Method number:	1005

Target concentration:	1 ppm
OSHA PEL:	1 ppm (3.19 mg/m³)(TWA); 5 ppm (16.0 mg/m³)(15-min STEL); 50 ppm (160 mg/m³)(10-min Peak) in General Industry (29 CFR 1910.1028)
	10 ppm (31.9 mg/m³)(TWA); 25 ppm (79.8 mg/m³)(15-min Ceiling) in sectors excluded from General Industry (29 CFR 1926.1028)
	1 ppm (3.19 mg/m³)(TWA); 5 ppm (16.0 mg/m³)(15-min STEL); 50 ppm (160 mg/m³)(10-min Peak) in Shipyard and Construction Industries
ACGIH TLV:	0.5 ppm (1.6 mg/m³) TWA; 2.5 ppm (8.0 mg/m³)(15-min STEL) (Skin)

Procedure:	Active samples are collected by drawing workplace air through charcoal tubes with personal sampling pumps. Diffusive samples are collected by exposing either SKC 575-002 Passive Samplers or 3M 3520 Organic Vapor Monitors (OVM) to workplace air. Samples are extracted with carbon disulfide and analyzed by GC using a flame ionization detector (FID).

Recommended sampling time and sampling rate:	
Charcoal tubes:	240 min at 50 mL/min (12 L)(TWA); 10 min at 50 mL/min (0.5 L)(Peak); 15 min at 50 mL/min (0.75 L)(STEL)

SKC 575-002 Passive Sampler and 3M 3520 OVM:	240 min (TWA); 10 min (Peak); 15 min (STEL) (Note: SKC 575-002 Passive Samplers and 3M 3520 OVMs must be exposed for at least 10 min)

Reliable quantitation limit (RQL) and standard error of estimate (SEE):

Media	RQL		SEE*
	(ppb)	(µg/m³)	(%)
Charcoal tube	3.32	11	5.1
SKC 575-002 Passive Sampler	4.25	14	8.8
3M 3520 OVM	3.55	11	7.4

*For samples where sampling site atmospheric pressure and temperature are known. When either or both of these values are unknown, see Section 4.4 for applicable standard errors of estimate.

Special requirements:	Report sampling site atmospheric pressure and temperature when using diffusive samplers.

Status of method:	Evaluated method. This method has been subjected to the established evaluation procedures of the Methods Development Team.

November 2001   Mary E. Eide

Methods Development Team
Industrial Hygiene Chemistry Division
OSHA Salt Lake Technical Center
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1. General Discussion

    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]

        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 myclotoxicant known to supress 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

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[1] OSHA Computerized Information System Database, Chemical Sampling Information, http://www.osha.gov, (accessed August 2001)

[2] OSHA Computerized Information System Database, Chemical Sampling Information, http://www.osha.gov, (accessed August 2001)

[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, http://www.osha.gov, (accessed August 2001)

times more likely to die from leukemia than an unexposed worker.[5] IARC has published a risk assesment 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]

1.1.4   Physical properties and descriptive information[11,12,13]

CAS number:	71-43-2	vapor pressure:	10 kPa at 20 °C
IMIS number[14]:	0320	lower explosive limit:	1.5 to 8% by volume
molecular weight:	78.11	flash point:	11 °C (12 °F) (cc)
boiling point:	80.1 °C	odor:	characteristic aromatic
melting point:	5.5 °C	appearance:	colorless liquid
specific gravity:	0.879 at 20 °C	molecular formula:	C_6H_6
synonyms:	benzol; coal naphtha; cyclohexatriene; phenyl hydride		
solubility:	slightly soluble in water; miscible in alcohol, acetone. carbon disulfide, carbon tetrachloride, chloroform, ether, glacial acetic acid, and oils		

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.

11 *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.

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

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

14 OSHA Computerized Information System Database, Chemical Sampling Information, http://www.osha.gov, (accessed August 2001)

structure:
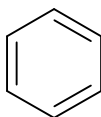
This method was evaluated according to the OSHA SLTC "Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis"[15]. The Guidelines define analytical parameters, specify required laboratory tests, statistical calculations and acceptance criteria. The analyte air concentrations throughout this method are based on the recommended sampling and analytical parameters. Air concentrations listed in ppm are referenced to 25 °C and 101.3 kPa (760 mmHg).

1.2   Limit defining parameters

1.2.1   Detection limit of the analytical procedure

The detection limit of the analytical procedure is 3.12 pg. This is the amount of analyte that will give a detector response that is significantly different from the response of a reagent blank. (Section 4.1)

1.2.2   Detection limit of the overall procedure

The detection limits of the overall procedure are 38 ng/sample for charcoal tubes, 49 ng/sample for SKC 575-002 Passive Samplers, and 41 ng/sample for 3M 3520 OVMs. These are the amounts of benzene spiked on the respective sampler that will give detector responses that are significantly different from the responses of respective sampler blanks. (Section 4.2)

Table 1.2.2
Detection Limits of the Overall Procedure

sampler	ng	ppb	$\mu g/m^3$
charcoal tube	38	0.99	3.17
SKC 575-002	49	1.28	4.08
3M 3520	41	1.07	3.42

1.2.3   Reliable quantitation limit

The reliable quantitation limits are 127 ng per sample (3.3 ppb or 11 $\mu g/m^3$) for charcoal tubes, 163 ng per sample (4.3 ppb or 14 $\mu g/m^3$) for SKC 575-002 Passive Samplers, and 136 ng per sample (3.6 ppb or 11 $\mu g/m^3$) for 3M 3520 OVMs. These are the amounts of benzene spiked on the respective samplers that will give detector responses that are considered the lower limits for precise quantitative measurements. (Section 4.2)

Table 1.2.3
Reliable Quantitation Limits

sampler	ng	ppb	$\mu g/m^3$	E_E
charcoal tube	127	3.32	10.6	96.6
SKC 575-002	163	4.26	13.6	93.1
3M 3520	136	3.55	11.3	97.9

1.2.4   Instrument calibration

The standard error of estimate is 0.34 µg over the range of 9.9 to 79.1 µg. This range corresponds to 0.25 to 2 times the TWA target concentration. (Section 4.3)

1.2.5   Precision

Charcoal tubes

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[15] Burright, D.; Chan, Y.; Eide, M.; Elskamp, C.; Hendricks, W.; Rose, M. C. *Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis,* http://www.osha.gov, (accessed August 2001).

The precision of the overall procedure at the 95% confidence level for the ambient temperature 19-day storage test for samples collected from a dynamically generated atmosphere of 1.2 ppm (3.84 mg/m^3) collected on charcoal tubes is $\pm$ 9.94%. This includes an additional 5% for sampling pump variability. (Section 4.4)

SKC 575-002 Passive Samplers

The precisions of the overall procedure at the 95% confidence level for the ambient temperature 19-day storage test for samples collected from a dynamically generated atmosphere of 1.2 ppm (3.84 mg/m^3) collected on SKC 575-002 Passive Samplers are given in Table 1.2.5.1.

Table 1.2.5.1
Precision of the Overall Procedure for SKC 575-002 Passive Samplers

known conditions	precision ($\pm$%)
both T & P	17.2
only T	18.1
only P	22.8
neither T nor P	23.6

They each include an additional 8.7% for sampling rate variability. There are different values given, depending on whether both, either, or neither temperature (T) or atmospheric pressure (P) are known at the sampling site. If the sampling site temperature is unknown, it is assumed to be 22.2 $\pm$ 15 °C (72 $\pm$ 27 °F) and a variability of $\pm$7.7% is included. If the atmospheric pressure is not known, it is estimated from the sampling site elevation and a variability of $\pm$3% is included. (Section 4.4)

3M 3520 OVMs

The precisions of the overall procedure at the 95% confidence level for the ambient temperature 19-day storage test for samples collected from a dynamically generated atmosphere of 1.2 ppm (3.84 mg/m^3) collected on 3M 3520 OVMs are given in Table 1.2.5.2. They each include an additional 6.4% for

Table 1.2.5.2
Precision of the Overall Procedure for 3M 3520 OVMs

known conditions	precision ($\pm$%)
both T & P	12.6
only T	13.9
only P	19.6
neither T nor P	20.6

sampling rate variability. There are different values given, depending on whether both, either, or neither temperature (T) or atmospheric pressure (P) are known at the sampling site. If the sampling site temperature is unknown, it is assumed to be 22.2 $\pm$ 15 °C (72 $\pm$ 27 °F) and a variability of $\pm$7.7% is included. If the atmospheric pressure is not known, it is estimated from the sampling site elevation and a variability of $\pm$3% is included. (Section 4.4)

1.2.6   Recovery

The recovery of benzene from samples used in a 19-day storage test remained above 98.0%, 96.5%, and 96.2% when the samples were stored at 23 °C for charcoal tubes, SKC 575-002 Passive Samplers, and 3M 3520 OVMs, respectively. (Section 4.5)

1.2.7   Reproducibility

Six samples for each of the three types of samplers were collected from a controlled test atmosphere and submitted for analysis by the OSHA Salt Lake Technical Center. The samples were analyzed according to a draft copy of this procedure after 7 days of storage at 4 °C. No individual sample result deviated from its theoretical value by more than the precision reported in Section 1.2.5. (Section 4.6)

2. Sampling Procedure

All safety practices that apply to the work area being sampled should be followed. The sampling equipment should be attached to the worker in a manner that will not interfere with work performance or safety.

2.1   Apparatus

    2.1.1   Charcoal tubes

        Samples are collected with 7-cm × 4-mm i.d. × 6-mm o.d. glass sampling tubes packed with two sections of coconut shell charcoal. The front section contains 100 mg and the back section contains 50 mg of charcoal. The sections are held in place with glass wool and polyurethane plugs. For this evaluation, commercially prepared charcoal tubes were purchased from SKC, Inc. (catalog no. 226-01, Anasorb CSC, lot 2000).

        Samples are collected using a personal sampling pump calibrated, with the sampling device attached, to within ±5% of the recommended flow rate.

    2.1.2   SKC 575-002 Passive Samplers and 3M 3520 OVMs

        Samples are collected with either SKC 575-002 Passive Samplers, or with 3M 3520 OVMs. Samplers were purchased from SKC, Inc. (catalog no. 575-002, contains 500 mg of Anasorb 747) or from 3M (catalog no. 3520, contains two charcoal adsorbent pads).

        A thermometer and barometer to determine the sampling site air temperature and atmospheric pressure.

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 manufacture'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 17.1 mL/min for SKC 575-002 Passive Samplers and 34.3 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 than the 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/m^3) 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 17.1 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 0.20 ppm (0.64 mg/m^3) 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 34.3 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/m^3) for benzene when 0.51 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 100.4%, when charcoal tubes containing 880 µg 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 99.7% 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/m^3 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/m^3 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/m^3 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 Plan[16]. 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.

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

3.1.3   An electronic integrator or other suitable means of measuring GC detector response. A Waters Millenium[32] 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.

3.1.7   Volumetric flasks - 10-mL and other convenient sizes for preparing standards.

3.1.8   Calibrated 10-μL syringe for preparing standards.

3.1.9   An SKC Desorption shaker with rack (226D-03K) was used to extract SKC 575-002 Passive Samplers in this evaluation.

3.1.10   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 (CS_2), [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).

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 μL/mL n-hexylbenzene (1-phenylhexane) in the CS_2. The n-hexylbenzene was added to the CS_2 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 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 (df = 5.0 µm)
retention times: 9.26 min (carbon disulfide) 13.66 min (benzene) 32.491 min (n-hexyl benzene)

FID conditions
hydrogen flow: 35 mL/min
air flow: 450 mL/min
nitrogen makeup
flow: 35 mL/min
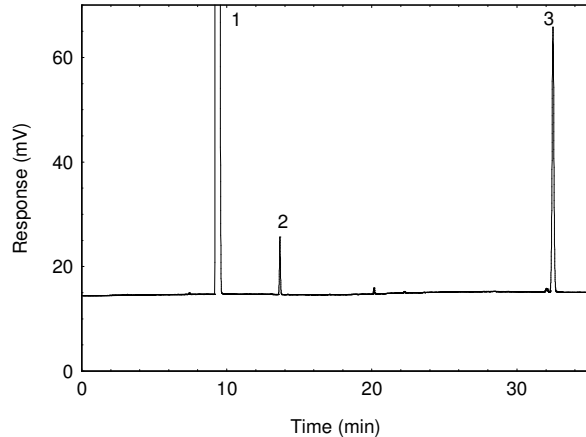
Figure 3.5.1. Chromatogram obtained at the target concentration with the recommended conditions. (1 = carbon disulfide; 2 = benzene; and 3 =n-hexylbenzene)

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.
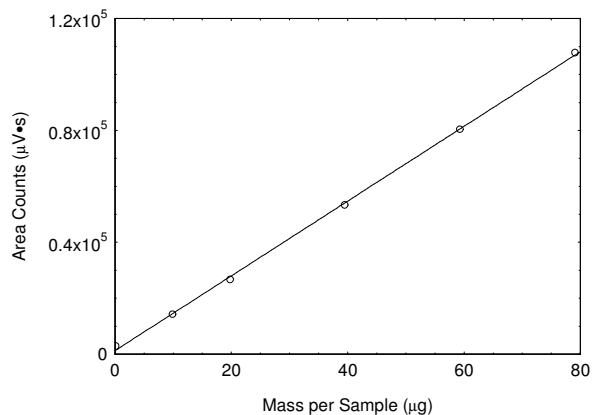
Figure 3.5.2. A calibration curve of benzene. (Y = 1356X + 199)

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 tubes

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.

$$C_M = \frac{M}{VE_E}$$

where C_M is concentration by weight (mg/m^3)
M is micrograms per sample
V is liters of air sampled
E_E is extraction efficiency, in decimal form

$$C_V = \frac{V_M C_M}{M_r}$$

where C_V is concentration by volume (ppm)
$V_M = 24.46$ at NTP
C_M is concentration by weight
M_r is molecular weight of 78.11

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.

$$R_{SS} = R_{NTP}\left(\frac{T_{SS}}{T_{NTP}}\right)^{\frac{3}{2}}\left(\frac{P_{NTP}}{P_{SS}}\right)$$

where R_{SS} is the sampling rate at sampling site
R_{NTP} is the sampling rate at NTP conditions (SKC 575-002 = 17.1 mL/min, 3M OVM = 34.3 mL/min)
T_{SS} is the sampling site temperature in K
T_{NTP} is 298.2 K
P_{SS} is the sampling site pressure in mmHg
P_{NTP} is 760 mmHg

$$C_M = \frac{10^3\, M}{tR_{SS}E_E}$$

where C_M is concentration by weight (mg/m^3)
M is micrograms per sample
R_{SS} is the sampling rate at the sampling site
t is the sampling time
E_E is extraction efficiency, in decimal form

$$C_V = \frac{V_M C_M}{M_r}$$

where C_V is concentration by volume (ppm)
$V_M = 24.46$ at NTP
C_M is concentration by weight
M_r is molecular weight of 78.11

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/ft^2
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-µL 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 (µV-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
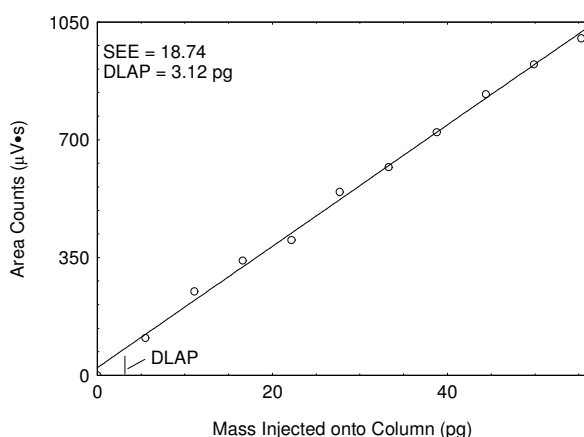
Figure 4.1. Plot of data to determine the DLAP. (Y = 18.0X + 22.8)

[17] Burright, D.; Chan, Y.; Eide, M.; Elskamp, C.; Hendricks, W.; Rose, M. C. *Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis,* http://www.osha.gov, (accessed August 2001).

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 0.958 and 15.58 were obtained for the slope and standard error of estimate for SKC 575-002 Passive Samplers, repsectively. The DLOP for SKC 575-002 Passive Samplers was calculated to be 49 ng/sample (4 ppb). Values of 0.918 and 12.45 were obtained for the slope and standard error of estimate for 3M 3520 OVMs, respectively. The DLOP for 3M 3520 OVMs was calculated to be 41 ng/sample (1 ppb).

Table 4.2.1
Detection Limit of the Overall Procedure
on Charcoal Tubes

mass per sample (ng)	area counts (µV-s)
0	0
105	103
211	175
316	293
422	383
527	488
633	563
738	683
844	784
949	889
1050	992
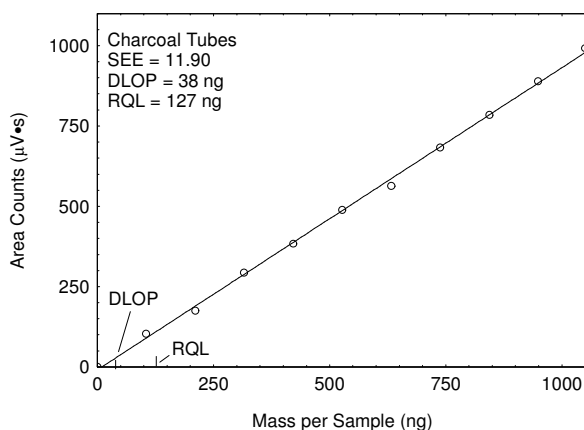
Figure 4.2.1. Plot of data to determine the DLOP/RQL on charcoal tubes (lot 2000). (y = 0.940x - 8.80)

Table 4.2.2
Detection Limit of the Overall Procedure
on SKC 575-002 Passive Samplers

mass per sample (ng)	area counts (µV•s)
0	0
105	114
211	255
316	346
422	409
527	551
633	623
738	728
844	841
949	944
1050	1040
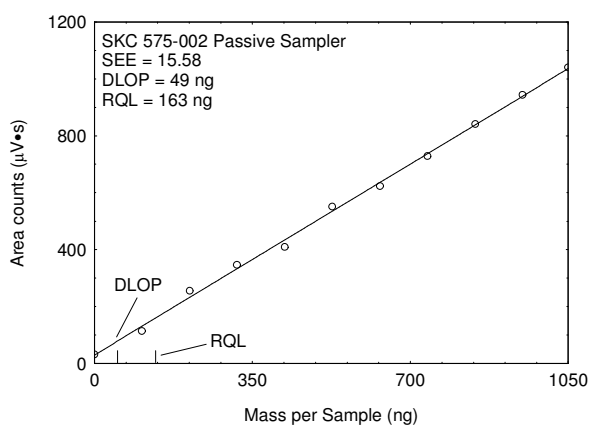
Figure 4.2.2. Plot of data to determine the DLOP/RQL on SKC 575-002 Passive Samplers. (y = 0.958x + 30.0)

Table 4.2.3
Detection Limit of the Overall Procedure
on 3M 3520 OVMs

mass per sample (ng)	area counts (μV•s)
0	0
105	111
211	211
316	296
422	391
527	517
633	606
738	687
844	786
949	862
1050	982
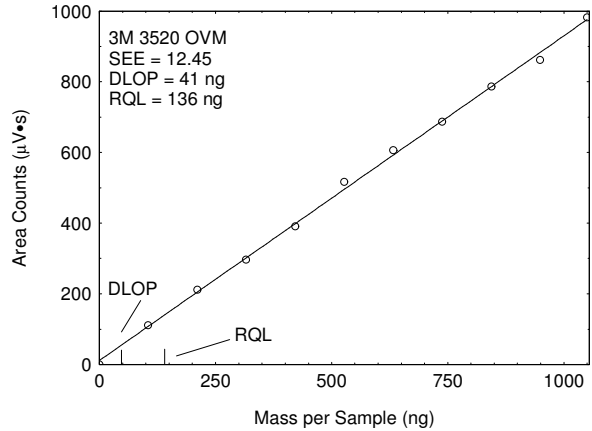
Figure 4.2.3. Plot of data to determine the DLOP/RQL on 3M 3520 OVMs. (y = 0.918x + 11.5)

The RQL is considered the lower limit for precise quantitative measurements. It is determined from the regression line parameters obtained for the calculation of the DLOP, providing 75% to 125% of the analyte is recovered. The RQLs for the various media are listed in Table 4.2.4.

Table 4.2.4
Reliable Quantitation Limits

sampler	ng	ppb	μg/m³	E_E
charcoal tube	127	3.32	10.6	96.6
SKC 575-002	163	4.26	13.6	93.1
3M 3520	136	3.55	11.3	97.9
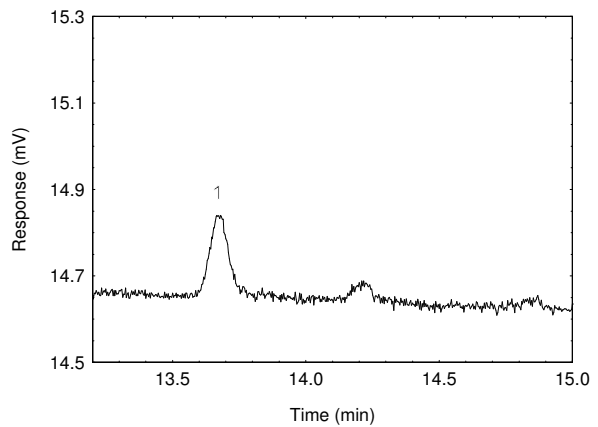
Figure 4.2.4. Chromatogram of the RQL. (1 = benzene)

4.3   Instrument calibration

The standard error of estimate was determined from the linear regression of data points from standards over a range that covers 0.25 to 2 times the TWA target concentration. A calibration curve was constructed and shown in Section 3.5.2 from the six injections of five standards. The standard error of estimate is 0.34 μg.

Table 4.3
Instrument Calibration

standard concn (μg/mL)	area counts (μV•s)					
9.9	14230	14187	14329	14284	14229	14219
19.8	26684	26783	26645	26743	26523	26589
39.5	53374	53487	53380	53409	53312	53287
59.3	80390	80450	80334	80299	80387	80401
79.1	107770	108450	107689	107651	107743	107812

4.4 Precision (overall procedure)

4.4.1 Charcoal tubes

The precision at the 95% confidence level is obtained by multiplying the standard error of estimate by 1.96 (the z-statistic from the standard normal distribution at the 95% confidence level). In Section 4.5, 95% confidence intervals are drawn about their respective regression lines in the storage graph figures. The precision of the overall procedure of ± 9.94 % was obtained from the standard error of estimate of 5.07% in Figure 4.5.1.1. The precision includes an additional 5% for sampling error.

4.4.2 SKC 575-002 Passsive Samplers

The precisions of the overall procedure at the 95% confidence level for the ambient temperature 19-day storage test (at the target concentration) from SKC 575-002 Passive Samplers are given in Table 4.4.2. They each include an additional 8.7% for sampling rate variability. There are different values given, depending on whether both, either, or neither temperature (T) or atmospheric pressure (P) are known at the sampling site. If the sampling site temperature is unknown, it is assumed to be 22.2 ± 15 °C (72 ± 27 °F) and a variability of ±7.7% is included. If the atmospheric pressure is not known, it is estimated from the sampling site elevation and a variability of ±3% is included.

Table 4.4.2
Standard Error of Estimate
and Precision of the Overall Procedure for
SKC 575-002 Passive Samplers

known condition	error (%)	precision (±%)
both T & P	8.75	17.2
only T	9.25	18.1
only P	11.65	22.8
neither T nor P	12.03	23.6

4.4.3 3M 3520 OVMs

The precisions of the overall procedure at the 95% confidence level for the ambient temperature 19-day storage test (at the target concentration) from 3M 3520 OVMs are given in Table 4.4.3. They each include an additional 6.4% for sampling rate variability. There are different values given, depending on whether both, either, or neither temperature (T) or atmospheric pressure (P) are known at the sampling site. If the sampling site temperature is unknown, it is assumed to be 22.2 ± 15 °C (72 ± 27 °F) and a variability of ±7.7% is included. If the atmospheric pressure is not known, it is estimated from the sampling site elevation and a variability of ±3% is included.

Table 4.4.3
Standard Error of Estimate and Precision of the
Overall Procedure for 3M 3520 OVMs

known condition	error (%)	precision (±%)
both T & P	6.45	12.6
only T	7.11	13.9
only P	10.0	19.6
neither T nor P	10.5	20.6

4.5 Storage test

4.5.1 Charcoal tubes

Storage samples for benzene were prepared by collecting samples from a controlled test atmosphere using the recommended sampling conditions. The concentration of benzene was at the target concentration and the absolute humidity was 15.7 milligrams of water per liter of air (about 80% at 22.2 °C). Thirty-three storage samples were prepared. Three samples were analyzed on the day of generation. Fifteen of the tubes were stored at reduced temperature (4 °C) and the other fifteen were stored in a closed drawer at ambient temperature (about 22 °C). At 2-5 day intervals, three samples were selected

from each of the two storage sets and analyzed. Sample results are not corrected for extraction efficiency.

Table 4.5.1
Storage Test for Benzene on Charcoal Tubes

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	98.9	99.9	100.4	98.9	99.9	100.4
5	99.4	98.9	97.9	98.8	100.3	99.7
8	97.9	99.4	99.1	99.5	100.4	98.8
12	98.1	99.9	97.9	100.1	99.9	97.9
15	98.5	98.9	96.9	97.7	99.1	98.5
19	96.8	99.1	98.4	97.9	99.8	98.4

Ambient Storage Charcoal Tubes
y = -0.0806 x + 99.5
Std Error of Estimate = 5.07%
95% Confidence Limits = ± (1.96)(5.07) = ± 9.94%

Refrigerated Storage Charcoal Tubes
y = -0.077 x + 100
Std Error of Estimate = 5.06%
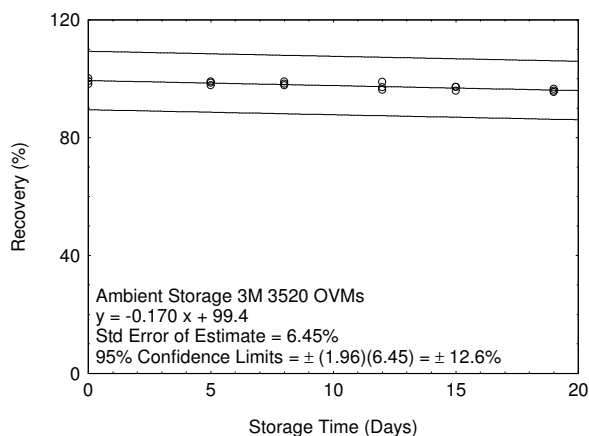95% Confidence Limits = ± (1.96)(5.06) = ± 9.92%
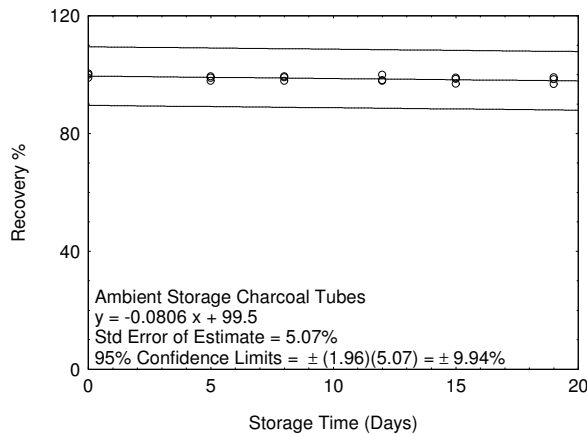
Figure 4.5.1.1. Ambient storage test for benzene collected on charcoal tubes.
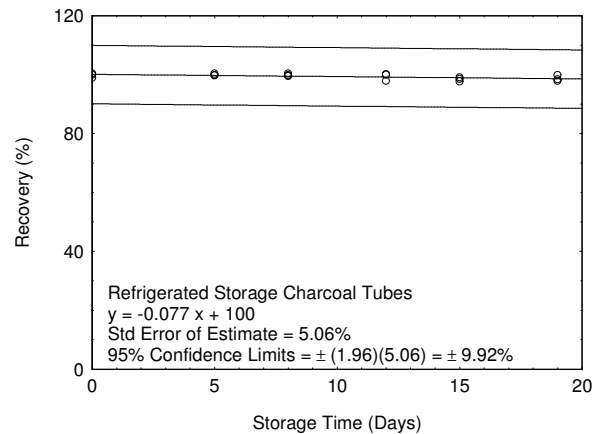
Figure 4.5.1.2. Refrigerated storage test for benzene collected on charcoal tubes.

4.5.2   SKC 575-002 Passive Samplers

Storage samples for benzene were prepared by collecting samples from a controlled test atmosphere using the recommended sampling conditions. The concentration of benzene was at the target concentration and the absolute humidity was 15.7 milligrams of water per liter of air (about 80% at 22.2 °C). Thirty-three storage samples were prepared. Three samples were analyzed on the day of generation. Fifteen of the samplers were stored at reduced temperature (4 °C) and the other fifteen were stored in a closed drawer at ambient temperature (about 22 °C). At 2-5 day intervals, three samples were selected from each of the two storage sets and analyzed. Sample results are not corrected for extraction efficiency.

Table 4.5.2
Storage Test for Benzene on SKC 575-002 Passive Samplers

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	100.5	100.6	98.9	100.5	100.6	98.9
5	99.6	100.1	98.8	99.3	99.4	100.3
8	99.4	98.8	96.8	99.9	99.1	98.8
12	97.9	98.8	98.2	100.1	98.6	99.5
15	96.6	98.6	96.1	98.9	99.6	97.5
19	97.5	96.5	95.8	99.3	97.5	99.1
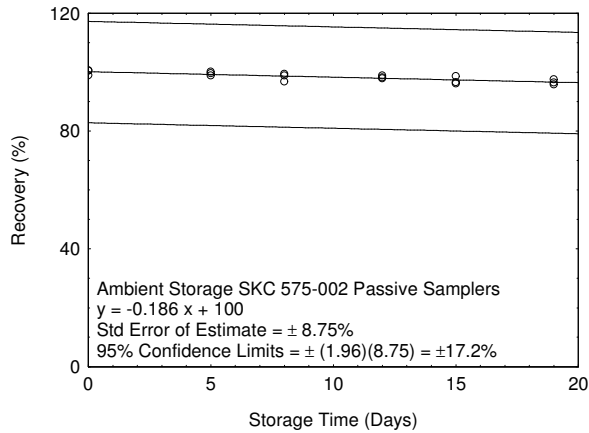
Figure 4.5.2.1. Ambient storage test for benzene collected on SKC 575-002 Passive Samplers.
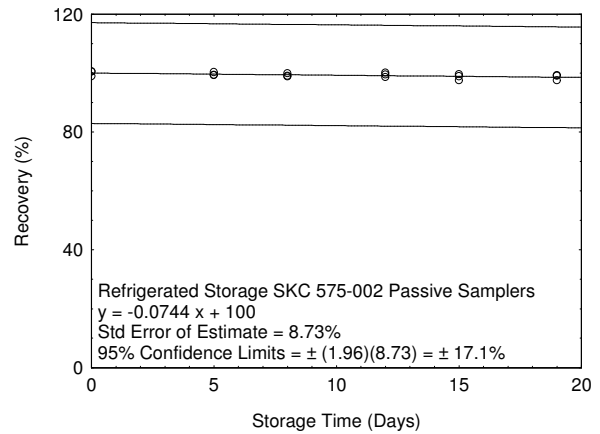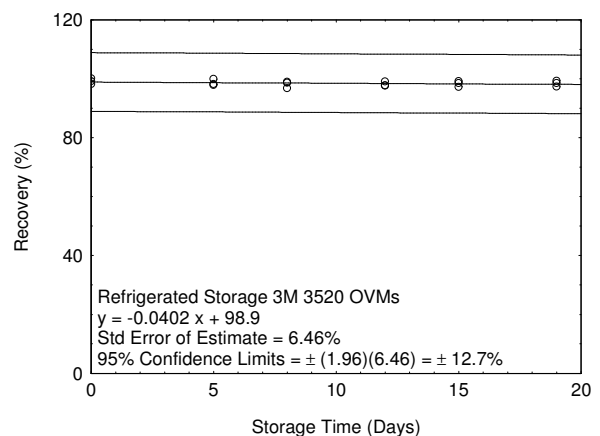

Figure 4.5.2.2. Refrigerated storage test for benzene collected on SKC 575-002 Passive Samplers.

4.5.3   3M 3520 OVMs

Storage samples for benzene were prepared by collecting samples from a controlled test atmosphere using the recommended sampling conditions. The concentration of benzene was at the target concentration and the absolute humidity was 15.7 milligrams of water per liter of air (about 80% at 22.2 °C). Thirty-three storage samples were prepared. Three samples were analyzed on the day of generation. Fifteen of the samplers were stored at reduced temperature (4 °C) and the other fifteen were stored in a closed drawer at ambient temperature (about 22 °C). At 2-5 day intervals, three samples were selected from each of the two storage sets and analyzed. Sample results are not corrected for extraction efficiency.

Table 4.5.3
Storage Test for Benzene on 3M 3520 OVMs

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	100.1	99.2	98.2	100.1	99.2	98.2
5	98.6	99.1	97.8	99.9	98.2	97.9
8	99.1	97.8	98.3	98.6	98.9	96.8
12	96.2	98.9	97.1	99.1	97.6	97.8
15	97.2	95.9	97.2	98.5	99.2	97.2
19	96.6	95.5	95.9	99.3	98.5	97.3

Figure 4.5.3.1. Ambient storage test for benzene collected on 3M 3520 OVMs.

Figure 4.5.3.2. Refrigerated storage test for benzene collected on 3M 3520 OVMs.

4.6   Reproducibility

Six samples were prepared for the three types of samplers by collecting them from a controlled test atmosphere similar to that which was used in the collection of the storage samples. The samples were submitted to the OSHA Salt Lake Technical Center for analysis, along with a draft copy of this method. The samples were analyzed after being stored for 7 days at 4 °C. Sample results were corrected for extraction efficiency. No sample result for benzene had a deviation greater than the precision of the overall procedure determined in Section 4.4.

Table 4.6.1
Reproducibility Data for Benzene on
Charcoal Tubes

theoretical (μg/sample)	recovered (μg/sample)	recovery (%)	deviation (%)
76.91	73.61	95.7	−4.3
83.34	81.58	97.9	−2.1
77.84	75.17	96.6	−3.4
88.56	85.62	96.7	−3.3
79.73	75.29	94.4	−5.6
78.98	74.88	94.8	−5.2

Table 4.6.2
Reproducibility Data for Benzene on SKC
575-002 Passive Samplers

theoretical (μg/sample)	recovered (μg/sample)	recovery (%)	deviation (%)
26.38	25.62	97.1	−2.9
26.38	25.03	94.9	−5.1
26.38	25.43	96.4	−3.6
26.38	25.21	95.6	−4.4
26.38	26.01	98.5	−1.5
26.38	25.33	96.0	−4.0

Table 4.6.3
Reproducibility Data for Benzene on
3M 3520 OVMs

theoretical (μg/sample)	recovered (μg/sample)	recovery (%)	deviation (%)
58.52	56.53	96.6	−3.4
58.52	56.18	96.0	−4.0
58.52	55.95	95.6	−4.4
58.52	57.06	97.5	−2.5
58.52	55.59	95.0	−5.0
58.52	57.01	97.4	−2.6

4.7   Sampler capacity

4.7.1   Charcoal tubes

The sampling capacity of the front section of a charcoal tube was tested by sampling from a dynamically generated test atmosphere of benzene (72.8 mg/m^3 or 23 ppm) with an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2 °C). This air concentration was twice the highest PEL. The samples were collected along with diffusive samplers. Three charcoal tubes and three of each kind of diffusive samplers were collected at 5, 10, 15, and 30 min, and 1, 2, 3, 4, 6, 8, and 10 hours. The charcoal tube samples were collected at 50 mL/min. There was no breakthrough observed in any of the charcoal tubes, therefore the sampler capacity was never exceeded. The interference study of gasoline showed that for samples taken up to 8 hours, with a benzene concentration of 32 mg/m^3 or 10 ppm, and a gasoline concentration of 890 mg/m^3 had no breakthrough for the benzene, though the gasoline did breakthrough after 4 hours (Section 4.9).

4.7.2   SKC 575-002 Passive Samplers

The sampling rate and sampler capacity are determined with samples collected for increasing time intervals from a controlled test atmosphere. Sampler capacity is exceeded when the sampling rate decreases (greater than 10 hours for SKC 575-002).   The concentration of the test atmosphere was two times the target concentration with an absolute humidity of 15.7 milligrams of water per liter of air (about 80% at 22.2 °C). The preliminary sampling rate was determined by averaging the nine values for the 0.5, 1 and

2 h samples. Horizontal lines were placed 10% above and below the preliminary sampling rate. For an atmosphere of 2.3 ppm the sampling rate is 17.2 mL/min at 760 mmHg and 25 °C and represents the average of all values between the lines. The standard deviation and RSD are 0.453 mL/min and 2.63%, respectively. For an atmosphere of 23 ppm the sampling rate is 16.9 mL/min at 760 mmHg and 25 °C and represents the average of all values between the lines. The standard deviation and RSD are 0.411 mL/min and 2.43%, respectively. The average sampling rate from both determinations was 17.1 mL/min. The data obtained are shown in Table 4.7.2.1 and Figure 4.7.2.1. Mass collected is corrected for extraction efficiency. The sampling rate for a 5-minute sample is significantly different from the calculated sampling rate indicating that samples should not be taken for that short of a time. The recommended sampling time is 4 h for TWA samples, 10 min for Peak samples, and 15 min for STEL samples.

Table 4.7.2.1
Determination of Sampling Rate and Time for SKC 575-002 Passive Samplers from a 2.3-ppm Atmosphere

time (h)	sampling rate (mL/min)		
	first	second	third
0.083	19.2	19.0	18.8
0.167	18.3	18.6	18.4
0.25	18.0	17.9	18.1
0.5	17.8	17.5	17.7
1	17.2	17.3	17.4
2	16.9	16.8	16.4
3	16.2	16.8	16.3
4	16.3	16.1	16.0
6	16.4	16.2	16.3
8	16.2	16.5	16.1
10	16.0	16.1	15.9
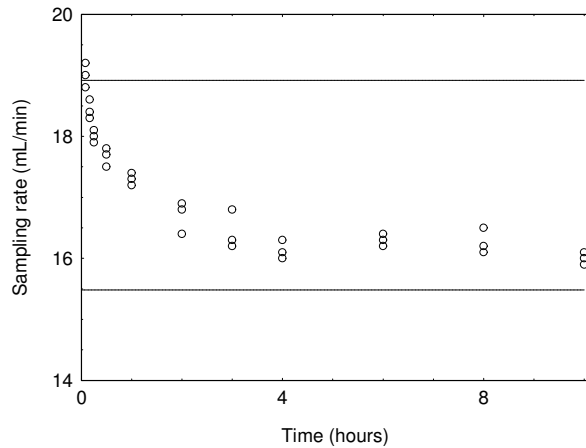
Figure 4.7.2.1. The SKC 575-002 Passive Sampler data plotted to determine the recommended sampling time and sampling rate from a 2.3-ppm atmosphere.

Table 4.7.2.2
Determination of Sampling Rate and Time for SKC 575-002 Passive Samplers from a 23-ppm Atmosphere

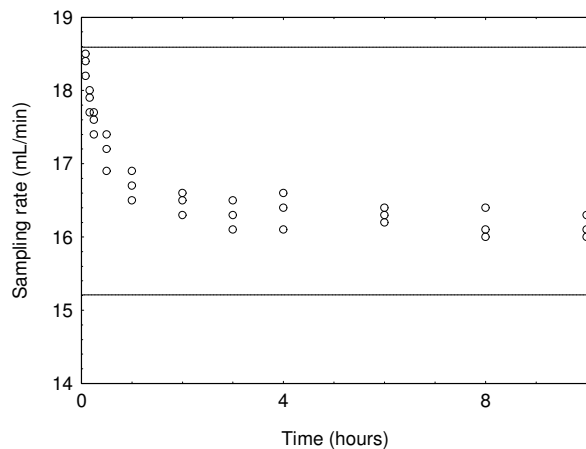| time (h)	sampling rate (mL/min)		
	first	second	third
0.083	18.4	18.5	18.2
0.167	18.0	17.7	17.9
0.25	17.4	17.7	17.6
0.5	17.2	17.4	16.9
1	16.7	16.5	16.9
2	16.5	16.3	16.6
3	16.1	16.3	16.5
4	16.4	16.1	16.6
6	16.4	16.3	16.2
8	16.4	16.1	16.0
10	16.3	16.0	16.1

Figure 4.7.2.2. The SKC 575-002 Passive Sampler data plotted to determine the recommended sampling time and sampling rate from a 23-ppm atmosphere.

4.7.3   3M 3520 OVMs

The sampling rate and sampler capacity are determined with samples collected for increasing time intervals from a controlled test atmosphere. Sampler capacity is exceeded when the sampling rate decreases(greater than 10 hours for 3M 3520 OVMs). The

concentration of the test atmosphere was two times the target concentration with an absolute humidity of 15.7 milligrams of water per liter of air (about 80% at 22.2 °C). The preliminary sampling rate was determined by averaging the nine values for the 0.5, 1 and 2 h samples. Horizontal lines were placed 10% above and below the preliminary sampling rate. For an atmosphere of 2.3 ppm the sampling rate is 34.3 mL/min at 760 mmHg and 25 °C and represents the average of all values between the lines. The standard deviation and RSD are 0.771 mL/min and 2.25%, respectively. The data obtained are shown in Table 4.7.3.1 and Figure 4.7.3.1. For an atmosphere of 23 ppm the sampling rate is 34.3 mL/min at 760 mmHg and 25 °C and represents the average of all values between the lines. The standard deviation and RSD are 0.466 mL/min and 1.36%, respectively. The data obtained are shown in Table 4.7.3.2 and Figure 4.7.3.2. Mass collected is corrected for extraction efficiency. The recommended sampling time is 4 h for TWA samples, 10 min for Peak samples, and 15 min for STEL samples.

Table 4.7.3.1
Determination of Sampling Rate and Time for 3M 3520
OVMs from a 2.3-ppm Atmosphere

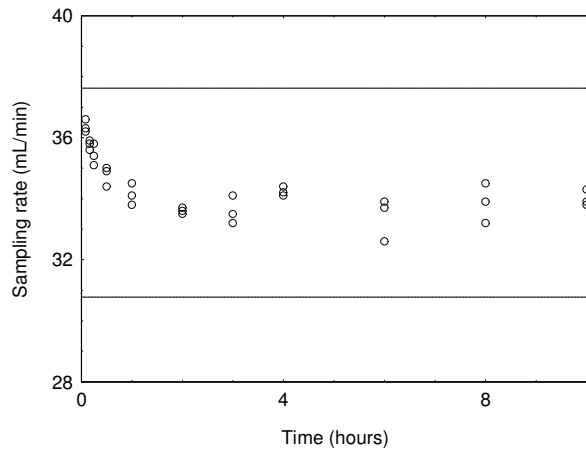| time (h)	sampling rate (mL/min)		
	first	second	third
0.083	36.2	36.3	36.6
0.167	35.6	35.9	35.8
0.25	35.1	35.8	35.4
0.5	34.4	35.9	34.9
1	34.5	34.1	33.8
2	33.5	33.6	33.7
3	34.1	33.5	33.2
4	34.2	34.4	34.1
6	32.6	33.9	33.7
8	34.5	33.2	33.9
10	34.3	33.8	33.9

Figure 4.7.3.1. The 3M 3520 OVM data plotted to determine the recommended sampling time and sampling rate for an atmosphere of 2.3 ppm.

Table 4.7.3.2
Determination of Sampling Rate and Time for 3M 3520
OVMs from a 23-ppm Atmosphere

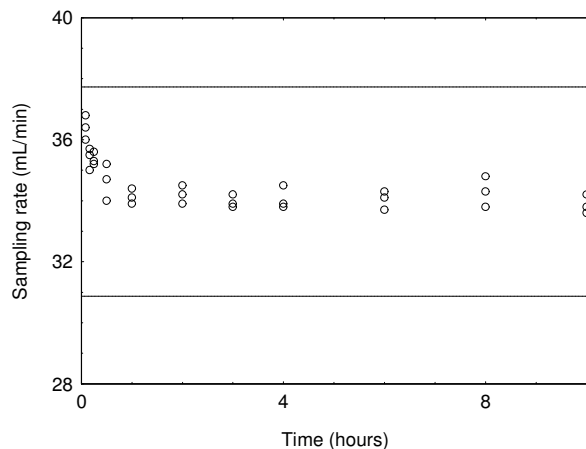| time (h)	sampling rate (mL/min)		
	first	second	third
0.083	36.8	36.0	36.4
0.167	35.5	35.0	35.7
0.25	35.2	35.6	35.3
0.5	34.0	35.2	34.7
1	34.1	34.4	33.9
2	33.9	34.5	34.2
3	33.9	34.2	33.8
4	33.8	33.9	34.5
6	34.1	33.7	34.3
8	34.3	33.8	34.8
10	34.2	33.6	33.8

Figure 4.7.3.2. The 3M 3520 OVM data plotted to determine the recommended sampling time and sampling rate for an atmosphere of 23 ppm.

4.8   Extraction efficiency and stability of extracted samples

The extraction efficiency is dependent on the extraction solvent as well as the internal standard. The extraction solvent used for this evaluation consisted of 0.25 µL/mL n-hexylbenzene (1-

phenylhexane) in the CS_2. Other extraction solvents or internal standards may be used provided that the new extraction solution or internal standard is tested. The new extraction solvent or internal standard should be tested as described below.

4.8.1   Charcoal tubes

Extraction efficiency

The extraction efficiencies of benzene were determined by liquid-spiking four charcoal tubes, at each concentration level, with the analyte from the RQL to 2 times the target concentration. These samples were stored overnight at ambient temperature and then analyzed. The mean extraction efficiency over the working range of the RQL to 2 times the target concentration is 97.0%. The extraction efficiency for the wet samplers was not included in the overall mean because it would bias the results. The test of wet samplers was performed to determine if the amount of water, that would collect under high humidity conditions at the recommended air volume, would affect the extraction efficiency.

Table 4.8.1.1
Extraction Efficiency of Benzene from Charcoal Tubes

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
RQL	0.13	98.5	97.3	95.3	95.1	96.6
0.25	9.9	98.6	95.3	96.6	97.3	97.0
0.5	19.8	97.6	98.2	97.6	98.2	97.9
1.0	39.5	96.7	97.1	96.3	97.0	96.8
1.5	59.3	96.9	95.5	96.9	97.3	96.7
2.0	79.1	97.2	96.5	97.2	97.1	97.0
1.0 (wet)	39.5	97.1	95.6	96.8	97.2	96.7

Stability of extracted samples

The stability of extracted samples was investigated by reanalyzing the target concentration samples 24 h after initial analysis. After the original analysis was performed two vials were recapped with new septa while the remaining two retained their punctured septa. The samples were reanalyzed with fresh standards. The average percent change was 0.9% for samples that were resealed with new septa and 3.4% for those that retained their punctured septa. Each septum was punctured 5 times for each injection. The test was performed at room temperature.

Table 4.8.1.2
Stability of Extracted Samples for Benzene on Charcoal Tubes

punctured septa replaced			punctured septa retained		
initial (%)	after one day (%)	difference (%)	initial (%)	after one day (%)	difference (%)
96.7	95.6	−1.1	96.3	92.1	−4.2
97.1	96.3	−0.8	97.0	94.5	−2.5
	(mean)			(mean)	
96.9	96.0	−0.9	96.7	93.3	−3.4

4.8.2   SKC 575-002 Passive Sampler

Extraction efficiency

The extraction efficiencies of benzene were determined by liquid-spiking four SKC 575-002 Passive Samplers, at each concentration level, with the analyte at the RQL to 2 times the target concentration. These samples were stored overnight at ambient temperature and

then extracted and analyzed. The average extraction efficiency over the working range of RQL to 2 times the target concentration was 93.6%. The extraction efficiency for the wet samplers was not included in the overall mean because it would bias the results. The test of wet samplers was performed to determine if the amount of water, that would collect under high humidity conditions at the recommended air volume, would affect the extraction efficiency.

Table 4.8.2.1
Extraction Efficiency of Benzene from SKC 575-002 Passive Samplers

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
RQL	0.13	93.8	92.4	91.4	94.6	93.1
0.25	3.08	95.2	94.3	93.4	93.1	94.0
0.5	6.15	93.3	94.3	93.8	92.6	93.5
1.0	12.3	94.9	93.6	94.3	92.2	93.8
1.5	18.5	92.4	93.8	93.5	93.3	93.3
2.0	24.6	94.2	93.4	94.2	93.1	93.7
1.0 (wet)	12.3	93.5	94.5	93.6	94.0	93.9

Stability of extracted samples

The stability of extracted samples was investigated by reanalyzing the target concentration samples 24 h after initial analysis. After the original analysis was performed two vials were recapped with new septa while the remaining two retained their punctured septa. The samples were reanalyzed with fresh standards. The average percent change was 1.3% for samples that were resealed with new septa and 2.6% for those that retained their punctured septa. Each septum was punctured 5 times for each injection. The test was performed at room temperature.

Table 4.8.2.2
Stability of Extracted Samples for Benzene on SKC 575-002 Passive Samplers

punctured septa replaced			punctured septa retained		
initial (%)	after one day (%)	difference (%)	initial (%)	after one day (%)	difference (%)
94.9	93.1	−1.8	94.3	91.2	−3.1
93.6	92.8	−0.8	92.2	90.2	−2.0
	(mean)			(mean)	
94.3	93.0	−1.3	93.3	90.7	−2.6

4.8.3   3M 3520 OVMs

Extraction efficiency

The extraction efficiencies of benzene were determined by liquid-spiking four 3M 3520 OVMs, at each concentration level, with the analyte at the RQL to 2 times the target concentration. These samples were stored overnight at ambient temperature and then extracted and analyzed. The average extraction efficiency over the working range of RQL to 2 times the target concentration was 97.9%. The extraction efficiency for the wet samplers was not included in the overall mean because it would bias the results. The test of wet samplers was performed to determine if the amount of water, that would collect under high humidity conditions at the recommended air volume, would affect the extraction efficiency.

Table 4.8.3.1
Extraction Efficiency of Benzene from 3M 3520 OVMs

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
RQL	0.13	98.5	97.7	98.2	97.2	97.9
0.25	6.81	97.4	98.1	97.7	97.8	97.8
0.5	13.6	97.3	98.8	97.8	98.1	98.0
1.0	27.2	97.2	98.2	97.4	98.5	97.8
1.5	40.9	98.0	97.6	97.7	98.1	97.9
2.0	54.5	98.4	98.0	98.6	97.8	98.2
1.0 (wet)	27.2	98.4	97.9	97.7	98.2	98.1

Stability of extracted samples

The stability of extracted samples was investigated by reanalyzing the target concentration samples 24 h after initial analysis. After the original analysis was performed two vials were recapped with new septa while the remaining two retained their punctured septa. The samples were reanalyzed with fresh standards. The average percent change was 0.6% for samples that were resealed with new septa and 1.9% for those that retained their punctured septa. Each septum was punctured 5 times for each injection. The test was performed at room temperature.

Table 4.8.3.2
Stability of Extracted Samples for Benzene on 3M 3520 OVMs

punctured septa replaced			punctured septa retained		
initial (%)	after one day (%)	difference (%)	initial (%)	after one day (%)	difference (%)
97.2	96.1	−1.1	97.4	95.9	−1.5
98.2	98.0	−0.2	98.5	96.3	−2.2
	(mean)			(mean)	
97.7	97.1	−0.6	98.0	96.1	−1.9

4.9   Interferences (sampling)

4.9.1   Charcoal tubes

Retention

The ability of a charcoal tube to retain benzene after it has been collected was tested by sampling an atmosphere containing 73.4 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). Six samplers had contaminated air drawn through them

Table 4.9.1
Retention of Benzene on Charcoal tubes

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

at 50 mL/min 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 having contaminant-free air drawn through them at 50 mL/min for 180 min and then all six samplers were analyzed. The mean of the samples in the second set had retained more than 100.4% of the mean collected by the first three samples.

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

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

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

(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.

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.

4.9.3   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

Table 4.9.3
Reverse Diffusion of Benzene
on 3M 3520 OVMs

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

(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 99.2% 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.

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

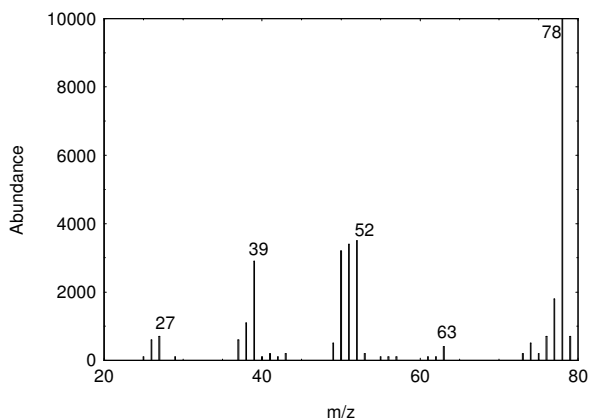The identity of benzene may be confirmed by GC/mass spectrometry. The mass spectrum of benzene is in Figure 4.10.

Figure 4.10. Mass spectrum for benzene.