configuration used in this work and was expected to have the ability to detect small masses of analyte.

(3) The model MSI-301B benzene vapor monitor (BVM) by Microsensor Systems, Inc., (Bowling Green, Ky.) described by its manufacturer as a "gas chromatograph [with a proprietary] solid-state detector."(12,13) This instrument was being used by marine chemists who assisted in the West Coast study and who offered to analyze field samples collected during that evaluation. It weighed approximately 5.4 kg (12 lb), was 33 cm (13 inches) wide by 9 cm (3.5 inches) high by 37 cm (14.5 inches) deep, and used line current or optional internal rechargeable batteries for power. It used scrubbed

ambient air for carrier gas (no compressed gas cylinder is necessary for carrier supply). Sample intake was via an internal pump onto a thermally desorbed concentrator. The BVM contained a 0.32 cm (1/8 inch) by 0.9 m (3 ft) isothermal packed column (unspecified). Instrument operation was controlled by a front panel keyboard, and data was displayed on a two-line, 24-character dot matrix liquid crystal display or an optional printer.

The Photovac and Sentex GCs were operated according to manufacturers' instructions after on-site calibration using a commercial 1-ppm benzene in air calibration gas (Scott Specialty Gases, Troy, Mich.) that had been analyzed to confirm its concentration. The Microsensor System benzene vapor monitor was calibrated and operated by the assisting CMC using his calibration gas, which was in turn verified against the 1-ppm standard mentioned above.

The bag samples were also analyzed by three detector tubes in addition to the portable GCs. These detector tubes included the Draeger 0.5/a, 2/a, and 0.5/c benzene tubes (National Draeger, Inc., Pittsburgh, Pa.). Tests by Reinhart, et al.(14) indicate that the Draeger tubes are at least as good as the Sensidyne and Kitagawa brand tubes at lower levels of contaminant. According to the manufacturer, the Draeger 0.5/a tube can detect benzene at a concentration of 0.5 ppm, but is not specific for benzene in the presence of other aromatic hydrocarbons.(15) The Draeger 2/a tube has a precleanse layer to absorb interfering components, but has a limit of detection of 2 ppm.(16) A Draeger 0.5/c tube that entered production during the study and therefore was not available for the first field test, was designed to have a precleanse layer, as with the 2/a tube, but with the sensitivity to 0.5 ppm benzene of the 0.5/a tube.(17) An Accuro 2000 automated pump system (National Draeger, Inc.), precalibrated using the wet film flow meter, was used to facilitate detector tube sampling from bags.

Replicate analyses of bag samples were conducted by portable GCs and detector tubes. Charcoal tube samples from the bags also were obtained, and these were returned to the laboratory for analysis by capillary column programmed temperature flame ionization detector gas chromatography (GC/FID). The charcoal tube samples were collected and analyzed as described in the NMAM,(18) modified by using a 30 m × 0.32 mm capillary column coated with 0.5 μm of DB-WAX. Sampling was at a flow rate of 200 cc/min for 15 to 30 minutes using sampling pumps (SKC, Inc., Eighty Four, Pa.) pre- and post-calibrated using a wet film flow meter (Gilian Instrument Co., Wayne, N.J.).

Subsequent to the first field study, GC/FID analyses of the charcoal tube samples were noted to be significantly higher than the results from the portable GCs. Therefore, a second analysis of selected charcoal tube samples collected during the second and third studies was requested. This analysis was done using a mass spectrometer (MS) detector instead of the flame ionization detector, since quantitation by GC/MS using extracted ions (characteristic of benzene and not aliphatic hydrocarbons) is much more selective than GC/FID. The chromatographic column used in the GC/MS instrument was a 30 m × 0.32 mm open tubular column with 1.0 μm DB-5 coating. Integration of the peak with mass-to-charge ratio 78 was used to quantitate benzene. Due to the complicated and costly nature of this analysis, one charcoal tube from each bag sample was selected for GC/MS analysis, and no information on variance was available.

Approximately 12 bag samples were collected during each field study. For the first study 4 replicate analyses of each bag by each portable GC, plus 4 replicate charcoal tube samples, plus 2 to 4 replicates of the 0.5/a and 2/a tubes provided a total of 16 to 20 analyses per bag. For the second study 4 replicate analyses of each bag by each portable GC, plus 2 replicates by the benzene monitor, plus 4 replicate charcoal tube samples, plus 2 to 4 replicates of the 0.5/a, 2/a, and 0.5/c tubes provided a total of 20 to 26 analyses per bag. For the third field study 4 replicate analyses of each bag with the PID, plus 4 replicates using the AID instrument, plus 3 replicate charcoal tube samples, plus 2 to 4 replicates with the 0.5/c tubes provided 13 to 15 analyses per bag.

For each bag sample collected in the field, the mean, range, and coefficient of variation for each analytical technique were calculated when possible. The data obtained using the various field analytical techniques was compared with each other and with data obtained from charcoal tube analyses.

RESULTS

The first field study was conducted on the Gulf Coast (near New Orleans, La.) in August 1992. Ambient temperatures ranged from 24 to 34°C (76 to 93°F) and relative humidity from 42 to 95%. The second field study was conducted on the northern West Coast (near Portland, Ore., and Seattle, Wash.) during October 1992, with temperature and humidity ranges from 8 to 23°C (47 to 74°F) and 45 to 82%, respectively. The third field study was again on the Gulf Coast (New Orleans and Baton Rouge, La.) during May 1993, with temperature and humidity ranges from 20 to 33°C (68 to 92°F) and 32 to 74%, respectively.

Table I describes the samples collected during these studies, giving the location (Gulf versus West Coast), vessel type (barge, tanker, or carrier), the last cargo(s) if known, and brief comments. The samples were divided into seven groups, based on the last cargo(s) of the vessel from which they were taken. Those groups and their respective samples are as follows.

- Diesel/gas—Samples D1 through D10 were taken from eight different holds on three barges, the last cargoes of which were diesel oil. For samples D4 through D9, taken from Barge B, the diesel cargo was preceded by gasoline.
- Crude oil—Samples C1 to C5 were taken from five different holds on three oil tankers.
- Six oil—Samples S1 to S5 were taken from four different holds on three barges, the last three cargoes of all barges being #6 oil.
- JP-5—Samples J1 through J3 were taken from three different tanks on an aircraft carrier that had been emptied and ventilated, but had last contained JP-5 fuel.
- Hydrocarbons—Samples H1 to H4 were taken from two different holds on the same barge, the last cargoes of

which were hydrocarbon mixtures of uncertain composition. Samples H5 to H8 were all from different barges whose last cargoes, indicated in Table I, were various hydrocarbon mixtures.

- Gasoline—Samples G1 and G2 were taken from two different barges, located in different shipyards. The most recent cargoes on both barges were gasoline.
- Chemical vessels—Samples X1 and X2 were collected from barges that had been carrying benzene and cumene, respectively. No information was available on the purity, other components, origin, or destination of these materials.

Table II shows the mean benzene concentration in parts per million for each sample by analytical instrument or technique, along with the corresponding coefficient of variation (CV) for that mean, except for the detector tube results and GC/MS analyses. Some measurements made by detector tubes are marked "$>$" (greater than) or "$\gg$" (much greater than) either 10 ppm or 60. Ten ppm is the upper limit of the range of measurements for the 0.5/a and 0.5/c tubes, using the requisite number of pump strokes. Sixty ppm is the upper limit of the range of measurements for the 2/a tubes. When the color was developed using fewer than (or much fewer than) the requisite number of pump strokes, the benzene was estimated to be "greater than" (or "much greater than") either 10 or 60 ppm. One sample (H1) shows a 2/a measurement of > 53 ppm. This is the mean of four measurements made by those tubes, two of which were > 60 ppm and two of which were finite measurements less than 60 ppm. In a few instances the 0.5/c tubes did not detect benzene, and those samples are so indicated on the table. Charcoal tube (GC/FID and GC/MS) measurements reported as "less than" values were calculated from the limit of detection reported by the laboratory doing those analyses and from the air volume sampled. "Less than" values reported for the portable GCs were estimated based on the instrument response to other compounds in the same or a similar matrix. Missing values indicate that the sample was not analyzed by the technique indicated.

In considering the data in Table II, it is important to realize that these benzene measurements are not an indication of the relative amount of benzene within each type of cargo, but rather are related more to the degree to which the vessel or individual hold had been cleaned and/or ventilated prior to sampling. For that reason, and for better visualization, the data were retabulated before plotting to indicate the response of the various analytical techniques for each sample compared to the response of the GC/FID measurement for that sample. The GC/FID measurements were selected for this comparison, since this was the only analytical technique for which all samples were analyzed.

Figures 1 through 6 show those plots of response, relative to GC/FID measurements, for the various cargo types indicated. The data from the 0.5/a and 2/a detector tubes were omitted from the plots because in most instances these measurements were much higher than those of other techniques. In several instances the vertical columns indicating magnitude of response are truncated, with the actual benzene measurement (relative to GC/FID response) indicated above the column, since showing the actual magnitude would force the vertical axes of the plots to be disproportionately high, reducing the effectiveness of the plot.

The high measurements obtained from the 0.5/a and 2/a detector tubes were not unexpected, but rather were predicted because of interferences according to the instructions provided by the manufacturer.(15,16) The measurements were made and the data included in Table II, since it is thought that some inspectors have used these devices to measure benzene in similar situations. These tubes were not used in the third field test, since doing so was considered redundant.

The variation in weather conditions between the Gulf and West Coast studies did not have a noticeable effect on the results. In both locations the analytical instruments that had heated columns were operated isothermally at temperatures 10 to 20°C above ambient. No condensation was noted in bag samples. Detector tubes were always operated within specifications stated by their manufacturer.

DISCUSSION

The most obvious trend throughout all field samples was that the data obtained from detector tube analyses were almost universally higher than any other technique. With the exception of one diesel sample (D7), one #6 oil sample (S5), and the three JP-5 samples where the 0.5/c tube indicated benzene concentrations lower than the charcoal tube measurements, the detector tube measurements indicated higher benzene concentrations than all other techniques. The manufacturer of these devices provides information for cross sensitivities for each type of tube, stating for the 0.5/a tubes that "other aromates . . . are also indicated. Benzene measurement is not possible in such cases."(15) The 2/a and 0.5/c tubes each have a pretube containing an oxidation layer to remove interfering compounds provided their concentrations do not exceed certain levels, ranging from 50 to 1500 ppm. However, this may not have been the case in several of the samples in this study, and the outcome indicates what happens when the pretube capacity is exceeded. There does not appear to be, however, any correlation between measurable LEL values and high detector tube readings.

While the detector tubes read consistently higher than the other techniques, they also were essentially providing a conservative estimate of safety. A marine chemist or industrial hygienist, using detector tubes alone to determine benzene concentration, would not have authorized entry into any vessel considered unsafe by other techniques with the exception of the five charcoal tube measurements mentioned above. The 0.5/a and 2/a versions of the detector tubes in almost all instances indicated conditions as unsafe for entry (i.e., greater than 1 ppm), even when all other measurements indicated otherwise. The 0.5/c tube indicated unsafe entry three times when the AID instrument indicated otherwise (Samples D5, D7, and X1), and once when the GC/MS measurement indicated safe (Sample S5), and in all other situations agreed with other measurements when used to determine entry. The 0.5/c tube data indicate that these tubes provide a conservative measurement of safety with a minimum number of false positive values. It should be noted, however, that the color change in this tube is from white to very light brown and is difficult to detect in good light and almost impossible to see in the dim conditions inside the hold of a tanker.

TABLE II. Mean Benzene Concentration and Variation for Each Sample Analyzed by Various Techniques

	GC/FID		Detector Tube			PID		AID		BVM		
			0.5/a	2/a	0.5/c							
Sample	Mean PPM	CV %	Tube PPM	Tube PPM	Tube PPM	Mean PPM	CV %	Mean PPM	CV %	Mean PPM	CV %	GC/MS PPM
D1	13.54	5.9	>10	>60		10.90	10.0	12.39	4.5			
D2	3.40	3.6	>10	44		0.67	3.2	0.89	37.5			
D3	1.09	7.2	2	28		0.27	45.6	0.19	21.4			
D4	16.45	2.5	>10	≫60	8.3	18.80	5.0	5.13	13.4	9.0	0.2	12.8
D5	16.52	0.7	>10	≫60	≫10	28.30	5.4	0.17	55.9	11.5	8.3	13.4
D6	18.26	2.9	>10	≫60	≫10	19.33	2.8	5.70	8.8	9.9	1.1	13.9
D7	5.29	0.8	>10	≫60	3	3.45	6.3	<0.1	—	1.3	7.2	1.2
D8	8.00	11.1	>10	>60	>10	8.58	4.6	1.56	16.8	19.6	1.3	5.0
D9	3.64	1.0	7.3	>60		1.77	2.7	1.05	(N = 1)	<0.1	—	0.5
D10	<0.05	—			<0.5	0.076	2.7	<0.05				<0.01
C1	0.32	8.3	4.3	17.5	<0.5	0.08	6.0	0.06	2.6	<0.1	—	
C2	<0.14	—	1.5			0.19	0.0	0.02	4.8	<0.1	—	
C3	0.44	2.3	6.3	<2	<0.5	0.04	5.6	0.02	40.1	<0.1	—	0.05
C4	0.27	12.7	2	<2	<0.5	<0.1	—	<0.1	—	<0.1	—	
C5	<0.05	—			<0.5			0.21	103.5			<0.01
S1	57.90	2.3	≫10	≫60		5.26	4.0	0.30	67.6			
S2	1.02	1.9	2			0.36	22.5	0.38	24.4			
S3	0.16	1.5			0.5			0.051	47.7			0.087
S4	0.089	1.3			<0.5	0.19	14.0	0.053	53.7			0.044
S5	1.93	21.3			1.7	1.60	51.2					0.61
J1	4.28	0.8	7.3	46	<0.5	0.05	9.8	0.35	34.0			0.04
J2	2.21	2.0	2.5	23	<0.5	0.02	13.6	<0.1	—			
J3	1.95	1.8	5.7	43	<0.5	0.02	6.8	0.14	44.6			0.03
H1	2.99	3.7	>10	>53		0.74	3.5	2.32	32.6			
H2	3.23	1.3	>10	57		0.83	3.8	1.26	38.6			
H3	4.66	7.9	≫10	>60		2.50	5.3	2.82	72.3			
H4	2.03	1.3	4	35		0.44	7.2	0.69	8.3			
H5	<0.05	—				<0.05	—					<0.01
H6	1.96	9.2			2.3			1.99	6.8			1.3
H7	<0.05	—			<0.5	<0.05	—	<0.05	—			<0.01
H8	0.081	34.3			<0.5	<0.05	—	<0.05	—			0.12
G1	0.045	1.3			<0.5			<0.05	—			0.045
G2	0.049	1.2			<0.5	0.17	0.9	<0.05	—			0.097
X1	56.5	1.2			>10			<0.05	—			86.1
X2	0.49	4.5			0.5	0.43	0.4	0.28	11.6			0.27

The GC/FID analyses were also providing a conservative estimate of safety, although since charcoal tubes must be sent for laboratory analysis, the conditions of the vessel could change between the time the sample was collected and the time the results were available. It was noted that in all of the #6 oil and JP-5 samples, and in most of the other samples, the charcoal tube data (with analysis by GC/FID) were higher than the measurements by other methods (except detector tubes), in some instances by almost two orders of magnitude. From this, it would appear that the capillary column used in the laboratory FID analysis of the charcoal tubes was even less able to resolve the mixtures prior to elution into the flame ionization detector. Identification of coeluents by mass spectroscopy was not possible, since a different column coating (DB-5) was used for the GC/MS than for the GC/FID.

Further consideration led the authors to the possibility of two other mechanisms in the portable instruments that could enhance their specificity for benzene: selectivity due to the detector or, in the AID and BVM units, preconcentration. To study this question, a comparison of detector responses was done in the laboratory, subsequent to the field work, using a dual detector GC (HNu Model 301 with PID and FID). The CPSil5 column from the Photovac portable GC was installed into the laboratory GC, and the output was adjusted so that both detectors responded approximately equally to an aliquot of benzene in clean air. This was achieved by electronically decreasing the sensitivity of the PID by a factor of 40, since the FID is the less sensitive of the two detectors. Gasoline vapor at sufficient concentration to contain approximately 10 ppm benzene was then injected into the GC. The height of a peak with the retention time of benzene

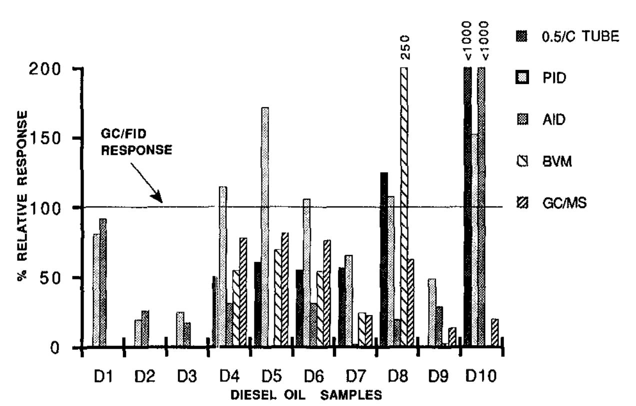

FIGURE 1. Response of five analytical techniques, compared with charcoal tube measurements, for samples collected from vessels whose last cargo was diesel oil

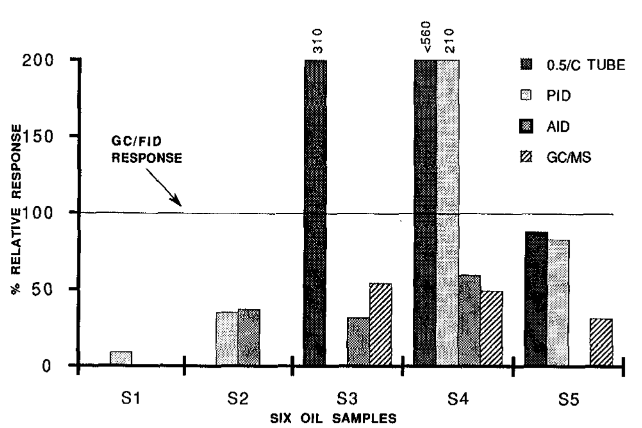

FIGURE 3. Response of four analytical techniques, compared with charcoal tube measurements, for samples collected from vessels whose last cargo was #6 oil

from the FID was approximately six times that from the PID. From this the authors conclude that much more than just benzene is eluting at that retention time, but the PID responds to much less of that material.

On the 35 total bag samples collected, a total of 73 sets of analyses were made by on-site direct reading instruments. (Of the 35 samples, 30 were analyzed by the PID, 33 by the AID, and 10 by the BVM.) Of these 73 sets of analyses there were 5 occasions when 1 portable instrument indicated the vessel was safe for entry (less than 1 ppm benzene) and the other(s) indicated it was not. For Sample H1 the PID measured 0.74 ppm benzene while the AID measured 2.32 ppm. For Sample S1 the AID measured 0.30 ppm benzene while the PID measured 5.26 ppm. For Samples D5 and D7 the AID indicated safe conditions (benzene at 0.17 ppm and ND) while measurements by the PID and BVM indicated otherwise. For Sample D9 the BVM indicated ND, while the PID and AID indicated 1.77 and 1.05 ppm. While the results obtained from the field instruments fell into the same range overall, that range was rather broad, and any one technique could be much higher or lower than the others in any given sample. The most probable reason for this would be variations in column capabilities or detector response between instruments. In addition, the coefficients of variation were often very low, but even these in some instances rise to greater than 50%, especially for the AID instrument. No explanation for this was apparent.

Comparison of the GC/MS data with other techniques indicated that these data were among the lowest of all measurements from a bag sample. This might be expected, since other compounds coeluting with benzene should not produce a positive interference with this technique. A comparison of data indicates that the PID estimates benzene concentration equal or greater than the GC/MS in 14 of 15 comparable samples. The AID and BVM estimate benzene concentration equal or greater than the GC/MS in 7 of 17 and 2 of 6 samples, respectively. That is to say, the PID appears to produce more conservative estimates

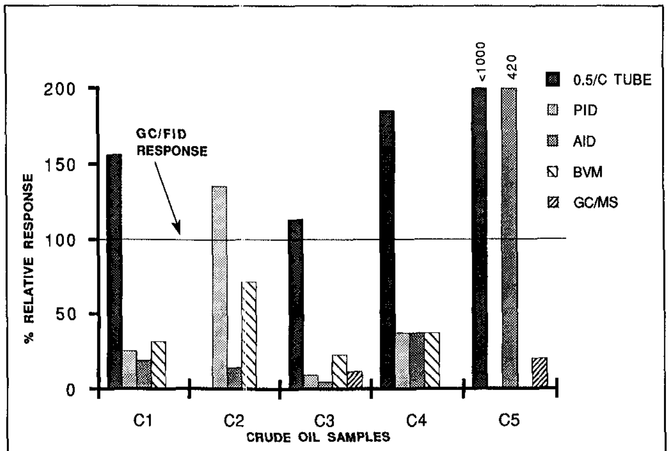

FIGURE 2. Response of five analytical techniques, compared with charcoal tube measurements, for samples collected from vessels whose last cargo was crude oil

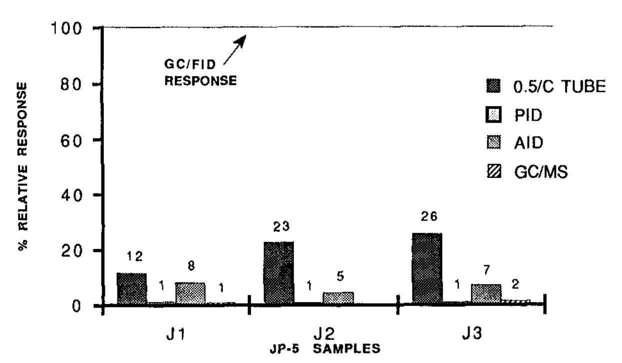

FIGURE 4. Response of five analytical techniques, compared with charcoal tube measurements, for samples collected from a vessel whose last cargo was JP-5 fuel

of safety than the GC/MS more frequently than the other portable GCs.

Another observation from these data involves the benzene exposure from JP-5 fuel. While it appears rather certain that there is some benzene in the environment of these tanks, the benzene would not appear to be the determining factor in dictating entry, since the total hydrocarbon concentration would be several hundred to a couple thousand parts per million before benzene exceeded 1 ppm.

CONCLUSIONS

Data from laboratory research indicated that ambient temperature, short column GC with photoionization detection, has the ability to separate benzene from toluene and xylene and detect sub-ppm levels of all three analytes. That same instrument can integrate peaks with the retention time of benzene vapor in samples generated from gasoline and crude and diesel oils, although in some instances the response was not due solely to the presence of benzene. Sequential analyses at 10-minute sampling intervals indicated no contaminant carried forward that interfered with subsequent benzene quantitation. Because these capabilities had been demonstrated in the laboratory, this technique was taken into the field for further evaluation.

Data from the field research indicate that the portable GCs tested are capable of providing a measure of benzene that may be an overestimate of actual concentration but less of an overestimate than that obtained by detector tubes, and in some cases less than what is obtained by laboratory analysis of charcoal tube samples using routine procedures with flame ionization detection. This appears to be due at least in part to the added specificity from the photoionization detector. The portable GC has the advantage of increased speed over the laboratory technique, being able to provide data on-site in a matter of minutes. It has the advantage of increased specificity over the detector tubes, being able to screen out larger numbers and higher concentrations of interfering substances. It also has greater sensitivity than the detector tubes, in most cases being capable of detecting benzene levels below the REL and TLV.

The first goal of this project, developing a screening procedure that would produce a minimum number of false positives for the detection of benzene, was considered fully met by the comparison of the PID data with all other techniques. The second goal, the ability to measure benzene accurately below the PEL and the REL, was considered to be partially met in that many benzene measurements were made by the PID below those levels with good precision and correlation with the GC/MS data. There does, however, appear to be a tendency to overestimate benzene concentration in some samples that coelute benzene with other photoionizable compounds.

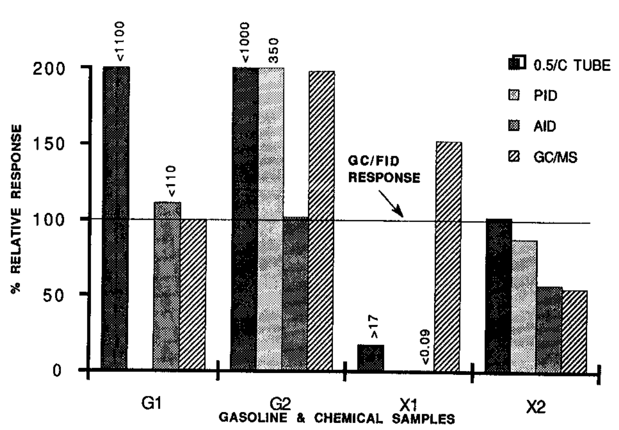

FIGURE 6. Response of four analytical techniques, compared with charcoal tube measurements, for samples collected from vessels whose last cargo was gasoline, benzene, or cumene

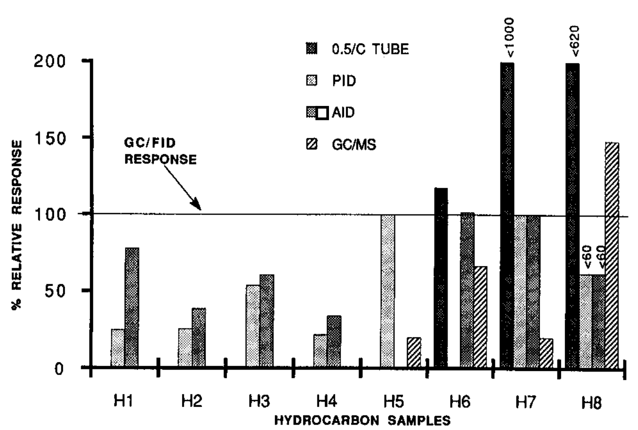

FIGURE 5. Response of four analytical techniques, compared with charcoal tube measurements, for samples collected from vessels whose last cargo was an undetermined hydrocarbon mixture

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