

1. General Discussion

For assistance with accessibility problems in using figures and illustrations presented in this method, please contact the Salt Lake Technical Center (SLTC) at (801) 233-4900. This procedure was designed and tested for internal use by OSHA personnel. Mention of any company name or commercial product does not constitute endorsement by OSHA.

1.1. Background

1.1.1. History

The collection of benzene using charcoal tubes (SKC lot 107) was evaluated in OSHA Method 12.¹ Since that time, many diffusive samplers have come on the market, and are becoming more popular for workplace sampling. The Methods Development Team at OSHA Salt Lake Technical Center is in the process of validating passive samplers for the top 10 organic chemicals. Benzene is in the top 10 organic chemicals requested, therefore an evaluation of its sampling performance with passive samplers was performed. This method includes two diffusive samplers, SKC 575-002 Passive Samplers and 3M 3520 OVMs, along with charcoal tubes (SKC lot 2000). Benzene PELs include a TWA, STEL, Ceiling, and Peak; therefore, these media were evaluated for both short term and long term sampling, for the various PELs.

The tests for the determination of the sampling rate show that SKC 575-002 Passive Samplers and 3M 3520 OVMs had a faster sampling rate in the first five minutes of sampling, than the rest of the times sampled. The sampling rate for the subsequent time periods each decreased until at 30 minutes it leveled off to the sampling rate used. The sampling rate was significantly higher in the first 5 minutes of sampling than the rest of the sampling period, so it is recommended that the sampling time for these passive samplers be at least 10 minutes. The Peak PEL for benzene is defined as a 10-minute sample.

Each of the media had good extraction efficiency and storage stability. The use of a capillary column in the analysis allowed for lower reliable quantitation limits in this method when compared to the limits obtained with the packed column in OSHA Method 12.²

In Version 2.1 the following calculations were corrected: detection limit of the overall procedure for SKC 575-002 Passive Samplers (Section 4.2), standard error of estimate of the instrument calibration (section 4.3), refrigerated storage line equation and related statistics for the charcoal tube sampler (Section 4.5.1), and the sampling rate for both SKC 575-002 Passive Samplers and 3M 3520 OVM samplers (Sections 4.7.2 and 4.7.3).

¹ OSHA Computerized Information System Database, [Chemical Sampling Information \(CSI\)](#), (accessed August 2001).

² OSHA Computerized Information System Database, [Chemical Sampling Information \(CSI\)](#), (accessed August 2001).

1.1.2. Toxic effects

(This section is for information only and should not be taken as the basis of OSHA policy.)

Benzene in high concentrations has narcotic effects similar to toluene and other aromatics. Benzene is a myelotoxicant known to suppress bone marrow cell proliferation and to induce hematologic disorders in humans and animals. Chronic exposure to benzene leads to aplastic anemia, and may lead to leukemia after 6 months to 6 years of chronic exposure. Benzene exposure can cause chromosomal aberrations in animals and humans. Chronic benzene exposure has also been associated with lung cancer in epidemiological studies. Benzene is classified as a human carcinogen by American Conference of Governmental Industrial Hygienists (ACGIH) and International Agency for Research on Cancer (IARC).³ Benzene is classified as a suspected human carcinogen by OSHA.⁴ A risk assessment for benzene exposure performed by Rinsky et al., reported that a worker exposed to 10 ppm benzene for 40 years was 155 times more likely to die from leukemia than an unexposed worker. A worker exposed to 1 ppm benzene was 1.7 times more likely to die from leukemia than an unexposed worker.⁵ IARC has published a risk assessment showing that workers exposed to a 10 ppm chronic exposure, had an increase of 14-140 leukemia cases per 1000 people above the rate for an unexposed worker. For 1 ppm chronic exposure, there was an increase of 1.4-14 cases per 1000 above the rate for an unexposed worker.⁶ The skin notation cited in the TLV is based on the skin absorption rate of 0.05% when neat benzene is applied to the skin, indicating benzene exposures through skin absorption can be significant.⁷

1.1.3. Workplace exposure

Benzene is used in the manufacture of industrial chemicals, as a solvent for waxes, resins, oils, natural rubber. Benzene may be present in gasoline and other petroleum products up to 1%, as a natural part of the cracking process.⁸ Benzene was the 16th highest chemical in the ranking of production by volume for 1995.⁹ Benzene production was 2.412 billion gallons in 2000.¹⁰

³ *Documentation of the Threshold Limit Values and Biological Exposure Indices*, 6th ed.; American Conference of Governmental Industrial Hygienists, Inc.: Cincinnati, OH, 1991, Vol. II, p 108.

⁴ OSHA Computerized Information System Database, [Chemical Sampling Information \(CSI\)](#), (accessed August 2001)

⁵ Rinsky, R.A., Smith A.B., Hormung R. et al, Benzene and Leukemia: An Epidemiologic Risk Assessment, *N Engl J Med*, 1987, 316 (17), pp1044-1050.

⁶ *International Agency for Research on Cancer: Benzene, IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Humans, Some Industrial chemicals and Dyestuffs*, IARC, Lyon, France, Vol 29, 1982, pp 93-148.

⁷ *Documentation of the Threshold Limit Values and Biological Exposure Indices*, 6th ed.; American Conference of Governmental Industrial Hygienists, Inc.: Cincinnati, OH, 1991, Vol. II, p 108.

⁸ Budavari, S., *The Merck Index*, 12th ed., Merck & Co. Inc.: Whitehouse Station, NJ, 1996, p 178.

⁹ Lewis, R., J., *Hawley's Condensed Chemical Dictionary*, 12th ed., Van Nostrand Reinhold Co.: New York, 1997, p 123.

¹⁰ McCoy, M. et al., Facts & Figures for the Chemical Industry, *Chem. Eng. News*, 2001, 79 (Jun 25), p 45.

2.2. Reagents

None required

2.3. Technique

2.3.1. Charcoal tubes

Immediately before sampling, break off the ends of the flame-sealed tube to provide an opening approximately half the internal diameter of the tube at each end. Wear eye protection when breaking ends. Use tube holders to minimize the hazard of broken glass. All tubes should be from the same lot.

The smaller section of the adsorbent tube is used as a back-up and is positioned nearest the sampling pump. Attach the tube holder to the sampling pump so that the adsorbent tube is in an approximately vertical position with the inlet facing down during sampling. Position the sampling pump, tube holder and tubing so they do not impede work performance or safety. Use tube holder to minimize the hazard to the worker from the broken end of the tube.

Draw the air to be sampled directly into the inlet of the tube holder. The air being sampled should not be passed through any hose or tubing before entering the sampling tube.

After sampling for the appropriate time, remove the adsorbent tube and seal it with plastic end caps. Seal each sample end-to-end with an OSHA 21 form as soon as possible.

Submit at least one blank sample with each set of samples. Handle the blank sampler in the same manner as the other samples except draw no air through it.

Record sample air volume (liters), sampling time (minutes) and sampling rate (mL/min) for each sample, along with any potential interferences on the OSHA 91A form.

Submit the samples to the laboratory for analysis as soon as possible after sampling. If delay is unavoidable, store the samples in a refrigerator. Ship any bulk samples separate from the air samples.

2.3.2. SKC 575-002 Passive Samplers (In general, follow the manufacturer's instructions.)

Remove the sampler enclosed in an air-tight clear bag from the container, just before sampling is to begin. **Caution - The sampler begins to sample immediately after the clear plastic bag is opened.** Keep the O-ring, press-on cover, cover retainer, port plugs and PTFE tube for later use.

Record the start time on the sampler label or on the OSHA 91A form.

Attach the sampler to the worker near his/her breathing zone with the perforations in the sampler facing forward. Assure that the area directly in front of the sampler is unobstructed throughout the sampling period.

At the end of the sampling period, immediately detach the sampler from the worker and attach the cover with the O-ring in place onto the sampler using the cover retainer. Visually inspect the O-ring to be sure it is forming a proper seal around the entire

circumference of the sampler. Record the stop time on sampler label or on OSHA 91A form.

Prepare a blank by removing an unused sampler from its clear package and immediately attaching a cover with the O-ring in place onto it.

Seal each sampler with an OSHA 21 form.

Verify that the sampling times are properly recorded on the OSHA 91A form for each sample. Also, identify blank samples on this form.

Record the room temperature and atmospheric pressure of the sampling site on the OSHA 91A form.

List any compounds that could be considered potential interferences, especially solvents, that are being used in the sampling area.

Submit the samples to the laboratory for analysis as soon as possible after sampling. If delay is unavoidable, store the samples in a refrigerator. Ship any bulk samples separate from the air samples. Include all port plugs and PTFE tubes which will be used in the laboratory analyses. Ship any bulk sample(s) in a container separate from the air samples.

2.3.3. 3M OVMs (In general, follow the manufacturer's instructions supplied with the samplers.)

The samplers come individually sealed in small metal cans. When ready to begin sampling, remove the plastic lid from the can and lift up on the revealed ring. Pull back on the ring to open the can. Discard the metal top of the can and remove the sampler. **Caution - The sampler begins to sample immediately after the can is unsealed.**

Keep the two closure caps with attached port plugs, cup and PTFE tubes in the can for later use. Close the can with the plastic lid.

Record the start time on the back of the sampler or on the OSHA 91A form.

Attach the sampler to the worker near his/her breathing zone with the white face forward. Assure that the area directly in front of the sampler is unobstructed throughout the sampling period. Do not remove the white film and ring from the sampler until the sampling period is terminated.

At the end of the sampling period, detach the sampler from the worker and remove the white film and retaining ring. Immediately snap a closure cap onto the primary (top) section of the sampler (where the white film and ring were removed). It is critical that this step be done as quickly as possible because the sampling rate is more than five times faster without the white film in place, which can be an important consideration, especially for short-term sampling. Assure that the attached port plugs are placed firmly into the port holes. The white film and ring can be discarded. Record the stop time on the back of the sampler and on the OSHA 91A form.

The following steps should be performed in a low background area for a set of samplers as soon as possible after sampling.

Ready a blank by removing the white film and ring and attaching a closure cap onto an unused sampler.

For each sampler (one at a time), separate the primary (top) and secondary (bottom) sections of the sampler using the edge of a coin as a pry.

Securely snap a cup onto the bottom of the primary section.

Snap a closure cap onto the secondary section of the sampler and assure that the attached port plugs are placed firmly into the port holes.

Return the sampler sections with closure caps and cup in place to the metal can which contains the PTFE tubes (which will be used by the laboratory). Close the can with the plastic lid, and seal it with an OSHA 21 form.

Verify that the sampling times are properly recorded on OSHA 91A form for each sample. Also, identify blank samples on this form.

Record the room temperature and atmospheric pressure of the sampling site on OSHA 91A form.

List any compounds that could be considered potential interferences, especially solvents, that are being used in the sampling area.

Submit the samples to the laboratory for analysis as soon as possible after sampling. If delay is unavoidable, store the samples in a refrigerator. Ship any bulk samples separate from the air samples.

2.4. Sampler capacity (Section 4.7)

2.4.1. Charcoal tubes

The sampling capacity of the front section of a charcoal tube was tested by sampling a dynamically generated test atmosphere of benzene (73.4 mg/m^3 or 23 ppm) at an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2°C). The samples were collected at 50 mL/min. No breakthrough was observed, even after sampling for 600 min.

2.4.2. SKC 575-002 Passive Samplers and 3M 3520 OVMs

The sampling rate and capacity of the SKC 575-002 Passive Sampler and the 3M 3520 OVM were determined by sampling a dynamically generated test atmosphere of benzene (7.34 mg/m^3 or 2.3 ppm and 73.4 mg/m^3 or 23 ppm) at an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2°C) for increasing time intervals. A sampling rate of 17.0 mL/min for SKC 575-002 Passive Samplers and 34.6 mL/min for 3M 3520 OVM was determined. The recommended sampling times for this method are 10 minutes for Peak, 15 minutes for STEL, and 240 minutes for TWA sampling. The tests showed a significant difference in the sampling rate for a 5 minute sample versus the determined sampling rate, therefore, these samplers cannot be used to sample for less than 10 minutes.

2.5. Extraction efficiency (Section 4.8)

It is the responsibility of each analytical laboratory to determine the extraction efficiency because the adsorbent material, internal standard, reagents and laboratory techniques may be different from those listed in this evaluation and influence the results.

2.5.1. Charcoal tubes

The mean extraction efficiency for benzene from dry charcoal tubes over the range of RQL to 2 times the target concentration (0.13 to 79.1 micrograms per sample) was 97.0%. The extraction efficiency was not affected by the presence of water (average recovery of 96.7%).

Extracted samples remain stable for at least 24 h.

2.5.2. SKC 575-002 Passive Samplers

The mean extraction efficiency for benzene from dry SKC 575-002 Passive Samplers over the range of RQL to 2 times the target concentration (0.13 to 24.6 micrograms per sample) was 93.6%. The extraction efficiency was not affected by the presence of water (average recovery of 93.9%).

Extracted samples remain stable for at least 24 h.

2.5.3. 3M 3520 OVMs

The mean extraction efficiency for benzene from dry 3M 3520 OVMs over the range of RQL to 2 times the target concentration (0.13 to 54.5 micrograms per sample) was 97.9%. The extraction efficiency was not affected by the presence of water (average recovery of 98.1%).

Extracted samples remain stable for at least 24 h.

2.6. Recommended sampling time and sampling rate

2.6.1. Charcoal tubes

Sample with charcoal tubes for up to 240 min at 50 mL/min (12 L) to collect TWA (long-term) samples, for 10 min at 50 mL/min (0.5 L) to collect Peak (short-term) samples, and for 15 min at 50 mL/min (0.75 L) collect STEL (short-term) samples.

When short-term samples are collected, the air concentration equivalent to the reliable quantitation limit becomes larger. For example, the reliable quantitation limit for charcoal tubes is 0.05 ppm (0.17 mg/m³) for benzene when 0.75 L are collected.

2.6.2. SKC 575-002 Passive Samplers

Sample with SKC 575-002 Passive Samplers for up to 240 min to collect TWA (long-term) samples, for 10 min to collect Peak (short-term) samples, and for 15 min to collect STEL (short-term) samples. The sampling rate is 17.0 mL/min.

When short-term samples are collected, the air concentration equivalent to the reliable quantitation limit becomes larger. For example, the reliable quantitation limit for SKC 575-002 Passive Samplers is 0.22 ppm (0.69 mg/m³) for benzene when 0.26 L (15 min) are collected.

2.6.3. 3M 3520 OVMs

Sample with 3M 3520 OVMs for up to 240 min to collect TWA (long-term) samples, for 10 min to collect Peak (short-term) samples, and for 15 min to collect STEL (short-term) samples. The sampling rate is 34.6 mL/min.

When short-term samples are collected, the air concentration equivalent to the reliable quantitation limit becomes larger. For example, the reliable quantitation limit for 3M 3520 OVMs is 0.08 ppm (0.26 mg/m³) for benzene when 0.52 L (15 min) are collected.

2.7. Interferences, sampling (Section 4.9)

2.7.1. Charcoal tubes

Retention

The mean retention efficiency for all samples was 100.3%, when charcoal tubes containing 880 g of benzene were allowed to sample 9 L of contaminant-free air having an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2°C).

Low humidity

The ability of a charcoal tube to collect benzene from a relatively dry atmosphere was determined by sampling an atmosphere of two times the target concentration of benzene and having an absolute humidity of 1.9 milligrams of water per liter of air (about 10% relative humidity at 22.2°C). The samples collected above 99.4% of theoretical.

Low concentration

The ability of a charcoal tube to collect benzene at low concentrations was determined by sampling a test atmosphere containing 0.1 times the target concentration of benzene and having an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2°C). The samples collected above 98.5% of theoretical.

Interference

The ability of charcoal tubes to collect benzene in the presence of an interference was determined from a test atmosphere containing one times the target concentration of benzene, 890 mg/m³ of gasoline, and having an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2°C). The benzene concentration on the samples remained above 98.9% of theoretical.

2.7.2. SKC 575-002 Passive Samplers

Reverse diffusion

Reverse diffusion is the measure of the ability of the sorbent within a diffusive sampler to retain the analyte collected. Reverse diffusion is measured by first exposing two sets of samplers to humid air containing the analyte, and then additionally exposing one of the sets to clean humid air of an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2°C). Comparison of the two sets of SKC 575-002 Passive Samplers showed that an average of 99.1% of the benzene was retained, indicating a loss of 0.9% to reverse diffusion. The loading of benzene on the samplers was 75.3 µg. (Section 4.9.2)

Low humidity

The ability of a SKC 575-002 Passive Sampler to collect benzene from a relatively dry atmosphere was determined by sampling an atmosphere of two times the target

concentration of benzene and having an absolute humidity of 1.9 milligrams of water per liter of air (about 10% relative humidity at 22.2°C). The samples collected above 98.9% of theoretical.

Low concentration

The recovery for all samples was above 98.7% of theoretical, when SKC 575-002 Passive Samplers were used to sample a test atmosphere containing 0.1 times the target concentration of benzene and having an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2°C)

Interference

The ability of SKC 575-002 Passive Samplers to collect benzene in the presence of an interference was determined from a test atmosphere containing one times the target concentration of benzene, 890 mg/m³ of gasoline, and having an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2°C). The benzene concentration on the samples remained above 99.3% of theoretical.

2.7.3. 3M 3520 OVMs

Reverse diffusion

Reverse diffusion is the measure of the ability of the sorbent within a diffusive sampler to retain the analyte collected. Reverse diffusion is measured by first exposing two sets of samplers to humid air containing the analyte, and then additionally exposing one of the sets to clean humid air of an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2°C). Comparison of the two sets of 3M 3520 OVMs showed that an average of 99.2% of the benzene was retained, indicating a loss of 0.8% to reverse diffusion. The loading of benzene on the samplers was 75.3 µg. (Section 4.9.3)

Low humidity

The ability of 3M 3520 OVMs to collect benzene from a relatively dry atmosphere was determined by sampling an atmosphere of two times the target concentration of benzene and having an absolute humidity of 1.9 milligrams of water per liter of air (about 10% relative humidity at 22.2°C). The samples collected above 98.7% of theoretical.

Low concentration

The ability of 3M 3520 OVMs to collect benzene at low concentrations was determined by sampling a test atmosphere containing 0.1 times the target concentration of benzene and having an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2°C). The samples collected above 99.5% of theoretical.

Interference

The ability of 3M 3520 OVMs to collect benzene in the presence of an interference was determined from a test atmosphere containing one times the target concentration of benzene, 890 mg/m³ of gasoline, and having an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2°C). The benzene concentration on the samples remained above 99.1% of theoretical.

3. Analytical Procedure

Adhere to the rules set down in your Chemical Hygiene Plan¹⁶. Avoid skin contact and inhalation of all chemicals and review all MSDSs before beginning this analytical procedure.

3.1. Apparatus

- 3.1.1. Gas chromatograph equipped with an FID. A Hewlett-Packard Model 5890 Series II GC equipped with an integrator, an automatic sample injector, and an FID was used in this evaluation.
- 3.1.2. A GC column capable of separating benzene from the extracting solvent, internal standard, and the components of gasoline. A J&W 60-m × 0.32-mm i.d. DB-1 (5-µm df) capillary column was used in this evaluation.
- 3.1.3. An electronic integrator or other suitable means of measuring GC detector response. A Waters Millennium³² Data System was used in this evaluation, along with a Hewlett Packard 3396 Series II integrator.
- 3.1.4. Glass vials with PTFE-lined caps. For this evaluation 2 and 4-mL vials were used.
- 3.1.5. A dispenser capable of delivering 1.0 or 2.0 mL of extracting solvent to prepare standards and samples. If a dispenser is not available, 1.0- and 2.0-mL volumetric pipets may be used.
- 3.1.6. Volumetric flasks - 10-mL and other convenient sizes for preparing standards.
- 3.1.7. Calibrated 10-L syringe for preparing standards.
- 3.1.8. An SKC Desorption shaker with rack (226D-03K) was used to extract SKC 575-002 Passive Samplers in this evaluation.
- 3.1.9. A mechanical shaker. An Eberbach mechanical shaker was used to extract the charcoal tubes in this evaluation.

3.2. Reagents

- 3.2.1. Benzene, [CAS no. 71-43-2], reagent grade or better. The benzene used in this evaluation was A.C.S. reagent grade (lot no. CU 03251PS) purchased from Aldrich (Milwaukee, WI).
- 3.2.2. Carbon disulfide (CS₂), [CAS no. 75-15-0], reagent grade or better. The carbon disulfide used in this evaluation was 99.9+% low benzene content grade (lot no. TI 01762PI) purchased from Aldrich (Milwaukee, WI).

¹⁶ Occupational Exposure to Hazardous Chemicals in Laboratories. *Code of Federal Regulations*, Part 1910.1450, Title 29, 1998.

3.2.3. 1-Phenylhexane (*n*-hexylbenzene) [CAS no. 1077-16-3], reagent grade or better. The 1-phenylhexane used in this evaluation was 97% reagent grade (lot no. 03006PZ) purchased from Aldrich (Milwaukee, WI).

3.2.4. The extraction solvent used for this evaluation consisted of 0.25 L/mL *n*-hexylbenzene (1-phenylhexane) in the CS₂. The *n*-hexylbenzene was added to the CS₂ as an internal standard. Other internal standards can be used provided they are fully tested.

3.3. Standard preparation

3.3.1. Prepare concentrated stock standards of benzene in the extracting solvent. At least two separate stock standard should be prepared. Prepare working analytical standards by diluting these stock standards with the extracting solution delivered from the same dispenser used to extract the samples. For example, to prepare a target standard (1 ppm), inject 4.5 µL of benzene in a 10-mL volumetric flask containing the extracting solvent and then make a 1/10 dilution with the extracting solvent to obtain the working standard at the target level. A second set of standards from a different primary standard should be prepared to check the quality of the first set of standards.

3.3.2. Bracket sample concentrations with standard concentrations. If upon analysis, sample concentrations fall outside the range of prepared standards, prepare and analyze additional standards to confirm instrument response, or dilute high samples with extraction solvent and reanalyze the diluted samples.

3.4. Sample preparation

3.4.1. Charcoal tubes

Remove the plastic end caps from the sample tube and carefully transfer each section of the adsorbent to separate 2-mL vials. Discard the glass tube and glass wool and polyurethane plugs.

Add 1.0 mL of extracting solution to each vial and immediately seal the vials with PTFE-lined caps.

Shake the vials on a shaker for 30 min (Shaking is necessary to obtain the extraction efficiency found in this method; without shaking the extraction efficiencies will be lower.)

3.4.2. SKC 575-002 Passive Samplers (In general, follow the manufacturer's instructions.)

Cut off the ends of the two protruding tubes of each sampler with a razor blade or sharp knife.

Slowly add 2.0 mL of extraction solvent through one of the protruding tubes (ports), stopping at least once to allow the bubbling to subside before adding the rest of the extraction solvent.

Immediately insert plugs into the ports.

Mount the samplers in the sampler rack (SKC Cat. No. 226-04-5) of a specialized shaker (SKC Cat. No. 226D-03-1) and shake the samplers for 1 hour.

Do not leave the extracted sample in the sampler. Transfer each extracted sample by removing the plugs from the sampler ports, firmly inserting the tapered end of a supplied

PTFE tube into the outer port and carefully pouring the solution through the PTFE tube into a labeled autosampler vial. Immediately cap each vial.

3.4.3. 3M 3520 OVMs (In general, follow the manufacturer's instructions.)

Remove both sampler sections from the metal cans, along with the sections of PTFE tubing. Assure that the closure caps are firmly snapped to the primary and secondary sections of all the samplers. Also, assure that all cap plugs are firmly seated in the cap ports. Any deviations must be noted. Make sure each section of the sampler is labeled properly for future reference.

Prepare one section of sampler at a time by temporarily removing the cap plugs from the ports and adding 2.0 mL of extraction solvent through the center port. Immediately replace the plugs in the ports. Repeat the process for the second section.

Allow the sampler sections to extract for 30 min. Periodically apply gentle agitation to the sampler sections during the extraction period.

Do not leave the extracted sample in the sampler. Transfer the solution from each sampler section by removing both plugs from the ports, inserting a decanting spout (a small section of PTFE tubing) into the rim port and pouring the liquid through the spout into a labeled autosampler vial. Immediately cap each vial.

3.5. Analysis

3.5.1. Analytical conditions

GC conditions

column temperature:	initial 60°C, hold 5 min, program at 10°/min to 220°C, hold 14 min
zone temperatures:	220°C (injector) 240°C (detector)
run time:	35 min
column gas flow:	2.4 mL/min (hydrogen)
septum purge:	3.5 mL/min (hydrogen)
injection size:	1.0 µL (19:1 split)
column:	60-m × 0.32-mm i.d. capillary DB-1 (d _f = 5.0 µm)
retention times:	9.26 min (carbon disulfide) 13.66 min (benzene) 32.49 min (n-hexyl benzene)

FID conditions

hydrogen flow:	35 mL/min
air flow:	450 mL/min
nitrogen makeup flow:	35 mL/min

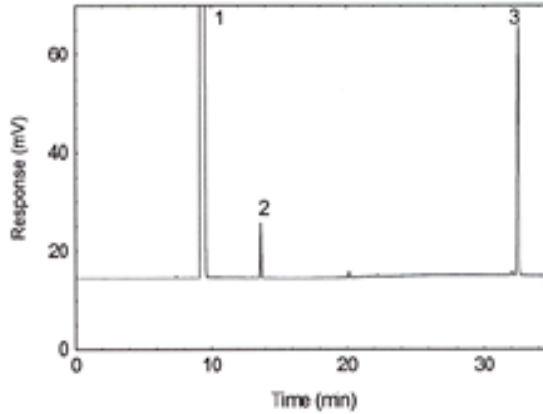


Figure 3.5.1. Chromatogram obtained at the target concentration with the recommended analytical conditions. There are three peaks: carbon disulfide at 9.26 min, benzene at 13.66 min, and n-hexyl benzene at 32.491 min.

3.5.2. An internal standard (ISTD) calibration method is used. The calibration curve was constructed by plotting the ISTD-corrected response of standard injections versus micrograms of analyte per sample. Bracket the samples with freshly prepared analytical standards over a range of concentrations.

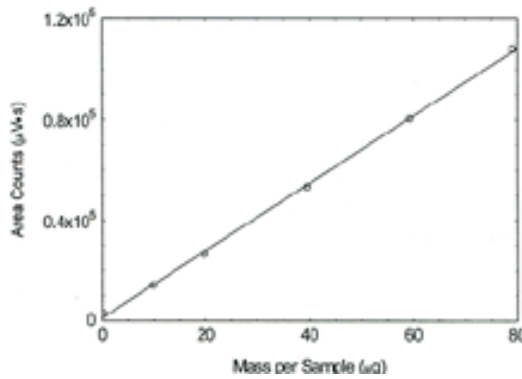


Figure 3.5.2. A plot of the calibration standards with mass per sample on the X-axis and area counts on the Y-axis. The points plotted here are: 79.1 µg, 107853 area counts; 59.3 µg, 80377 area counts; 39.5 µg, 53375 area counts; 19.8 µg, 26661 area counts; and 9.9 µg, 14246 area counts. ($y = 1356x + 199$)

3.6. Interferences (analytical)

- 3.6.1. Any compound that produces an FID response and has a similar retention time as the analyte or internal standard is a potential interference. If any potential interferences were reported, they should be considered before samples are extracted. Generally, chromatographic conditions can be altered to separate an interference from the analyte.
- 3.6.2. When necessary, the identity of an analyte peak may be confirmed with additional analytical data (Section 4.10).

3.7. Calculations

3.7.1. Charcoal

The amount of benzene per sampler is obtained from the appropriate calibration curve in terms of micrograms per sample, uncorrected for extraction efficiency. The back section is analyzed primarily to determine the extent of sampler saturation. (The charcoal tube is considered saturated when 25% of the amount found on the front section is found on the back section of the tube, and therefore, some of the sample may have been lost.) If any analyte is found on the back section, it is added to the amount on the front section. This total amount is then corrected by subtracting the total amount (if any) found on the blank. The air concentration is calculated using the following formulas.

$$C_M = \frac{M}{VE_E} \quad \text{where} \quad \begin{array}{l} C_M \text{ is concentration by weight (mg/m}^3\text{)} \\ M \text{ is micrograms per sample} \\ V \text{ is liters of air sampled} \\ E_E \text{ is extraction efficiency, in decimal form} \end{array}$$

$$C_M = \frac{C_V V_M}{M_r} \quad \text{where} \quad \begin{array}{l} C_V \text{ is concentration by volume (ppm)} \\ V_M = 24.46 \text{ at NTP} \\ C_M \text{ is concentration by weight} \\ M_r \text{ is molecular weight of 78.11} \end{array}$$

3.7.2. 3M 3520 OVMs and SKC 575-002 Passive Samplers

The amount of benzene for the samples is obtained from the appropriate calibration curve in terms of micrograms per sample, uncorrected for extraction efficiency. (In the case of the 3M 3520 OVMs, the back section is analyzed primarily to determine the extent of sampler saturation. If any analyte is found on the back section, the amount is multiplied by 2.2 (as per manufacturer's instructions) and then added to the amount on the front section. The sampler is saturated, affecting its ability to collect, when the corrected amount found on the back section is 50% of the amount found on the front section.) This total amount is then corrected by subtracting the total amount (if any) found on the blank. The air concentration is calculated using the following formulas.

$$R_{SS} = R_{NTP} \left(\frac{T_{SS}}{T_{NTP}} \right)^{3/2} \frac{P_{NTP}}{P_{SS}} \quad \text{where} \quad \begin{array}{l} R_{SS} \text{ is the sampling rate at sampling site} \\ R_{NTP} \text{ is the sampling rate at NTP conditions} \\ \text{(SKC 575-002 = 17.1 mL/min, 3M OVM = 34.3 mL/min)} \\ T_{SS} \text{ is the sampling site temperature in K} \\ T_{NTP} \text{ is 298.2 K} \\ P_{SS} \text{ is the sampling site pressure in mmHg} \\ P_{NTP} \text{ is 760 mmHg} \end{array}$$

$$C_M = \frac{10^3 M}{t R_{SS} E_E} \quad \text{where} \quad \begin{array}{l} C_M \text{ is concentration by weight (mg/m}^3\text{)} \\ M \text{ is micrograms per sample} \\ R_{SS} \text{ is the sampling rate at the sampling site} \\ t \text{ is the sampling time} \\ E_E \text{ is extraction efficiency, in decimal form} \end{array}$$

$$C_V = \frac{C_M V_M}{M_r} \quad \text{where} \quad \begin{array}{l} C_V \text{ is concentration by volume (ppm)} \\ V_M = 24.46 \text{ at NTP} \\ C_M \text{ is concentration by weight} \\ M_r \text{ is molecular weight of 78.11} \end{array}$$

3.7.3. If the sampling site temperature is not provided, assume that it is 22.2°C. If the sampling site atmospheric pressure is not given, calculate an approximate value based on the sampling site elevation from the following equation.

$$P_{SS} = AE^2 - BE + 760.0$$

where P_{SS} is the approximate atmospheric pressure
E is the sampling site elevation, ft
A is 3.887×10^{-7} mmHg/ft²
B is 0.02748 mmHg/ft

4. Backup Data

General background information about the determination of detection limits and precision of the overall procedure is found in the "Evaluation Guidelines for Air Sampling Methods Utilizing Chromatography Analysis"¹⁷. The Guidelines define analytical parameters, specify required laboratory tests, statistical calculations, and acceptance criteria.

4.1. Detection limit of the analytical procedure (DLAP)

The DLAP is measured as the mass of analyte introduced onto the chromatographic column. Ten analytical standards were prepared with equal increments with the highest standard containing 1050 ng/mL. This is the concentration that would produce a peak approximately 10 times the response of a reagent blank near the elution time of the analyte. These standards, and the reagent blank were analyzed with the recommended analytical parameters (1- μ L injection with a 19:1 split), and the data obtained were used to determine the required parameters (standard error of estimate and slope) for the calculation of the DLAP. Values of 18.0 and 18.74 were obtained for the slope and standard error of estimate respectively. DLAP was calculated to be 3.12 pg.

Table 4.1
Detection Limit of the Analytical Procedure

concentration (ng/mL)	mass on column (pg)	area counts (μ V·s)
0	0	0
105	5.5	111
211	11.1	249
316	16.6	341
422	22.2	402
527	27.7	545
633	33.3	618
738	38.8	722
844	44.4	835
949	49.9	924
1050	55.3	1001

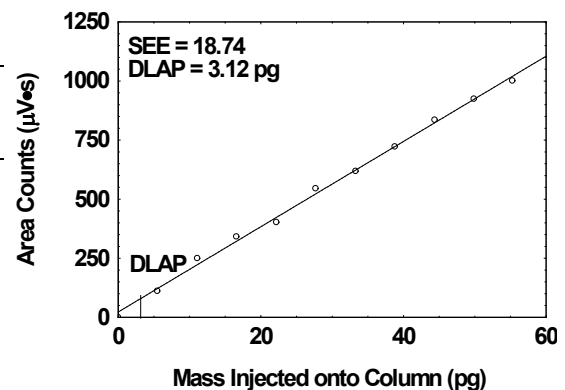


Figure 4.1. Plot of data in Table 4.1 used to determine the DLAP. ($y = 18.0x + 22.8$)

4.2. Detection limit of the overall procedure (DLOP) and reliable quantitation limit (RQL)

DLOP is measured as mass per sample and expressed as equivalent air concentrations, based on the recommended sampling parameters. Ten samplers were spiked with equal descending increments of analyte, such that the highest sampler loading was 1050 ng/sample. This is the amount spiked on a sampler that would produce a peak approximately 10 times the response of a sample blank. These spiked samplers, and the sample blank were analyzed with the recommended analytical parameters, and the data obtained used to calculate the required parameters (standard error of estimate and the slope) for the calculation of the DLOP. Values of 0.940 and 11.90 were obtained for the slope and standard error of estimate for charcoal tubes, respectively. The DLOP for charcoal tubes was calculated to be 38 ng/sample (1 ppb). Values of 0.972 and 17.50 were obtained for the slope and standard error of estimate for SKC 575-002 Passive Samplers, respectively. The DLOP for SKC 575-002 Passive Samplers was calculated

¹⁷ Burreight, D.; Chan, Y.; Eide, M.; Elskamp, C.; Hendricks, W.; Rose, M. C. [Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis](#), (accessed August 2001).

Table 4.9.1
Retention of Benzene on Charcoal tubes

set	percent recovery (%)			mean
	1	2	3	
first	98.7	99.2	99.6	99.2
second	99.1	99.0	100.5	99.5
second/first				100.3

Low humidity

The ability of a charcoal tube to collect benzene from a relatively dry atmosphere was tested by sampling an atmosphere containing 73.4 mg/m³ of benzene at an absolute humidity of 1.9 milligrams of water per liter of air (about 10% relative humidity at 22.2°C). Three samplers had contaminated air drawn through them at 50 mL/min for 240 min. All of the samples were immediately analyzed. The samples had collected 99.4%, 99.8% and 99.7% of theoretical.

Low concentration

The ability of a charcoal tube to collect benzene at low concentrations was tested by sampling an atmosphere containing 0.32 mg/m³ of benzene at an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2°C). The benzene concentration was achieved by diluting the benzene with toluene and pumping the mixture into the sampling chamber. Three samplers had contaminated air drawn through them at 50 mL/min for 240 min. All of the samples were immediately analyzed.

The samples had collected 100.4%, 98.5% and 98.9% of theoretical.

Interference

The ability of a charcoal tube to collect benzene was tested when other potential interferences are present by sampling an atmosphere containing 31.9 mg/m³ of benzene at an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2°C) and gasoline, whose concentration was 890 mg/m³. Three samplers had contaminated air drawn through them at 50 mL/min for 240 min. All of the samples were immediately analyzed. The samples had collected 99.8%, 100.1% and 98.9% of theoretical. There was no benzene on the backup portion of the charcoal tubes, though there was 5.25% gasoline.

4.9.2. SKC 575-002 Passive Sampler

Reverse diffusion

Reverse diffusion is the measure of the ability of the sorbent within a diffusive sampler to retain the analyte collected. Reverse diffusion is measured by first exposing two sets of samplers to humid air containing the analyte, and then additionally exposing one of the sets to clean humid air of an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2°C). Six samplers were exposed to contaminated air for 60 min. Sampling was discontinued and three samples set aside. The generation system was flushed with contaminant-free air. Sampling resumed with the other three samples being exposed to humid contaminant-free air for 180 min and then all six samplers were analyzed. Comparison of the two sets of SKC 575-002 Passive Samplers showed that an average of 99.1% of the benzene was retained, indicating a loss of 0.9% to reverse diffusion. The loading of benzene on the samplers was 75.3 µg.

Table 4.9.2
Reverse Diffusion of Benzene on
SKC 575-002 Passive Samplers

set	mass (μg)			mean
	1	2	3	
first	75.6	75.2	75.8	75.5
second	74.1	74.7	75.5	74.8
second/first				99.1%

4.9.3. Low humidity

The ability of a SKC 575-002 Passive Sampler to collect benzene from a relatively dry atmosphere was tested by sampling an atmosphere containing 73.4 mg/m^3 of benzene at an absolute humidity of 1.9 milligrams of water per liter of air (about 10% relative humidity at 22.2°C). Three samplers were exposed to contaminated air for 240 min. All of the samples were immediately analyzed. The samples had collected 99.2%, 98.9% and 100.3% of theoretical.

Low concentration

The ability of a SKC 575-002 Passive Sampler to collect benzene at low concentration was tested by sampling an atmosphere containing 0.32 mg/m^3 of benzene at an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2°C). The benzene concentration was achieved by diluting the benzene with toluene and pumping the mixture into the sampling chamber. Three samplers were exposed to contaminated air for 240 min. All of the samples were immediately analyzed. The samples had collected 100.3%, 98.7% and 99.8% of theoretical.

Interference

The ability of a SKC 575-002 Passive Sampler to collect benzene when other potential interferences are present was tested by sampling an atmosphere containing 31.9 mg/m^3 of benzene at an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2°C) and gasoline, whose concentration was 890 mg/m^3 . Three samplers were exposed to contaminated air for 240 min. All of the samples were immediately analyzed. The samples had collected 99.3%, 100.3% and 99.8% of theoretical.

4.9.4. 3M 3520 OVMs

Reverse diffusion

Reverse diffusion is the measure of the ability of the sorbent within a diffusive sampler to retain the analyte collected. Reverse diffusion is measured by first exposing two sets of samplers to humid air containing the analyte, and then additionally exposing one of the sets to clean humid air of an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2°C). Six samplers were exposed to contaminated air for 60 min. Sampling was discontinued and three samples set aside. The generation system was flushed with contaminant-free air. Sampling resumed with the other three samples being exposed to humid contaminant-free air for 180 min and then all six samplers were analyzed. Comparison of the two sets of 3M 3520 OVMs showed that an average of 99.2% of the benzene was retained, indicating a loss of 0.8% to reverse diffusion. The loading of benzene on the samplers was $75.3 \mu\text{g}$.

Table 4.9.3
Reverse Diffusion of Benzene on 3M 3520 OVMs

set	mass (μg)			mean
	1	2	3	
first	150.8	150.2	150.9	150.6
second	150.6	149.0	148.5	149.4
second/first				99.2

Low humidity

The ability of a 3M 3520 OVM to collect benzene from a relatively dry atmosphere was tested by sampling an atmosphere containing 73.4 mg/m^3 of benzene at an absolute humidity of 1.9 milligrams of water per liter of air (about 10% relative humidity at 22.2°C). Three samplers were exposed to contaminated air for 240 min. All of the samples were immediately analyzed. The samples had collected 99.9%, 98.7% and 100.2% of theoretical.

Low concentration

The ability of a 3M 3520 OVM to collect benzene at low concentration was tested by sampling an atmosphere containing 0.32 mg/m^3 of benzene at an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2°C). The benzene concentration was achieved by diluting the benzene with toluene and pumping the mixture into the sampling chamber. Three samplers were exposed to contaminated air for 240 min. All of the samples were immediately analyzed. The samples had collected 99.7%, 99.5% and 100.6% of theoretical.

Interference

The ability of a 3M 3520 OVM to collect benzene when other potential interferences are present was tested by sampling an atmosphere containing 31.9 mg/m^3 of benzene at an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2°C) and gasoline, whose concentration was 890 mg/m^3 . Three samplers were exposed to contaminated air for 240 min. All of the samples were immediately analyzed. The samples had collected 100.1%, 100.3% and 99.1% of theoretical. There was no benzene on the backup pad of the sampler, though there was 2.75% of the gasoline.

4.10. Qualitative analysis

The identity of benzene may be confirmed by GC/mass spectrometry. The mass spectrum of benzene is in Figure 4.10.

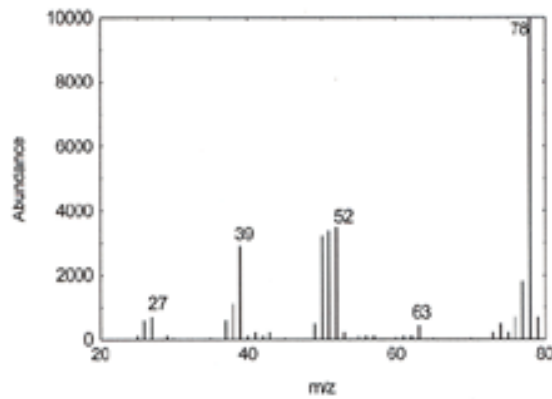


Figure 4.10. This is a plot of the mass spectrum of benzene. The major peaks are: a base peak (highest abundance peak) of 78 amu, the next highest are a triplet at 50, 51, and 52 amu, followed in intensity by 39, 27, 38, and 77.

5. Addendum for 1005: Wipe sampling for Benzene

5.1. Introduction

Benzene is a volatile organic solvent which will not collect onto the conventional wipe media of filters (e.g Smear tabs or Whatman filters) as it will evaporate off of these media within minutes of sampling. The charcoal pad from a 3M 3500 or 3520 Organic Vapor Monitor (OVM) was found to adsorb the benzene and retain it upon storage when placed in a tightly sealed vial. Note that an obviously dry surface will have no benzene on it, as the benzene will have already evaporated away. Wipe samples should be taken from surfaces where a residue of some sort can be observed.

The charcoal pads need to remain in a sealed container until just before use, and need to be placed immediately into a sealed container after sampling, as the charcoal pad can also adsorb organic vapors from the air. It is possible to remove the charcoal pads, in the office, from the 3M OVM and place in a 20-mL tightly capped sample vial, and take the vial to the workplace for sampling. Alternately, the charcoal pads may be placed in a sealed aluminized plastic bag, until used.

The charcoal pad may also be used to check for skin exposure due to the permeation of benzene through the worker's gloves. The charcoal pad is placed in the palm of the employee's hand, and the gloves are put on over it. The charcoal pad is removed when the gloves are changed or removed, immediately placed in a vial, sealed, and sent in for analysis. If benzene is found on the charcoal pad, it indicates that benzene permeated the glove and skin exposure may have occurred.

5.2. Wipe Technique

Prepare a sufficient number of 20-mL sample vials, or aluminized plastic bags, each labeled with a unique number, for the projected sampling needs.

Prepare a diagram of the area or rooms to be wipe sampled along with the locations of key surfaces.

Wear a new pair of clean gloves for each sample to prevent contamination of future samples as well as oneself. The selected gloves are to be resistant to penetration of the chemical being

sampled and any other chemicals expected to be present. Nitrile gloves are suggested for sampling benzene based on a review of several glove manufacturer's chemical resistivity and degradation information. Do not wear powdered gloves.

Record the sample vial number and the location where the sample is taken.

Remove the charcoal pad from the carrying container with clean tweezers or gloved hand.

Depending on the purpose of the sample, it may be useful to determine the surface loading of the contamination (e.g., in micrograms of analyte per area). For these samples, it is necessary to record the area of the surface wiped (e.g., 100 cm²). This would not be necessary for samples taken to simply show the presence of the contaminant.

Surfaces should not be wetted with water as the water may adsorb along the benzene, decreasing the capacity of the charcoal pad for benzene.

Firm pressure should be applied when wiping. Start at the outside edge and progress toward the center making concentric squares of decreasing size. Fold the filter with the contaminant side inward and repeat.

Without allowing the charcoal pad to come into contact with any other surface, fold the charcoal pad with the exposed side inward. Place the charcoal pad in a sample vial and tightly cap it (or place in aluminized plastic bag and seal it), and place a corresponding number at the sample location on the diagram. Include notes with the sketch giving any further description that may prove useful when evaluating the sample results (e.g., a description of the surface sampled, such as pencil, doorknob, safety glasses, lunch table, inside respirator, employee names, etc.).

Submit at least one blank charcoal pad, treated in the same fashion (ie. take it out of the original container and place in sample vial or aluminized plastic bag), but without wiping.

Record sample location, employees names, surface area (if pertinent), work description, type of operation, personal protective equipment, and any other necessary information, along with any potential interferences on the OSHA-91A form.

Submit the samples to the OSHA Salt Lake Technical Center together with OSHA-91A forms as soon as possible after sampling. Ship any bulk samples separate from the surface samples.

5.3. Results and Discussion

The extraction studies performed in OSHA Method 1005 for the 3M 3520 OVM pertain also to these wipe samples. The mean extraction efficiency for benzene from dry 3M 3520 OVMs over the range of RQL to 2 times the target concentration (0.13 to 54.5 micrograms per sample) was 97.9% when using carbon disulfide to extract the samples. The extraction efficiency was not affected by the presence of water (average recovery of 98.1%).

The sampler removal efficiency was evaluated using the ideal surface of a glass plate. This type of surface approaches the smooth and non-porous characteristics of an ideal surface. The variety of surfaces found in workplaces will likely be less than ideal, so the media will have a lower removal efficiency. The amount of analyte found on the charcoal pad after sampling will indicate that at least that amount was present on the surface that was sampled. The glass plate was spiked with a solution of benzene in carbon disulfide, and immediately wiped with the charcoal pad, to avoid loss due to evaporation from the glass plate. Six surfaces were spiked at the target concentration of benzene, 25 µg/100 cm². The average recovery was 94.1% (Table 5.1).

Table 5.1
 Sampler Removal Efficiency
 Data for Benzene

theoretical ($\mu\text{g}/\text{surface}$)	recovered ($\mu\text{g}/\text{sample}$)	recovery (%)
25	23.2	92.8
25	24.1	96.4
25	22.9	91.6
25	23.1	92.4
25	24.5	98.0
25	23.4	93.6

The storage studies were performed by spiking a glass plate with a solution containing benzene, wiping immediately, and then the charcoal pad was placed into a 20-mL vial and tightly capped. Three samples were analyzed immediately. Fifteen of the samples were stored at ambient temperature and fifteen were stored at refrigerated temperature. The recovery was 93.6% for ambient storage and 95.0% for refrigerated storage for the fifteen days stored (Table 5.2).

Table 5.2
 Storage Test for Benzene

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
	0	97.3	94.8	95.3	97.3	94.8
4	96.9	95.1	95.5	95.2	96.4	93.3
8	95.8	94.3	92.4	96.1	92.9	94.5
15	92.8	95.1	93.2	97.1	95.5	93.8

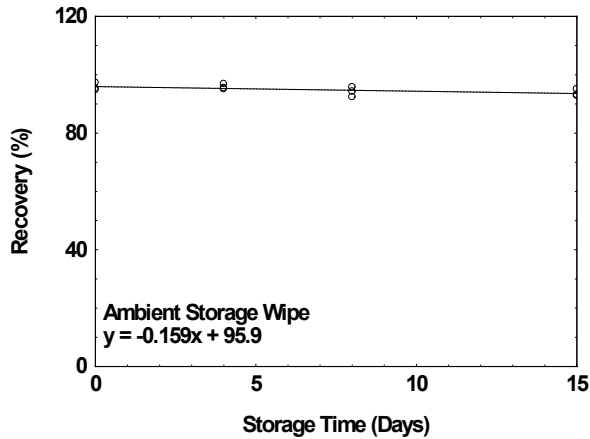


Figure 5.1 This is a plot of the benzene wipe ambient storage data found in Table 5.2.

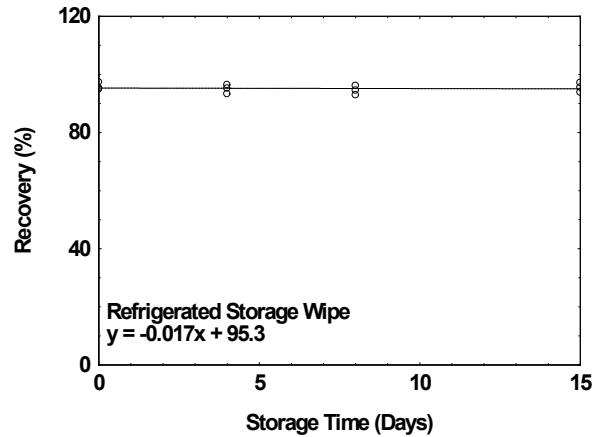


Figure 5.2 This is a plot of the benzene wipe refrigerated storage data found in Table 5.2.

Sampling reproducibility studies were performed by having a chemist, other than the one developing the method, conduct sampling on the glass plate using the charcoal pad. The test was repeated with a second chemist performing the sampling. The samples were analyzed. The first chemist was able to achieve a removal efficiency of 94.1% and the second chemist 93.3% (Tables 5.3 and 5.4).

Table 5.3
Sampling Reproducibility
1st Chemist Samples for Benzene

theoretical ($\mu\text{g}/\text{surface}$)	recovered ($\mu\text{g}/\text{sample}$)	recovery (%)
25	24.0	96.0
25	23.5	94.0
25	22.6	90.4
25	23.9	95.6
25	24.1	96.4
25	23.1	92.4

Table 5.4
Sampling Reproducibility
2nd Chemist Samples for Benzene

theoretical ($\mu\text{g}/\text{surface}$)	recovered ($\mu\text{g}/\text{sample}$)	recovery (%)
25	24.1	96.4
25	22.5	90.0
25	23.9	95.6
25	22.9	91.6
25	23.6	94.4
25	22.9	91.6

The reproducibility of the analytical wipe method was tested by taking six samples from the glass plate and submitting them, with a copy of the method, to the OSHA SLTC for analysis. The samples were analyzed after being stored for 10 days at 23 °C. The average recovery was 94.0% (Table 5.5).

Table 5.5
Analytical Reproducibility
Data for Benzene

theoretical ($\mu\text{g}/\text{surface}$)	recovered ($\mu\text{g}/\text{sample}$)	recovery (%)
25	23.1	92.4
25	24.2	96.8
25	22.8	91.2
25	22.7	90.8
25	23.9	95.6
25	24.3	97.2

5.4. Conclusion

Wipe samples for benzene can be collected on charcoal pads. The surface to be sampled should have some residue on it, as a dry surface will have no benzene on it. It is important to tightly seal the vials the charcoal pads are placed in, and to send a blank, as the charcoal pads can absorb any organic chemical they may come into contact with.