Benzene

*Related Information: Chemical Sampling -* [*Benzene*](https://www.osha.gov/dts/chemicalsampling/data/CH_220100.html)

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| Method no.: | 1005 |
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| Control no.: | T-1005-FV-01-0111-M |
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| Target Concentration: | 1 ppm |
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| 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 |
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| ACGIH TLV: | 0.5 ppm (1.6 mg/m³) TWA; 2.5 ppm (8.0 mg/m³)(15-min STEL) (Skin) |
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| 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). |
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| Recommended air volume and  sampling rate and 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) |
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| 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) |
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| Reliable quantitation limit (RQL) and standard error of estimate (SEE): |  |

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| --- | --- | --- | --- |
|  | | | |
| 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 |
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| \*For samples where sampling site atmospheric pressure and temperature are known. When either or both of these values are unknown, see [Section 4.4](https://www.osha.gov/dts/sltc/methods/validated/1005/1005.html#sec44) for applicable standard errors of estimate. | |
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| Special requirements: | Report sampling site atmospheric pressure and temperature when using diffusive samplers. |
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| Wipe sampling: | A 10 cm × 10 cm area is wiped with the charcoal pad from 3M 3520 OVM and immediately placed into a capped vial. |
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| Status of method: | Evaluated method. This method has been subjected to the established evaluation procedures of the Methods Development Team. |
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| Date: | November 2001 |
|  |  |
| Revised: | September 2002 |
|  |  |
| Chemist: | Mary E. Eide |
|  |  |
| Methods Development Team Industrial Hygiene Chemistry Division  OSHA Salt Lake Technical Center Sandy UT 84070-6406 | |

1.1 Background

1.1.1 History   
  
The collection of benzene using charcoal tubes (SKC lot 107) was evaluated in OSHA Method 12.[1](https://www.osha.gov/dts/sltc/methods/validated/1005/1005.html#ref1) 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](https://www.osha.gov/dts/sltc/methods/validated/1005/1005.html#ref2)   
  
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 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](https://www.osha.gov/dts/sltc/methods/validated/1005/1005.html#ref3) Benzene is classified as a suspected human carcinogen by OSHA.[4](https://www.osha.gov/dts/sltc/methods/validated/1005/1005.html#ref4) 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](https://www.osha.gov/dts/sltc/methods/validated/1005/1005.html#ref5) 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](https://www.osha.gov/dts/sltc/methods/validated/1005/1005.html#ref6) 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](https://www.osha.gov/dts/sltc/methods/validated/1005/1005.html#ref7)   
  
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](https://www.osha.gov/dts/sltc/methods/validated/1005/1005.html#ref8) Benzene was the 16th highest chemical in the ranking of production by volume for 1995.[9](https://www.osha.gov/dts/sltc/methods/validated/1005/1005.html#ref9) Benzene production was 2.412 billion gallons in 2000.[10](https://www.osha.gov/dts/sltc/methods/validated/1005/1005.html#ref10)  
  
1.1.4 Physical properties and descriptive information[11](https://www.osha.gov/dts/sltc/methods/validated/1005/1005.html#ref11),[12](https://www.osha.gov/dts/sltc/methods/validated/1005/1005.html#ref12),[13](https://www.osha.gov/dts/sltc/methods/validated/1005/1005.html#ref13)

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| CAS number: IMIS number[14](https://www.osha.gov/dts/sltc/methods/validated/1005/1005.html#ref14): molecular weight: boiling point: melting point: specific gravity: | 71-43-2 0320 78.11 80.1°C 5.5°C 0.879 at 20°C | vapor pressure: lower explosive limit: flash point: odor:  appearance: molecular formula: | 10 kPa at 20°C 1.5 to 8% by volume 11°C (52°F) (cc) characteristic aromatic colorless liquid C6H6 |
| 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 | | |
| structure: | For problems with accessibility in using figures and illustrations in this method, please contact the SLTC at (801) 233-4900. | | |

This method was evaluated according to the OSHA SLTC "Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis"[15](https://www.osha.gov/dts/sltc/methods/validated/1005/1005.html#ref15). 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](https://www.osha.gov/dts/sltc/methods/validated/1005/1005.html#sec41))   
  
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](https://www.osha.gov/dts/sltc/methods/validated/1005/1005.html#sec42))

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| --- | --- | --- | --- |
| Table 1.2.2 Detection Limits of the Overall Procedure | | | |
|  | | | |
| **sampler** | **ng** | **ppb** | **µg/m3** |
|  | | | |
| charcoal tube SKC 575-002 3M 3520 | 38 49 41 | 0.99 1.28 1.07 | 3.17 4.08 3.42 |
|  | | | |

1.2.3 Reliable quantitation limit  
  
The reliable quantitation limits are 127 ng per sample (3.3 ppb or 11 g/m³) for charcoal tubes, 163 ng per sample (4.3 ppb or 14 g/m³) for SKC 575-002 Passive Samplers, and 136 ng per sample (3.6 ppb or 11 µg/m³) 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](https://www.osha.gov/dts/sltc/methods/validated/1005/1005.html#sec42))

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| --- | --- | --- | --- | --- |
| Table 1.2.3 Reliable Quantitation Limits | | | | |
|  | | | | |
| **sampler** | **ng** | **ppb** | **µg/m3** | **EE** |
|  | | | | |
| charcoal tube SKC 575-002 3M 3520 | 127 163 136 | 3.32 4.26 3.55 | 10.6 13.6 11.3 | 96.6 93.1 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](https://www.osha.gov/dts/sltc/methods/validated/1005/1005.html#sec43))   
  
1.2.5 Precision   
  
Charcoal Tubes   
  
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/m³) collected on charcoal tubes is ±9.94%. This includes an additional 5% for sampling pump variability. ([Section 4.4](https://www.osha.gov/dts/sltc/methods/validated/1005/1005.html#sec44))   
  
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/m³) collected on SKC 575-002 Passive Samplers are given in Table 1.2.5.1. 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. ([Section 4.4](https://www.osha.gov/dts/sltc/methods/validated/1005/1005.html#sec44))

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| --- | --- |
| Table 1.2.5.1 Precision of the Overall Procedure of SKC 575-002 Passive Samplers | |
|  | |
| **know conditions** | **precision (±%)** |
|  | |
| both *T* & *P* only *T* only *P* neither *T* nor *P* | 17.2 18.1 22.8 23.6 |
|  | |

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/m³) collected on 3M 3520 OVMs are given in Table 1.2.5.2. 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. ([Section 4.4](https://www.osha.gov/dts/sltc/methods/validated/1005/1005.html#sec44))

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| --- | --- |
| Table 1.2.5.2 Precision of Overall Procedure for 3M 3520 OVMs | |
|  | |
| **know conditions** | **precision (±%)** |
|  | |
| both *TP* only T only *P* neither *T* nor *P* | 12.6 13.9 19.6 20.6 |
|  | |

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](https://www.osha.gov/dts/sltc/methods/validated/1005/1005.html#sec45))   
  
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](https://www.osha.gov/dts/sltc/methods/validated/1005/1005.html#sec46))

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](https://www.osha.gov/dts/sltc/methods/validated/1005/1005.html#sec47))

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/m³ 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/m³ or 2.3 ppm and 73.4 mg/m³ 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](https://www.osha.gov/dts/sltc/methods/validated/1005/1005.html#sec48))  
  
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/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 17.1 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/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 34.3 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/m³) for benzene when 0.51 L (15 min) are collected.

2.7 Interferences, sampling ([Section 4.9](https://www.osha.gov/dts/sltc/methods/validated/1005/1005.html#sec49))

2.7.1 Charcoal tubes  
  
Retention  
  
The mean retention efficiency for all samples was 100.4%, 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 99.7% 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/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 3M 3520 OVMs 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](https://www.osha.gov/dts/sltc/methods/validated/1005/1005.html#sec492))  
  
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](https://www.osha.gov/dts/sltc/methods/validated/1005/1005.html#sec493))  
  
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 Plan[16](https://www.osha.gov/dts/sltc/methods/validated/1005/1005.html#ref16). 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 Millenium32 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-L 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 (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).  
  
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 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 4.5µL 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 | For problems with accessibility in using figures and illustrations in this method, please contact the SLTC at (801) 233-4900.  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. |
| 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 |  |
|  |  |  |

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.

|  |  |  |
| --- | --- | --- |
|  | For problems with accessibility in using figures and illustrations in this method, please contact the SLTC at (801) 233-4900.  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](https://www.osha.gov/dts/sltc/methods/validated/1005/1005.html#sec410)).

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.

|  |  |  |  |
| --- | --- | --- | --- |
| CM = |  | where | *CM* is concentration by weight (mg/m³) *M* is micrograms per sample *V* is liters of air sampled *EE* is extraction efficiency, in decimal form |
| M |
|  |
| VEE |

|  |  |  |  |
| --- | --- | --- | --- |
| CV = |  | where | *CV* is concentration by volume (ppm) *VM* = 24.46 at NTP *CM* is concentration by weight *Mr* is moleculary weight of 78.11 |
| VMCM |
|  |
| Mr |

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.

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | | | | | | | | | | where | *RSS* is the sampling rate at sampling site |
| RSS | = | RNTP | ( | TSS | ) | 3/2 | ( | PNTP | ) | RNTP is the sampling rate at NTP conditions (SKC 575-002 = 17.1 mL/min, 3M OVM = 34.3 mL/min) |
|  |  |  | *TSS* is the sampling site temperature in K |
| TNTP | PSS | *TNTP* is 298.2 K |
|  | | | | | | | | | | *PSS* is the sampling site pressure in mmHg |
| *PNTP* is 760 mmHg |

|  |  |  |  |
| --- | --- | --- | --- |
| CM = | 103 M | where | *CM* is concentration by weight (mg/m3) |
| *M* is micrograms per sample |
|  | *RSS* is the sampling rate at the sampling site |
| tRSSEE | *t* is the sampling time |
| *EE* is the extration efficiency, in decimal form |

|  |  |  |  |
| --- | --- | --- | --- |
|  | VMCM | where | *CV* is concentration by volume (ppm) |
| CV = |  | *VM* = 24.46 at NTP |
|  | Mr | *CM* is concentration by weight |
|  |  | *Mr* 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.

|  |  |  |
| --- | --- | --- |
| PSS = AE2 - BE + 760.0 | where | *PSS* is the approximate atmospheric pressure |
|  |  | *E* is the sampling site elevation, ft |
|  |  | *A* is 3.887x10-7 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](https://www.osha.gov/dts/sltc/methods/validated/1005/1005.html#ref17). 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 | | |  |
|  | | | For problems with accessibility in using figures and illustrations in this method, please contact the SLTC at (801) 233-4900.  Figure 4.1.  Plot of data in Table 4.1 used to determine the DLAP. (y = 18.0x + 22.8) |
| **concentration (ng/mL)** | **mass on column (pg)** | **area counts** (µV-s) |
|  | | |
| 0 105 211 316 422 527 633 738 844 949 1050 | 0 5.5 11.1 16.6 22.2 27.7 33.3 38.8 44.4 49.9 55.3 | 0 111 249 341 402 545 618 722 835 924 1001 |
|  | | |

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 | |  |
|  | | For problems with accessibility in using figures and illustrations in this method, please contact the SLTC at (801) 233-4900.  Figure 4.2.1.  Plot of data in Table 4.2.1 used to determine the DLOP/RQL of benzene collected on charcoal tubes (lot 2000). (y = 0.904x + 8.80) |
| **mass per sample (ng)** | **area counts (µV-s)** |
|  | |
| 0 105 211 316 422 527 633 738 844 949 1050 | 0 103 175 293 383 488 563 683 784 889 992 |
|  | |

|  |  |  |
| --- | --- | --- |
| Table 4.2.2 Detection Limit of the Overall Procedure on SKC 575-002 Passive Samplers | |  |
|  | | For problems with accessibility in using figures and illustrations in this method, please contact the SLTC at (801) 233-4900.  Figure 4.2.2.  Plot of data in Table 4.2.2 used to determine the DLOP/RQL of benzene collected on SKC 575-002 Passive Samplers. (y = 0.958x + 30.0) |
| **mass per sample (ng)** | **area counts (µV·s)** |
|  | |
| 0 105 211 316 422 527 633 738 844 949 1050 | 0 114 255 346 409 551 623 728 841 944 1040 |
|  | |

|  |  |  |
| --- | --- | --- |
| Table 4.2.3 Detection Limit of the Overall Procedure on 3M 3520 OVMs | |  |
|  | | For problems with accessibility in using figures and illustrations in this method, please contact the SLTC at (801) 233-4900.  Figure 4.2.3.  Plot of data in Table 4.2.3 used to determine the DLOP/RQL of benzene collected on 3M 3520 OVMs. (y = 0.918x + 11.5) |
| **mass per sample (ng)** | **area counts (µV·s)** |
|  | |
| 0 105 211 316 422 527 633 738 844 949 1050 | 0 111 211 296 391 517 606 687 786 862 982 |
|  | |

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** | **EE** |
|  | | | | |
| charcoal tube SKC 575-002 3M 3520 | 127 163 136 | 3.32 4.26 3.55 | 10.6 13.6 11.3 | 96.6 93.1 97.9 |
|  | | | | |

|  |
| --- |
| For problems with accessibility in using figures and illustrations in this method, please contact the SLTC at (801) 233-4900.  Figure 4.2.4.  Chromatogram of the benzene peak near the RQL on charcoal tubes, and the peak has an area count of 174. |

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](https://www.osha.gov/dts/sltc/methods/validated/1005/1005.html#sec352) 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 19.8 39.5 59.3 79.1 | 14230 26684 53374 80390 107770 | 14187 26783 53487 80450 108450 | 14329 26645 53380 80334 107689 | 14284 26743 53409 80299 107651 | 14229 26523 53312 80387 107743 | 14219 26589 53287 80401 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](https://www.osha.gov/dts/sltc/methods/validated/1005/1005.html#fig4511). The precision includes an additional 5% for sampling error.  
  
4.4.2 SKC 575-002 Passive 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 | | |
|  | | |
| **know condition** | **error (%)** | **precision (±%)** |
|  | | |
| both *T* & *P* only *T* only *P* neither *T* nor *P* | 8.75 9.25 11.65 12.03 | 17.2 18.1 22.8 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 | | |
|  | | |
| **know condition** | **error (%)** | **precision (±%)** |
|  | | |
| both *T* & *P* only *T* only *P* neither *T* nor *P* | 6.45 7.11 10.0 10.5 | 12.6 13.9 19.6 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 5 8 12 15 19 | 98.9 99.4 97.9 98.1 98.5 96.8 | 99.9 98.9 99.4 99.9 98.9 99.1 | 100.4 97.9 99.1 97.9 96.9 98.4 | 98.9 98.8 99.5 100.1 97.7 97.9 | 99.9 100.3 100.4 99.9 99.1 99.8 | 100.4 99.7 98.8 97.9 98.5 98.4 |
|  | | | | | | |

|  |
| --- |
| For problems with accessibility in using figures and illustrations in this method, please contact the SLTC at (801) 233-4900.  Figure 4.5.1.1.  A plot of the storage data in Table 4.5.1 for benzene under ambient conditions collected on charcoal tubes. |

|  |
| --- |
| For problems with accessibility in using figures and illustrations in this method, please contact the SLTC at (801) 233-4900.  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 5 8 12 15 19 | 100.5 99.6 99.4 97.9 96.6 97.5 | 100.6 100.1 98.8 98.8 98.6 96.5 | 98.9 98.8 96.8 98.2 96.1 95.8 | 100.5 99.3 99.9 100.1 98.9 99.3 | 100.6 99.4 99.1 98.6 99.6 97.5 | 98.9 100.3 98.8 99.5 97.5 99.1 |
|  | | | | | | |

|  |
| --- |
| For problems with accessibility in using figures and illustrations in this method, please contact the SLTC at (801) 233-4900.  Figure 4.5.2.1. A plot of the storage data in Table 4.5.2 for benzene under ambient conditions collected on SKC 575-002 Passive Samplers. |

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| --- |
| For problems with accessibility in using figures and illustrations in this method, please contact the SLTC at (801) 233-4900.  Figure 4.5.2.2. A plot of the storage data in Table 4.5.2 for benzene under refrigerated conditions collected on 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 4.5.3 Storage Test for Benzene on 3M 3520 OVMs | | | | | | |
|  | | | | | | |
| **time (days)** | **ambient storage recovery (%)** | | | **refrigerated storage recovery (%)** | | |
|  | | | | | | |
| 0 5 8 12 15 19 | 100.1 98.6 99.1 96.2 97.2 96.6 | 99.2 99.1 97.8 98.9 95.9 95.5 | 98.2 97.8 98.3 97.1 97.2 95.9 | 100.1 99.9 98.6 99.1 98.5 99.3 | 99.2 98.2 98.9 97.6 99.2 98.5 | 98.2 97.9 96.8 97.8 97.2 97.3 |
|  | | | | | | |

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| For problems with accessibility in using figures and illustrations in this method, please contact the SLTC at (801) 233-4900.  Figure 4.5.3.1.  A plot of the storage data in Table 4.5.3 for benzene under ambient conditions collected on 3M 3520 OVMs. |

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| --- |
| For problems with accessibility in using figures and illustrations in this method, please contact the SLTC at (801) 233-4900.  Figure 4.5.3.2. A plot of the storage data in Table 4.5.3 for benzene under ambient conditions 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](https://www.osha.gov/dts/sltc/methods/validated/1005/1005.html#sec44).

|  |  |  |  |
| --- | --- | --- | --- |
| Table 4.6.1 Reproducibility Data for Benzene on Charcoal Tubes | | | |
|  | | | |
| **theoretical (µg/sample)** | **recovered  (µg/sample)** | **recovery (%)** | **deviation (%)** |
|  | | | |
| 76.91 83.34 77.84 88.56 | 73.61 81.58 75.17 85.62 | 95.7 97.9 96.6 96.7 | -4.3 -2.1 -3.4 -3.3 |
|  | | | |

|  |  |  |  |
| --- | --- | --- | --- |
| Table 4.6.2 Reproducibility Data for Benzene on SKC 575-002 Passive Samplers | | | |
|  | | | |
| **theoretical (µg/sample)** | **recovered  (µg/sample)** | **recovery (%)** | **deviation (%)** |
|  | | | |
| 26.38 26.38 26.38 26.38 26.38 | 25.62 25.03 25.43 25.21 26.01 | 97.1 94.9 96.4 95.6 98.5 | -2.9 -5.1 -3.6 -4.4 -1.5 |
|  | | | |

|  |  |  |  |
| --- | --- | --- | --- |
| Table 4.6.3 Reproducibility Data for Benzene on 3M 3520 OVMs | | | |
|  | | | |
| **theoretical (µg/sample)** | **recovered (µg/sample)** | **recovery (%)** | **deviation (%)** |
|  | | | |
| 58.52 58.52 58.52 58.52 58.52 58.52 | 56.53 56.18 55.95 57.06 55.59 57.01 | 96.6 96.0 95.6 97.5 95.0 97.4 | -3.4 -4.0 -4.4 -2.5 -5.0 -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/m³ 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/m³ or 10 ppm, and a gasoline concentration of 890 mg/m³ had no breakthrough for the benzene, though the gasoline did breakthrough after 4 hours ([Section 4.9](https://www.osha.gov/dts/sltc/methods/validated/1005/1005.html#sec49)).   
  
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 | | | |
|  | | | |
|  | **sampling rate (mL/min)** | | |
| **time (h**) | **first** | **second** | **third** |
|  | | | |
| 0.083 0.167 0.25 0.5 1 2 3 4 6 8 10 | 19.2 18.3 18.0 17.8 17.2 16.9 16.2 16.3 16.4 16.2 16.0 | 19.0 18.6 17.9 17.5 17.3 16.8 16.8 16.1 16.2 16.5 16.1 | 18.8 18.4 18.1 17.7 17.4 16.4 16.3 16.0 16.3 16.1 15.9 |
|  | | | |

|  |
| --- |
| For problems with accessibility in using figures and illustrations in this method, please contact the SLTC at (801) 233-4900.  Figure 4.7.2.1.  This is a plot of the data in Figure 4.7.2.1 of time versus sampling rate, used to determine the recommended sampling time and sampling rate from a 2.3-ppm atmosphere for SKC 575-002 Passive Samplers. |

|  |  |  |  |
| --- | --- | --- | --- |
| Table 4.7.2.2 Determination of Sampling Rate and Time for SKC 575-002 Passive Samplers from a 23-ppm Atmosphere | | | |
|  | | | |
|  | sampling rate (mL/min) | | |
| **time (h)** | **first** | **second** | **third** |
|  | | | |
| 0.083 0.167 0.25 0.5 1 2 3 4 6 8 10 | 18.4 18.0 17.4 17.2 16.7 16.5 16.1 16.4 16.4 16.4 16.3 | 18.5 17.7 17.7 17.4 16.5 16.3 16.3 16.1 16.3 16.1 16.0 | 18.2 17.9 17.6 16.9 16.9 16.9 16.5 16.6 16.2 16.0 16.1 |
|  | | | |

|  |
| --- |
| For problems with accessibility in using figures and illustrations in this method, please contact the SLTC at (801) 233-4900.  Figure 4.7.2.2. This is a plot of the data in Figure 4.7.2.2 of time versus sampling rate, used to determine the recommended sampling time and sampling rate from a 23-ppm atmosphere for SKC 575-002 Passive Samplers. |

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

|  |
| --- |
| For problems with accessibility in using figures and illustrations in this method, please contact the SLTC at (801) 233-4900.  Figure 4.7.3.1.  This is a plot of the data in Figure 4.7.3.1 of time versus sampling rate, used to determine the recommended sampling time and sampling rate from a 2.3-ppm atmosphere for 3M 3520 OVMs. |

|  |  |  |  |
| --- | --- | --- | --- |
| Table 4.7.3.2 Determination of Sampling Rate and Time for 3M 3520 OVMs from a 23-ppm Atmosphere | | | |
|  | | | |
|  | **sampling rate (mL/min)** | | |
| **time (h)** | **first** | **second** | **third** |
|  | | | |
| 0.083 0.167 0.25 0.5 1 2 3 4 6 8 10 | 36.8 35.5 35.2 34.0 34.1 33.9 33.9 33.8 34.1 34.3 34.2 | 36.0 35.0 35.6 35.2 34.4 34.5 34.2 33.9 33.7 33.8 33.6 | 36.4 35.7 35.3 34.7 33.9 34.2 33.8 34.5 34.3 34.8 33.8 |
|  | | | |

|  |
| --- |
| For problems with accessibility in using figures and illustrations in this method, please contact the SLTC at (801) 233-4900.  Figure 4.7.3.2.  This is a plot of the data in Figure 4.7.3.2 of time versus sampling rate, used to determine the recommended sampling time and sampling rate from a 23-ppm atmosphere for 3M 3520 OVMs. |

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 CS2. 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 0.25 0.5 1.0 1.5 2.0  1.0 (wet) | 0.13 9.9 19.8 39.5 59.3 79.1  39.5 | 98.5 98.6 97.6 96.7 96.9 97.2  97.1 | 97.3 95.3 98.2 97.1 95.5 96.5  95.6 | 95.3 96.6 97.6 96.3 96.9 97.2  96.8 | 95.1 97.3 98.2 97.0 97.3 97.1  97.2 | 96.6 97.0 97.9 96.8 96.7 97.0  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 Samples for Benzene on Charcoal Tubes | | | | | |
|  | | | | | |
| **punctured septa replaced** | | | **punctured septa retained** | | |
| **initial (%)** | **after one day (%)** | **difference (%)** | **initial (%)** | **after one day (%)** | **difference (%)** |
|  | | | | | |
| 96.7 97.1  96.9 | 95.6 96.3 (mean) 96.0 | -1.1 -0.8  -0.9 | 96.3 97.0  96.7 | 92.1 94.5 (mean) 93.3 | -4.2 -2.5  -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 0.25 0.5 1.0 1.5 2.0  1.0 (wet) | 0.13 3.08 6.15 12.3 18.5 24.6  12.3 | 93.8 95.2 93.3 94.9 92.4 94.2  93.5 | 92.4 94.3 94.3 93.6 93.8 93.4  94.5 | 91.4 93.4 93.8 94.3 93.5 94.2  93.6 | 94.6 93.1 92.6 92.2 93.3 93.1  94.0 | 93.1 94.0 93.5 93.8 93.3 93.7  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 93.6  94.3 | 93.1 92.8 (mean) 93.0 | -1.8 -0.8  -1.3 | 94.3 92.2  93.3 | 91.2 90.2 (mean) 90.7 | -3.1 -2.0  -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 0.25 0.5 1.0 1.5 2.0  1.0 (wet) | 0.13 6.81 13.6 27.2 40.9 54.5  27.2 | 98.5 97.4 97.3 97.2 98.0 98.4  98.4 | 97.7 98.1 98.8 98.2 97.6 98.0  97.9 | 98.2 97.7 97.8 97.4 97.7 98.6  97.7 | 97.2 97.8 98.1 98.5 98.1 97.8  98.2 | 97.9 97.8 98.0 97.8 97.9 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 98.2  97.7 | 96.1 98.0 (mean) 97.1 | -1.1 -0.2  -0.6 | 97.4 98.5  98.0 | 95.9 96.3 (mean) 96.1 | -1.5 -2.2  -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/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). Six samplers had contaminated air drawn through them 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.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Table 4.9.1 Retention of Benezene on Charcoal tubes | | | | |
|  | | | | |
|  | **percent recovery (%)** | | |  |
| **set** | **1** | **2** | **3** | **mean** |
|  | | | | |
| first second  second/first | 98.7 99.1 | 99.2 99.0 | 99.6 100.5 | 99.2 99.5  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 | | | | |
|  | | | | |
|  | **mass (µg)** | | |  |
| **set** | **1** | **2** | **3** | **mean** |
|  | | | | |
| first second  second/first | 75.6 74.1 | 75.2 74.7 | 75.8 75.5 | 75.5 74.8  99.1% |
|  | | | | |

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/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 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/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 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/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 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 (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 µg.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Table 4.9.3 Reverse Diffusion of Benzene on 3M 3520 OVMs | | | | |
|  | | | | |
|  | **mass (µg)** | | |  |
| **set** | **1** | **2** | **3** | **mean** |
|  | | | | |
| first second  second/first | 150.8 150.6 | 150.2 149.0 | 150.9 148.5 | 150.6 149.4  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/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 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/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 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/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 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.

|  |  |  |
| --- | --- | --- |
|  | For problems with accessibility in using figures and illustrations in this method, please contact the SLTC at (801) 233-4900.  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   
  
Introduction   
  
Benzene is a volatile organic solvent which will not collect onto the conventional wipe media of filters, ie.  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 employees 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.   
  
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.   
  
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 (µg/surface) | recovered (µg/sample) | recovery (%) |
|  | | |
| 25 25 25 25 25 25 | 23.2 24.1 22.9 23.1 24.5 23.4 | 92.8 96.4 91.6 92.4 98.0 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 4 8 15 | 97.3 96.9 95.8 92.8 | 94.8 95.1 94.3 95.1 | 95.3 95.5 92.4 93.2 | 97.3 95.2 96.1 97.1 | 94.8 96.4 92.9 95.5 | 95.3 93.3 94.5 93.8 |
|  | | | | | | |

|  |  |  |
| --- | --- | --- |
| For problems with accessibility in using figures and illustrations in this method, please contact the SLTC at (801) 233-4900.  Figure 5.1  This is a plot of the benzene wipe ambient storage data found in Table 5.2. |  | For problems with accessibility in using figures and illustrations in this method, please contact the SLTC at (801) 233-4900.  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 (µg/surface) | recovered (µg/sample) | recovery (%) |
|  | | |
| 25 25 25 25 25 25 | 24.0 23.5 22.6 23.9 24.1 23.1 | 96.0 94.0 90.4 95.6 96.4 92.4 |
|  | | |

|  |  |  |
| --- | --- | --- |
| Table 5.4 Sampling Reproducibility 2nd Chemist Samples for Benzene | | |
| theoretical (µg/surface) | recovered (µg/sample) | recovery (%) |
|  | | |
| 25 25 25 25 25 25 | 24.1 22.5 23.9 22.9 23.6 22.9 | 96.4 90.0 95.6 91.6 94.4 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 (µg/surface) | recovered (µg/sample) | recovery (%) |
|  | | |
| 25 25 25 25 25 25 | 23.1 24.2 22.8 22.7 23.9 24.3 | 92.4 96.8 91.2 90.8 95.6 97.2 |
|  | | |

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.   
  
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