

Styrene
(Diffusive Samplers)



Method no.: 1014

Control no.: T-1014-FV-01-0911-M

Target concentration: 100 ppm (420 mg/m³) (TWA), 200 ppm (850 mg/m³) (15 min ceiling)
 OSHA PEL: 100 ppm (420 mg/m³) (TWA), 200 ppm (850 mg/m³) (15 min ceiling), 600 ppm (2550 mg/m³) (5 min peak in any 3 hour period)
 ACGIH TLV: 20 ppm (85 mg/m³) (TWA), 40 ppm (170 mg/m³) (STEL)

Procedure: Diffusive samplers are collected by exposing them to workplace air. Samples are extracted with toluene and analyzed by gas chromatography (GC) using a flame ionization detector (FID).

Recommended sampling time: 240 min (TWA); 15 min (ceiling); (cannot be used for peak sampling)

Reliable quantitation limit:

sampler	ceiling (15 min) ppm	ceiling (15 min) mg/m ³	TWA (240 min) ppm	TWA (240 min) mg/m ³
3M 3520 OVM	0.52	2.2	0.035	0.15
SKC 575-006 Passive Sampler	1.3	5.5	0.082	0.35

Standard error of estimate (SEE)*:

sampler	ceiling (15 min) (%)	TWA (240 min) (%)
3M 3520 OVM	6.52	6.47
SKC 575-006 Passive Sampler	8.74	8.79

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

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

Status of method: Validated method. This method has been subjected to the established evaluation procedures of the OSHA Salt Lake Technical Center Methods Development Team.

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Mary E. Eide

Methods Development Team
 Industrial Hygiene Chemistry Division
 OSHA Salt Lake Technical Center
 Sandy UT 84070-6406

1. General Discussion

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

1.1 Background

1.1.1 History

OSHA's first method for styrene specified sample collection using sampling tubes containing coconut-shell charcoal, sample extraction with carbon disulfide, and analysis by gas chromatography with a flame ionization detector (GC/FID).¹ The method suffered from low and non-constant extraction efficiency at lower levels which required the use of a non-linear curve to correct analytical results. The low and non-constant extraction efficiency issue was resolved in OSHA Method 89 which specifies sample collection using sampling tubes containing coconut-shell charcoal which has been coated with *p*-*tert*-butylcatechol (TBC), sample extraction with toluene, and analysis by GC/FID.² OSHA presently uses TBC-coated sampling media to collect several other analytes.³ This media was used specifically to resolve recovery and stability issues with the other analytes. TBC is commercially used as an antioxidant, a stabilizer, and a polymerization inhibitor for several reactive chemicals including styrene and butadiene.⁴

OSHA is presently developing sampling and analytical methods that permit use of diffusive samplers as a sampling option for the organic chemicals most requested by compliance officers for analysis at OSHA SLTC. This work was performed to provide a diffusive sampling option for styrene which was the 5th most requested organic chemical analyzed at SLTC in 2008. Two different diffusive samplers were tested. The first one was the 3M 3520 Organic Vapor Monitor (OVM) which contains two charcoal pads. The second one was a special sampler prepared by SKC, Inc. which contains a carbon bead adsorbent that had been coated with TBC. It is anticipated that the SKC sampler could be used to validate methods for some of the other analytes which specify the use of TBC-coated sampling media.

The results of this validation showed that the two tested diffusive samplers provided excellent storage stability, and excellent recovery was obtained at all tested levels, including the detection limits when the samples were extracted with toluene. Extraction with toluene gave high constant recoveries for both media, therefore, this extraction solvent was used in this method. Carbon disulfide (containing 1% *N,N*-dimethylformamide) was tested as an alternative extraction solvent because it is extensively used at OSHA SLTC. Considerably lower but constant recoveries were obtained using 99:1 carbon disulfide: *N,N*-dimethylformamide. However, toluene is the preferred extraction solvent and is recommended in this method (Section 4.8).

¹ Shulsky, M., OSHA Method 9 Styrene. <https://www.osha.gov/dts/sltc/methods/organic/org009/org009.html> (accessed 1/30/09).

² Burreight, D., OSHA Method 89 Divinylbenzene Ethylvinylbenzene Styrene. <http://www.osha.gov/dts/sltc/methods/organic/org089/org089.html> (accessed 1/30/09).

³ OSHA Chemical Sampling Information, 2009, U.S. Department of Labor, Occupational Safety and Health Administration website. https://www.osha.gov/dts/chemicalsampling/toc/toc_chemsamp.html (accessed 1/30/09).

⁴ *p*-*tert*-Butylcatechol, 2009, National Toxicology Program website <http://ntp.niehs.nih.gov/index.cfm?objectid=BDA6C602-123F-7908-7BA456A1C3784AB7> (accessed 1/30/09).

1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.)^{5,6}

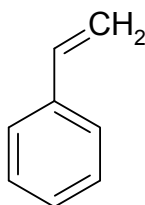
Styrene causes eye, nose, and respiratory irritation, headache, fatigue, dizziness, confusion, drowsiness, weakness and unsteady gait. Styrene exposure can cause deficits in color vision and high frequency hearing. Higher exposures can cause narcosis, defatting dermatitis, liver injury, and reproductive effects.

1.1.3 Workplace exposure

Styrene is used in production of polystyrene plastics, fiberglass, co-polymer plastics, synthetic rubber, co-polymer resins with acrylonitrile and butadiene, protective coatings, and as a chemical intermediate.⁷ Styrene production in 2007 was 5,100,000 metric tons in the U.S.⁸

1.1.4 Physical properties and other descriptive information^{9,10}

synonyms:	cinnamene; phenylethylene; vinylbenzene
IMIS: ¹¹	2280
CAS number:	100-42-5
boiling point:	145-146 °C (293-295 °F)
melting point:	-30.6 °C (-23.1 °F)
density:	0.9059
molecular weight:	104.15
vapor pressure:	0.573 kPa @ 15 °C
flash point:	31 °C (88 °F) (closed cup)
appearance:	colorless to light yellow liquid
vapor density:	3.6 g/m ³
molecular formula:	C ₈ H ₈
odor:	penetrating
solubility:	sparingly soluble in water, soluble in alcohol, ether, methanol, acetone, and carbon disulfide
autoignition temperature:	480 °C (896 °F)
structural formula:	



⁵ O'Neil, M.J., Ed., *The Merck Index*, 13th ed., Merck & Co., Inc., Whitehouse Station, NJ, 2001, p 1578.

⁶ *Documentation of the Threshold Limit Values for Chemical Substances*, 7th ed., American Conference of Governmental Industrial Hygienists Inc., Cincinnati, OH, 2001, vol. 3, p Styrene 1.

⁷ *Documentation of the Threshold Limit Values for Chemical Substances*, 7th ed., American Conference of Governmental Industrial Hygienists Inc., Cincinnati, OH, 2001, vol. 3, p Styrene 1.

⁸ Gains in Chemical Output Level Off. *Chem. Eng. News* **2008**, 86, 61-70.

⁹ O'Neil, M.J., Ed., *The Merck Index*, 13th ed., Merck & Co., Inc., Whitehouse Station, NJ, 2001, p 1051.

¹⁰ Lewis, R. J. Sr., Ed. *Hawley's Condensed Chemical Dictionary*, 14th ed.; Van Nostrand Reinhold Co.: New York, 2001, p 172.

¹¹ Styrene (OSHA Chemical Sampling Information), 2009, U.S. Department of Labor, Occupational Safety and Health Administration website. http://www.osha.gov/dts/chemicalsampling/data/CH_268200.html (accessed 1/15/09).

This method was evaluated according to the OSHA SLTC "Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis".¹² 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 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 9.78 pg. This is the amount of analyte that will give a detector response that is significantly different from the response of a reagent blank. (Section 4.1)

1.2.2 Detection limit of the overall procedure

The detection limits of the overall procedure are listed in Table 1.2.2. These are the amounts of analyte spiked on the respective sampler that will give detector responses that are significantly different from the responses of the respective sampler blanks. (Section 4.2)

Table 1.2.2
Detection Limit of the Overall Procedure

sampler	µg	ppb	µg/m ³
3M 3520	0.31	10.5	44.7
SKC 575-006	0.34	24.3	103

1.2.3 Reliable quantitation limit

The reliable quantitation limits are listed in Table 1.2.3. These are the amounts of analyte spiked on the respective samplers that will give detector responses that are considered the lower limits for precise quantitative measurements. (Section 4.2)

Table 1.2.3
Reliable Quantitation Limit

sampler	µg	ppb	µg/m ³	E _E
3M 3520	1.0	35.2	150	96.1
SKC 575-006	1.1	81.7	351	96.2

1.2.4 Instrument calibration

The standard error of estimate was 22.3 µg/sample over the range of 1 to 3080 µg/sample for styrene. This range corresponds to the RQL to 2 times the TWA PEL target concentration for 3M 3520 OVMs. (Section 4.3)

1.2.5 Precision

3M 3520 OVMs

The precision of the overall procedure at the 95% confidence level for the ambient temperature 17-day storage test for samples collected on 3M 3520 OVMs was determined at the target concentration. The precisions are given in Table 1.2.5.1. They each include an additional 6.4% for sampling rate variability. There are different values given, depending on whether both, either, or

Table 1.2.5.1
Precision of the Overall Procedure at Ceiling and TWA PELs for 3M 3520 OVMs

known conditions	ceiling precision (±%)	TWA precision (±%)
both <i>T</i> & <i>P</i>	12.8	12.7
only <i>T</i>	14.1	14.0
only <i>P</i>	19.7	19.7
neither <i>T</i> nor <i>P</i>	20.6	20.6

¹² Burright, D.; Chan, Y.; Eide, M.; Elskamp, C.; Hendricks, W.; Rose, M.; *Evaluation Guidelines For Air Sampling Methods Utilizing Chromatographic Analysis*. <http://www.osha.gov/dts/sltc/methods/chromguide/index.html>, OSHA Salt Lake Technical Center, U.S. Department of Labor: Salt Lake City, UT, 1999 (accessed 3/15/09).

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)

SKC 575-006 Passive Samplers

The precision of the overall procedure at the 95% confidence level for the ambient temperature 17-day storage test for samples collected on SKC 575-006 Passive Samplers was determined at the target concentration. The precisions are given in Table 1.2.5.2. 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. (Section 4.4)

Table 1.2.5.2
Precision of the Overall Procedure at Ceiling and TWA PELs for SKC 575-006 Passive Samplers

	ceiling PEL precision (±%)	TWA PEL precision (±%)
known conditions		
both <i>T</i> & <i>P</i>	17.1	17.2
only <i>T</i>	18.1	18.2
only <i>P</i>	22.8	22.9
neither <i>T</i> nor <i>P</i>	23.6	23.6

1.2.6 Recovery

The recoveries of styrene, calculated on day 17 from the equations of the storage graphs that were prepared from samples used in 17-day ambient (23 °C) storage tests are shown in Table 1.2.6. (Section 4.5)

Table 1.2.6
Storage Test Recovery

sampler	target concentration	recovery (%)
3M 3520 OVM	ceiling	94.5
3M 3520 OVM	TWA	94.1
SKC 575-006	ceiling	94.6
SKC 575-006	TWA	94.5

1.2.7 Reproducibility

Six samples for each of the two types of samplers were collected from dynamically generated controlled test atmosphere at 1 x TWA PEL (101 ppm) for a 240-min sample and at 1 x ceiling PEL (202 ppm) for a 15-min sample, and submitted for analysis by the OSHA Salt Lake Technical Center. The samples were analyzed according to a draft copy of this procedure after being stored at 4 °C for 4 days. No individual sample result deviated from its theoretical value by more than the precision reported in Section 1.2.5. (Section 4.6)

2. Sampling Procedure

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

2.1 Apparatus

Samples are collected with either 3M 3520 OVMs or with SKC 575-006 Passive Samplers. Samplers were purchased from 3M (catalog no. 3520, containing two charcoal adsorbent pads, lot no. 830411); or from SKC, Inc. (catalog no. 575-006, containing 500 mg of Anasorb 747 coated with 10% *p*-*tert*-butylcatechol, lot no. CPM012809-002).

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

2.2 Reagents

None required

2.3 Technique

2.3.1 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 and on Form OSHA-91A.

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 15-min ceiling 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 Form OSHA-91A.

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

Prepare a blank by removing the white film and ring and attaching the closure cap onto the 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 tool.

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 a Form OSHA-21.

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

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

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. As a precaution, store the samples at refrigerator temperature if a delay in shipment is unavoidable.

Ship any bulk samples separate from the air samples.

2.3.2 SKC 575-006 Passive Samplers (In general, follow the manufacturer's instructions.)

Open the top of the aluminum bag and remove the sampler. Remove the cover retainer and press-on cover. **Caution- The sampler begins to sample immediately after the press-on cover is removed.** Save the O-ring, press-on cover, cover retainer, port plugs and PTFE tube in the aluminum bag for later use.

Record the start time on the sampler label and on Form OSHA-91A.

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, first place the O-ring on the side with the perforations, followed by the press-on cover and cover retainer ring. 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 the sampler label and on Form OSHA-91A. Place the sampler in the aluminum bag. Include all port plugs and PTFE tubes which will be used by the laboratory for analyses in the aluminum bag. Close the bag and place a Form OSHA-21 seal over the closure.

The following steps should be performed in a low background area for a set of samplers as soon as possible after sampling. Prepare a blank by removing an unused sampler from its aluminum package, removing the cover retainer and press-on cover, place O-ring on the side with perforations followed by the press-on cover, and cover retainer. Replace the sampler into the aluminum bag, close the bag, and seal with a Form OSHA-21 over the closure.

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

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

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

Submit the samples to the laboratory for analysis as soon as possible after sampling. As a precaution, store the samples at refrigerator temperature if a delay in shipment is unavoidable.

Ship any bulk sample(s) in a container separate from the air samples.

2.4 Sampler capacity (Section 4.7)

The sampling rate and capacity of 3M 3520 OVMs and of SKC 575-006 Passive Samplers were determined by using dynamically generated test atmospheres containing styrene at two times the target concentration with an average relative humidity of approximately 80% at 23 °C. The concentration of styrene was 858 mg/m³ or 202 ppm. Samples were collected for increasing time intervals. Sampler capacity is exceeded when the sampling rate decreases (greater than 8 hours for styrene on 3M OVMs and SKC 575-006 Passive Samplers). The average sampling rate for 3M 3520 OVMs was determined to be 29.93 mL/min and for SKC 575-006 Passive Samplers it was 13.55 mL/min. The recommended sampling times for this method are 15 min for ceiling sampling, and 240 min for TWA sampling. These samplers should not be used for 5 min peak sampling.

2.5 Extraction efficiency (Section 4.8)

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

2.5.1 3M 3520 OVMs

The mean extraction efficiency from dry 3M 3520 OVMs over the range of the RQL to 2 times the target concentration was 97.2% for samples extracted with toluene (0.001 to 6.16 mg/sample). The extraction efficiency was not affected by the presence of water.

Extracted samples remain stable for at least 72 h.

2.5.2 SKC 575-006 Passive Samplers

The mean extraction efficiency from dry SKC 575-006 Passive Samplers over the range of the RQL to 2 times the target concentration was 96.7% for samples extracted with toluene (0.001 to 2.72 mg/sample). The extraction efficiency was not affected by the presence of water.

Extracted samples remain stable for at least 72 h.

2.6 Recommended sampling time and sampling rate

2.6.1 3M 3520 OVMs

Sample with 3M 3520 OVMs for up to 240 min to collect TWA (long-term) samples, and for 15 min to collect ceiling samples. The sampling rate is 29.93 mL/min.

When 15-min ceiling 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 0.52 ppm (2.2 mg/m³) when an air volume of 0.45 L (15 min x 29.93 mL/min) is collected.

2.6.2 SKC 575-006 Passive Samplers

Sample with SKC 575-006 Passive Samplers for up to 240 min to collect TWA (long-term) samples, and for 15 min to collect ceiling samples. The sampling rate is 13.55 mL/min.

When 15-min ceiling samples are collected, the air concentration equivalent to the reliable quantitation limit becomes larger. For example, the reliable quantitation limit for SKC 575-006 Passive Samplers is 1.3 ppm (5.5 mg/m³) when an air volume of 0.20 L (15 min x 13.55 mL/min) is collected.

2.7 Interferences, sampling (Section 4.9)

2.7.1 3M 3520 OVMs

Reverse diffusion

Reverse diffusion is the measure of the ability of the sorbent within a diffusive sampler to retain the collected analyte. Reverse diffusion is measured by first exposing two sets of samplers to humid air with an average relative humidity of 80% at 23 °C containing the analyte and then additionally exposing one of the sets to clean humid air. Comparison of the two sets of 3M 3520 OVMs showed an average recovery of 99.5%. (Section 4.9.1)

Low humidity

The ability of 3M 3520 OVMs to collect styrene from a relatively dry atmosphere was tested at the ceiling PEL by sampling a test atmosphere containing 1704 mg/m³ (400 ppm) of styrene at an average relative humidity of 20% at 23 °C for 15 min, and at the TWA PEL by sampling a test atmosphere containing 852 mg/m³ (200 ppm) of styrene at an average relative humidity of 20% at 23 °C for 240 min. The mean recoveries (% of theoretical) were 98.1% for the 15-min ceiling samples and 97.8% for the 240-min TWA samples. (Section 4.9.1)

Low concentration

The ability of 3M 3520 OVMs to collect styrene at a low concentration of 0.1 x the ceiling PEL was tested by sampling an atmosphere containing 85.2 mg/m³ (20 ppm) of styrene at an average relative humidity of 80% at 23 °C for 15 min, and at 0.1 x the TWA PEL by sampling a test atmosphere containing 42.6 mg/m³ (10 ppm) of styrene at an average relative humidity of 80% at 23 °C for 240 min. The mean recoveries (% of theoretical) were 97.4% for the 15-min ceiling samples and 98.4% for the 240 min TWA samples. (Section 4.9.1)

Sampling interference

The ability of 3M 3520 OVMs to collect the analyte when other potential interferences are present was tested by creating a test atmosphere at the TWA PEL level of acetone and styrene in humid air having an average relative humidity of 80% at 23 °C. The concentrations of the analytes in the test atmospheres were: acetone (2400 mg/m³ or 1000 ppm), and styrene (429 mg/m³ or 101 ppm). Three samplers were exposed for 60 min due to potential capacity problems with the high concentration of acetone. All of the samples were immediately analyzed. The mean recovery (% of theoretical) for styrene was 100.5%. There was no styrene on the backup pad of the sampler for any of the samples, but there was acetone on the back-up pads. Over half of the styrene samples analyzed at OSHA Salt Lake Technical Center in 2005-2008 were from fiberglass operations. To test the ability of 3M 3520 OVMs to collect styrene at the recommended TWA sampling time of 240 min with acetone concentrations at a similar level, as would be found in fiberglass operations where the acetone is present in the mix at a near equal level to the styrene, a test atmosphere was created at the TWA PEL for styrene and 0.1 x the TWA PEL for acetone in humid air having an average relative humidity of 80% at 22 °C. The concentrations of the test atmosphere were:

acetone (240 mg/m³ or 100 ppm) and styrene (429 mg/m³ or 101 ppm). To test the ability of 3M 3520 OVMs to collect styrene at the recommended ceiling sampling time of 15 min with acetone concentrations at a similar level, a test atmosphere was created at the ceiling PEL for styrene and 0.2 x the TWA PEL for acetone in humid air having an average relative humidity of 80% at 22 °C. The concentrations of the test atmosphere were: acetone (480 mg/m³ or 200 ppm) and styrene (858 mg/m³ or 202 ppm). The mean recovery (% of theoretical) was 97.0% for the 15-min ceiling samples and 99.7% for the 240-min TWA samples. There was no styrene or acetone on the backup pad of the 15-min ceiling samplers. There was no styrene on the back-up pad of the 240-min TWA samplers, but there was a small amount of acetone on the back-up pad.

The ability of 3M 3520 OVMs to collect styrene in the presence of a potential interfering chemical at the same concentration was tested by sampling atmospheres containing styrene and an interference of methyl methacrylate at 1 x the ceiling PEL of styrene for 15 min and 1 x the TWA PEL of styrene for 240 min. The concentrations of the analytes in the 1 x ceiling PEL test atmosphere at an average humidity of 80% at 23 °C were: styrene (858 mg/m³ or 202 ppm), and methyl methacrylate (826 mg/m³ or 202 ppm). The concentrations of the analytes in the 1 x the TWA PEL test atmosphere at an average humidity of 79% at 23 °C were: styrene (429 mg/m³ or 101 ppm), and methyl methacrylate (413 mg/m³ or 101 ppm). Thirty three samplers were exposed to contaminated air (air containing the analyte and interferences) for each set of samples collected. Three samples from each set were immediately analyzed. The average recoveries (% of theoretical) on day 0 for styrene were: 97.4% for 15-min ceiling samples and 97.4% for 240-min TWA samples. Since methyl methacrylate can polymerize with styrene, a storage study was done with the remaining samplers to determine if there was a loss of styrene upon storage. The recoveries, calculated from the equation of the storage graph on day 17, for 15-min ceiling samples were 90.2% for ambient and 94.8% for refrigerated storage, and for 240-min TWA samples recoveries were 90.0% for ambient and 94.5% for refrigerated storage. (Section 4.9.1)

2.7.2 SKC 575-006 Passive Samplers

Reverse diffusion

Reverse diffusion is the measure of the ability of the sorbent within a diffusive sampler to retain the collected analyte. Reverse diffusion is measured by first exposing two sets of samplers to humid air with an average relative humidity of 80% at 23 °C containing the analyte, and then additionally exposing one of the sets to clean humid air. Comparison of the two sets of SKC 575-006 Passive Samplers showed an average of 98.8% was retained. (Section 4.9.2)

Low humidity

The ability of SKC 575-006 Passive Samplers to collect styrene from a relatively dry atmosphere was tested at the ceiling PEL by sampling a test atmosphere containing 1704 mg/m³ (400 ppm) of styrene at an average relative humidity of 20% at 23 °C for 15 min, and at the TWA PEL by sampling a test atmosphere containing 852 mg/m³ (200 ppm) of styrene at an average relative humidity of 20% at 23 °C for 240 min. The mean recoveries (% of theoretical) were 96.4% for the 15-min ceiling samples and 97.5% for the 240-min TWA samples. (Section 4.9.2)

Low concentration

The ability of SKC 575-006 Passive Samplers to collect styrene at a low concentration of 0.1 x the ceiling PEL was tested by sampling an atmosphere containing 85.2 mg/m³ (20 ppm) of styrene at an average relative humidity of 80% at 23 °C for 15 min, and at

0.1 x the TWA PEL was tested by sampling an atmosphere containing 42.6 mg/m³ (10 ppm) of styrene at an average relative humidity of 80% at 23 °C for 240 min. The mean recoveries (% of theoretical) were 97.7% for the 15-min ceiling samples and 98.4% for the 240-min TWA samples. (Section 4.9.2)

Sampling interference

A test of the ability of SKC 575-006 Passive Samplers to collect styrene in the presence of acetone was performed by creating a test atmosphere at the PEL level of acetone and styrene in humid air having an average relative humidity of 80% at 22 °C. The concentrations of the test atmospheres were: acetone (2400 mg/m³ or 1000 ppm) and styrene (429 mg/m³ or 101 ppm). Three SKC 575-006 Passive Samplers were exposed for 60 min due to potential capacity problems with the high concentrations of acetone. The mean recovery (% of theoretical) for styrene was 98.2%. Over half of the styrene samples analyzed at OSHA Salt Lake Technical Center in 2005-2008 were from fiberglass operations. To test the ability of SKC 575-006 Passive Samplers to collect styrene at the recommended TWA sampling time of 240 min with acetone concentrations at a similar level, as would be found in fiberglass operations where the acetone is present in the mix at a near equal level to the styrene, a test atmosphere was created at the TWA PEL styrene and 0.1 x TWA PEL acetone in humid air having an average relative humidity of 80% at 22 °C. The concentrations of the test atmospheres were: acetone (240 mg/m³ or 100 ppm) and styrene (429 mg/m³ or 101 ppm). To test the ability of SKC 575-006 Passive Samplers to collect styrene at the recommended ceiling sampling time of 15 min with acetone concentrations at a similar level a test atmosphere was created at the ceiling PEL styrene and 0.2 x the TWA PEL acetone in humid air having an average relative humidity of 80% at 22 °C. The concentrations of the test atmospheres were: acetone (480 mg/m³ or 200 ppm) and styrene (858 mg/m³ or 202 ppm). The mean recovery (% of theoretical) was 98.2% for the 15-min ceiling samples, and 98.5% for the 240-min TWA samples.

The ability of SKC 575-006 Passive Samplers to collect styrene in the presence of a potential interfering chemical at the same concentration was tested by sampling atmospheres containing styrene and an interference of methyl methacrylate at 1 x the ceiling PEL of styrene for 15 min and 1 x the TWA PEL of styrene for 240 min. The concentrations of the analytes in the 1 x the ceiling PEL test atmosphere at an average humidity of 80% at 23 °C were: styrene (858 mg/m³ or 202 ppm), and methyl methacrylate (826 mg/m³ or 202 ppm). The concentrations of the analytes in the 1 x the TWA PEL test atmosphere at an average humidity of 79% at 23 °C were: styrene (429 mg/m³ or 101 ppm), and methyl methacrylate (413 mg/m³ or 101 ppm). Thirty three samplers were exposed to contaminated air (air containing the analyte and interferences) for each set of samples collected. Three samples from each set were immediately analyzed. The average recoveries (% of theoretical) on day 0 for styrene were: 96.5% for 15-min samples and 97.4% for 240-min samples. Since methyl methacrylate can polymerize with styrene, a storage study was done with the remaining samplers to determine if there was a loss of styrene upon storage. The recoveries, calculated from the equation of the storage graph on day 17, for 15-min ceiling samples were 91.5% for ambient and 95.1% for refrigerated storage, and for 240-min TWA samples recoveries were 91.4% for ambient and 94.6% for refrigerated storage. (Section 4.9.2)

3. Analytical Procedure

Adhere to the rules set down in your Chemical Hygiene Plan.¹³ Avoid skin contact and inhalation of all chemicals and review all MSDSs before beginning this analytical procedure.

¹³ Occupational Exposure to Hazardous Chemicals in Laboratories. *Code of Federal Regulations*, Part 1910.1450, Title 29, 2003.

3.1 Apparatus

Gas chromatograph equipped with an FID. An Agilent Model 6890 GC equipped with an integrator, an automatic sample injector, and an FID was used in this evaluation.

A GC column capable of separating styrene from the extracting solvent, potential interferences, and internal standard. A J&W 60-m × 0.32-mm i.d. DB-WAX (0.5- μ m df) capillary column was used in this evaluation. An Agilent 5183-4647 injection port liner was used in this evaluation.

An electronic integrator or other suitable means of measuring GC detector response. A Waters Empower 2 Data System was used in this evaluation.

Glass vials with PTFE-lined caps. For this evaluation 2 and 4-mL vials were used.

A dispenser capable of delivering 2.0 mL of extracting solvent to prepare standards and samples. If a dispenser is not available, 2.0-mL volumetric pipettes can be used.

Class A volumetric flasks - 10-mL and other convenient sizes for preparing standards.

Calibrated 10- μ L syringe for preparing standards.

An SKC Desorption Shaker with rack (226D-03K) was used to extract SKC 575-006 Passive Samplers in this evaluation.

A mechanical shaker. An Eberbach mechanical shaker was used to extract the 3M pads in this evaluation.

3.2 Reagents

Styrene, [CAS no. 100-42-5], reagent grade or better. The styrene used in this evaluation was \geq 99% (lot no. 06501PE) purchased from Sigma-Aldrich (Milwaukee, WI).

Toluene, [CAS no. 108-88-3], reagent grade or better. The toluene used in this evaluation was 99.9% (lot no. 051343) purchased from Fisher Scientific (Pittsburg, PA).

n-Hexylbenzene [CAS no. 1077-16-3], reagent grade or better. The *n*-hexylbenzene (listed as 1-phenylhexane on bottle) used in this evaluation was 97% (lot no. 06202KO) purchased from Aldrich (Milwaukee, WI).

The extraction solvent used in this evaluation of SKC-006 Passive Samplers consisted of 1 μ L/mL *n*-hexylbenzene in toluene. The *n*-hexylbenzene was added to toluene as an internal standard. Other internal standards can be used provided they are fully tested.

While toluene extraction is the preferred procedure an alternative extraction solvent, which gives lower extraction efficiencies than the toluene extraction solvent, is a mixture of 99:1 carbon disulfide:*N,N*-dimethylformamide.

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. 11561HC) purchased from Aldrich (Milwaukee, WI).

N,N-Dimethylformamide (DMF), [CAS no. 68-12-2], anhydrous reagent grade or better. The DMF used in this evaluation was 99.8% (lot no. 08197EJ) purchased from Sigma-Aldrich (Milwaukee, WI).

The alternative extraction solvent consisted of 99:1 carbon disulfide:*N,N*-dimethylformamide with 1 µL/mL *n*-hexylbenzene as an internal standard. Other internal standards can be used provided they are fully tested.

3.3 Standard preparation

The diffusive samplers are extracted with 2 mL of the extraction solvent. Prepare analytical standards by injecting microliter amounts of the analyte into 2-mL volumetric flasks and diluting with extraction solvent. For example: a TWA target concentration level (for 3M 3520 OVM) standard for styrene was prepared by injecting 3.4 µL of styrene into a 2-mL volumetric flask containing about 1.75 mL of extraction solvent and then diluting to the mark with extraction solvent (3.08 mg/sample or 1.54 mg/mL). Lower concentration standards can be prepared from microliter injections of a stock solution of styrene in toluene or from dilutions of the higher concentration standards.

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 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 and 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 the sampler at a time by temporarily removing the cap plugs from the ports and pipetting 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 2-mL autosampler vial. Immediately cap each vial.

An alternative means of extraction for the 3M 3520 OVMs is to remove the cap, pull off the interior retaining ring, remove the charcoal pad, and place the pad into a labeled 4-mL vial. Remove the pad from the second section of the sampler in similar fashion. Add 2-mL of the extraction solvent to each vial and cap the vial. Shake the vials for 30 min. Transfer the sample into a labeled 2-mL autosampler vial. Immediately cap each vial. This alternative means was used in this method validation.

3.4.2 SKC 575-006 Passive Samplers (In general, follow the manufacturer's instructions.)

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

Slowly pipette 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 of a specialized shaker (SKC catalog no. 226D-03K) 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.

3.5 Analysis

3.5.1 Gas chromatography conditions:

Zone temperatures:

column: initial 60 °C, hold 4 min, program at 10 °C/min to 160 °C, hold 8 min

injector: 250 °C

detector: 260 °C

run time: 22 min

column gas flow: 1.5 mL/min (hydrogen)

column mode: 6.9 psi (constant pressure)

injection size: 1.0 µL (10:1 split)

inlet liner: Agilent 5183-4647 or equivalent

column: 60-m × 0.32-mm i.d. DB-WAX capillary column (df = 0.5 µm)

retention times: toluene 10.86 min, styrene 14.58 min, and *n*-hexylbenzene 19.56 min

FID conditions:

hydrogen flow: 30 mL/min

air flow: 400 mL/min

nitrogen

makeup flow: 20 mL/min

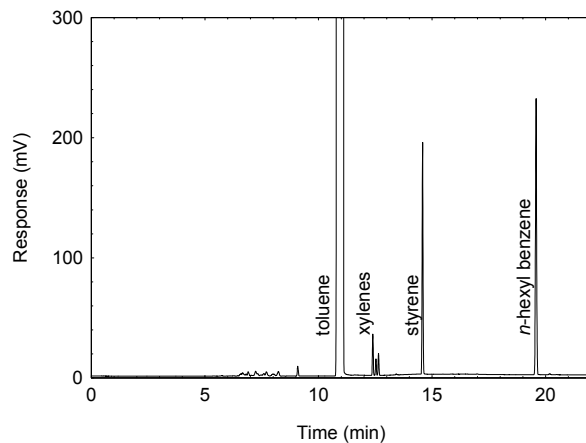


Figure 3.5.1. A chromatogram obtained at the target concentration with the recommended analytical conditions of styrene in the extraction solution (xylenes are contaminants in the toluene).

Peak areas are measured with an integrator or other suitable means.

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

3.5.3

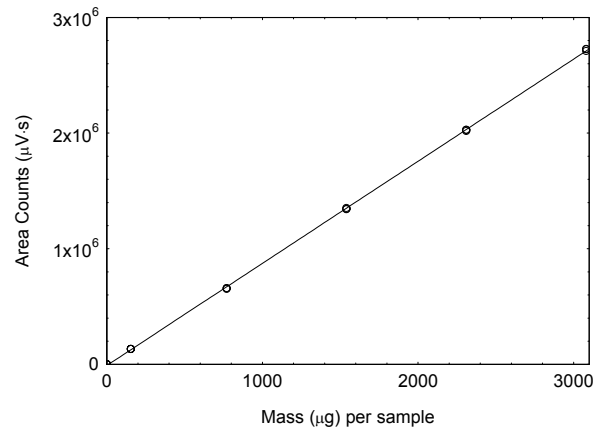


Figure 3.5.2. Calibration curve for styrene.
($y = 883x - 9224$)

3.6 Interferences (analytical)

Any compound that produces a GC response and has a similar retention time as the analyte 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 any interference from the analyte.

When necessary, the identity or purity of an analyte peak can be confirmed by GC-mass spectrometry, or by another analytical procedure (Section 4.10).

3.7 Calculations

3M 3520 OVMs and SKC 575-006 Passive Samplers

The amount of analyte 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 3M 3520 OVM sampler is saturated, affecting its ability to retain styrene, 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 SKC 575-006 Passive Samplers have only one section. The total micrograms per sample is the amount found on the sampler minus the amount found on the blank (if any).

The air concentration is calculated using the following formulas.

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

where: R_{SS} is the sampling rate at sampling site (mL/min)
 T_{SS} is the sampling site temperature in K
 T_{NTP} is 298.2 K
 P_{SS} is the sampling site pressure in mmHg
 P_{NTP} is 760 mmHg
 R_{NTP} is the sampling rate at NTP conditions (mL/min)

$$C_M = \frac{M1000}{tR_{SS}E_E}$$

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

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

where: C_V is concentration by volume (ppm)
 V_M is molar volume at $25\text{ }^\circ\text{C} = 24.46$
 C_M is concentration by weight (mg/m^3)
 M_r is molecular weight of analyte (styrene = 104.15)

If the sampling site temperature is not provided, assume that it is $22.2\text{ }^\circ\text{C}$. If the sampling site atmospheric pressure is not given, calculate an approximate value based on the sampling site elevation from the following equation.

$$P_{SS} = AE^2 - BE + 760$$

where: P_{SS} is the approximate atmospheric pressure (mmHg)
 E is the sampling site elevation, ft
 A is $3.768 \times 10^{-7}\text{ mmHg}/\text{ft}^2$
 B is $0.02741\text{ mmHg}/\text{ft}$

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 Chromatographic Analysis".¹⁴ 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 equally descending increments with the highest standard containing $4.98\text{ }\mu\text{g}/\text{mL}$ styrene. 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 ($1\text{-}\mu\text{L}$ injection with a 1:10 split), and the data obtained were used to determine the required parameters (standard error of estimate and slope) for the calculation of the DLAP. The slope and standard error of estimate, respectively, for styrene were 7.89 and 25.7. DLAP was calculated to be 9.78 pg .

¹⁴ Burreight, D.; Chan, Y.; Eide, M.; Elskamp, W.; Rose, M.; *Evaluation Guidelines For Air Sampling Methods Utilizing Chromatographic Analysis*. <http://www.osha.gov/dts/sltc/methods/chromguide/index.html>, OSHA Salt Lake Technical Center, U.S. Department of Labor: Salt Lake City, UT, 1999 (accessed 3/15/09).

Table 4.1
Detection Limit of the Analytical Procedure
for Styrene

concentration ($\mu\text{g}/\text{mL}$)	mass on column (pg)	area counts ($\mu\text{V}\cdot\text{s}$)
0	0	0
0.50	50	413
1.00	100	793
1.49	149	1134
1.99	199	1572
2.49	249	1963
2.99	299	2324
3.49	349	2766
3.98	398	3167
4.48	448	3494
4.98	498	3945

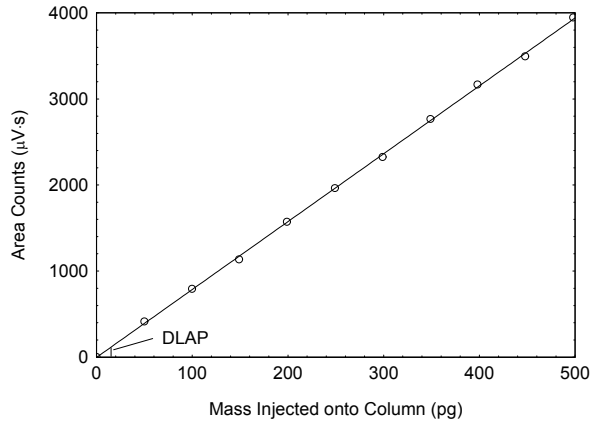


Figure 4.1. Plot of data to determine the DLAP for styrene. ($y = 7.89x - 2.78$)

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 equally descending increments of analyte. The highest amount is the amount spiked on the 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. The slope and standard error of estimate, respectively, were 40.4 and 387 for the 3M OVM and 41.6 and 366 for the SKC 575-006. The DLOP for the 3M OVM was $0.31 \mu\text{g}$ (10.5 ppb or $44.7 \mu\text{g}/\text{m}^3$), and for the SKC 575-006 was $0.34 \mu\text{g}$ (24.3 ppb or $103 \mu\text{g}/\text{m}^3$).

Table 4.2.1
Detection Limit of the Overall
Procedure for Styrene Collected on
3M OVM

mass per sample (μg)	area counts ($\mu\text{V}\cdot\text{s}$)
0	0
1.0	416
1.99	734
2.99	1156
3.98	1545
4.98	1963
5.98	2318
6.97	2647
7.97	3013
8.96	3493
9.96	3909

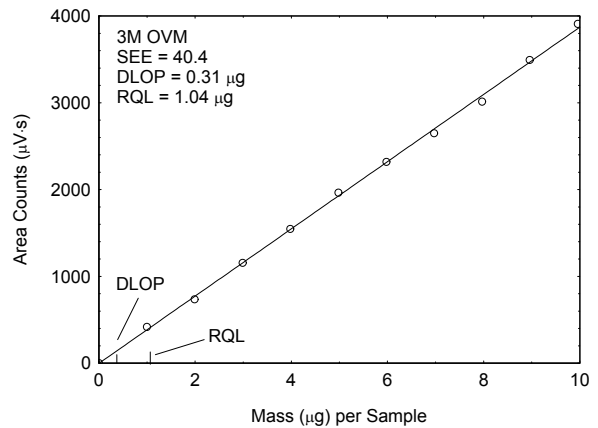


Figure 4.2.1. Plot of data to determine the DLOP/RQL for styrene on 3M OVM. ($y = 387x - 2.95$)

Table 4.2.2
Detection Limit of the Overall
Procedure for Styrene Collected on
SKC 575-006 Passive Samplers

mass per sample (μg)	area counts ($\mu\text{V}\cdot\text{s}$)
0	0
1.00	397
1.99	722
2.99	1144
3.98	1405
4.98	1843
5.98	2189
6.97	2502
7.97	2882
8.96	3274
9.96	3718

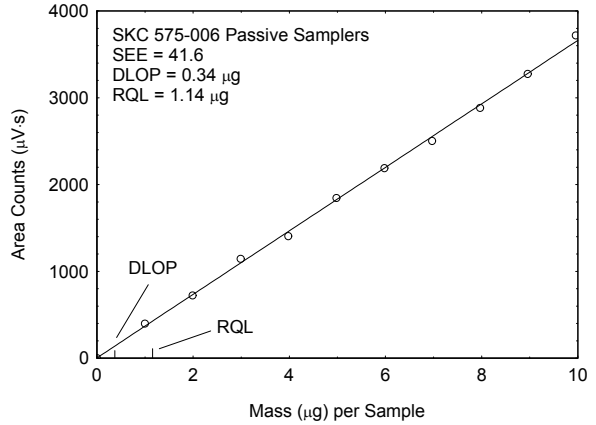


Figure 4.2.2. Plot of data to determine the DLOP/RQL for styrene on SKC 575-006 Passive Samplers. ($y = 366x + 2.96$)

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 4.2.3. In Table 4.2.3, E_E means the extraction efficiency.

Table 4.2.3
Reliable Quantitation Limit

sampler	μg	ppb	$\mu\text{g}/\text{m}^3$	E_E
3M 3520	1.0	35.2	150	96.1
SKC 575-006	1.1	81.7	351	96.2

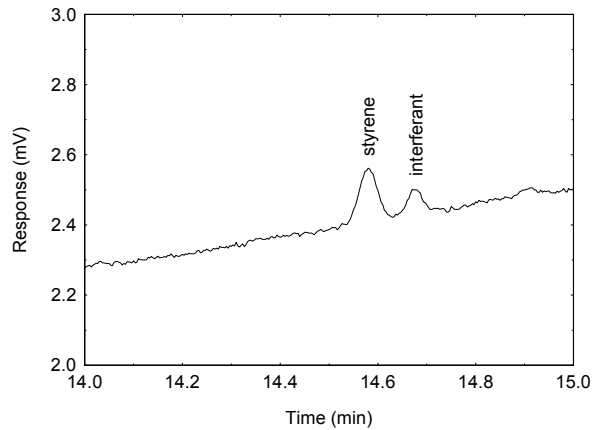


Figure 4.2.3. A chromatogram of the RQL collected on SKC 575-006 Passive Samplers.

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 the RQL to 2 times the TWA target concentration for 3M 3520 OVMs. This was the sampler with the highest mass loadings. The calibration curve was constructed and shown in Section 3.5.2 from the three injections each of five standards. The standard error of estimate was 22.3 μg .

Table 4.3
Instrument Calibration for Styrene

x target concn ($\mu\text{g}/\text{sample}$)	RQL	0.1 x	0.5 x	1.0 x	1.5 x	2.0 x
area counts	395	133612	652388	1341136	2029032	2727777
($\mu\text{V}\cdot\text{s}$)	386	133048	658062	1344095	2018949	2725023
	402	132041	659231	1352911	2027415	2710012

4.4 Precision (overall procedure)

4.4.1 3M 3520 OVMs

The precision of the overall procedure at the 95% confidence level for the ambient temperature 17-day storage test (at target concentration of both ceiling and TWA PELs) for samples collected on 3M 3520 OVMs are given in Table 4.1.1. 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 $\pm 7.7\%$ is included. If the atmospheric pressure is not known, it is estimated from the sampling site elevation and a variability of $\pm 3\%$ is included.

Table 4.4.1
Standard Error of Estimate and Precision of the Overall Procedure
at Ceiling and TWA PELs for 3M 3520 OVMs

known conditions	ceiling PEL error (%)	ceiling PEL precision ($\pm\%$)	TWA PEL error (%)	TWA PEL precision ($\pm\%$)
both T & P	6.52	12.8	6.47	12.7
only T	7.18	14.1	7.13	14.0
only P	10.1	19.7	10.1	19.7
neither T nor P	10.5	20.6	10.5	20.6

4.4.2 SKC 575-006 Passive Samplers

The precision of the overall procedure at the 95% confidence level for the ambient temperature 17-day storage test (at the target concentration of both ceiling and TWA PELs) for samples collected on SKC 575-006 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 $\pm 7.7\%$ is included. If the atmospheric pressure is not known, it is estimated from the sampling site elevation and a variability of $\pm 3\%$ is included.

Table 4.4.2
Standard Error of Estimate and Precision of the Overall Procedure
at Ceiling and TWA PELs for SKC 575-006 Passive Samplers

known conditions	ceiling PEL error (%)	ceiling PEL precision ($\pm\%$)	TWA PEL error (%)	TWA PEL precision ($\pm\%$)
both T & P	8.74	17.1	8.79	17.2
only T	9.24	18.1	9.29	18.2
only P	11.65	22.8	11.69	22.9
neither T nor P	12.03	23.6	12.06	23.6

4.5 Storage test

4.5.1 3M 3520 OVMs

Storage samples for styrene were prepared by collecting samples from a dynamically generated test atmosphere using the recommended sampling conditions for 3M 3520 OVMs. Two sets of samples at different loadings were prepared. The first set of samples was collected for 240 min from a test atmosphere at the TWA target concentration (429 mg/m^3 or 101 ppm), with an average relative humidity of 80% at 23 °C. The second set of samples was collected for 15 min from a test atmosphere at the ceiling target concentration (858 mg/m^3 or 202 ppm), with an average relative humidity of 80% at 23 °C. Each set contained thirty-three storage samples. Three samples were analyzed on the day of generation from each set of samples. In each set, fifteen of the 3M 3520 OVMs were stored at reduced temperature (4 °C) and the other fifteen were stored in a closed drawer at ambient temperature (about 23 °C). At 3 to 4-day intervals, three samples were selected from each set and analyzed. Sample results are not corrected for extraction efficiency. The recoveries on day 17, calculated from the equation of the storage graph, for the samples collected for the 15-min ceiling were 94.5% for ambient and 95.5% for refrigerated; and for 240-min TWA samples recoveries were 94.1% for ambient and 95.4% for refrigerated storage.

Table 4.5.1.1
Storage Test for Styrene on 3M 3520 OVMs Collected for 15 min at Ceiling PEL

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	98.8	96.3	97.0			
3	97.5	98.2	96.2	97.8	98.3	96.6
7	95.4	98.5	96.9	96.7	96.1	97.5
10	94.3	95.1	97.0	96.2	97.0	97.8
14	96.6	94.5	93.2	95.0	96.2	97.0
17	93.9	96.1	94.1	95.1	96.3	94.1

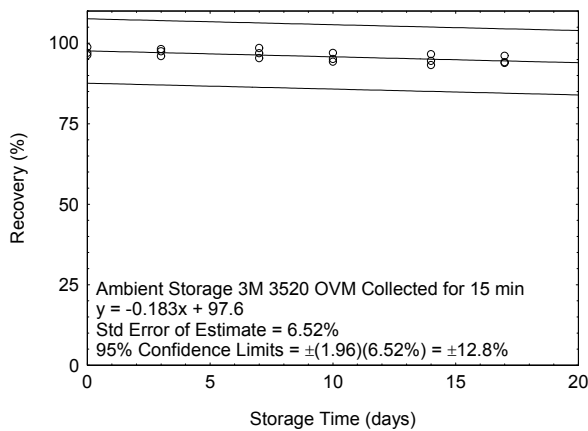


Figure 4.5.1.1. Ambient storage test for styrene at the ceiling PEL collected for 15 min on 3M 3520 OVMs.

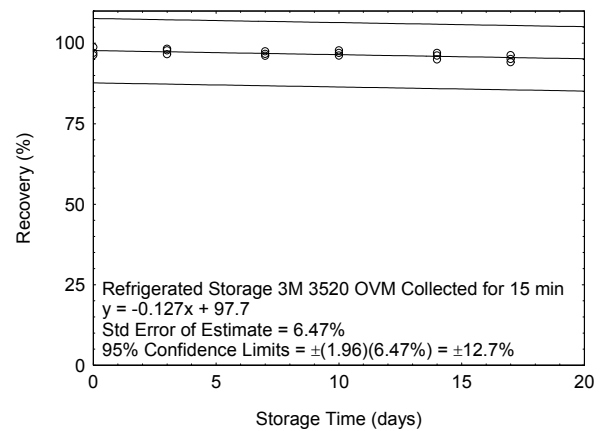


Figure 4.5.1.2. Refrigerated storage test for styrene at the ceiling PEL collected for 15 min on 3M 3520 OVMs.

Table 4.5.1.2

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
	0	98.1	96.5	97.4		
3	97.9	96.0	96.8	98.5	95.8	97.7
7	96.3	97.0	95.1	98.0	97.0	96.1
10	96.9	94.0	95.0	97.9	96.7	95.3
14	96.1	93.9	94.7	94.9	97.0	95.4
17	95.1	93.6	92.9	96.6	95.3	94.0

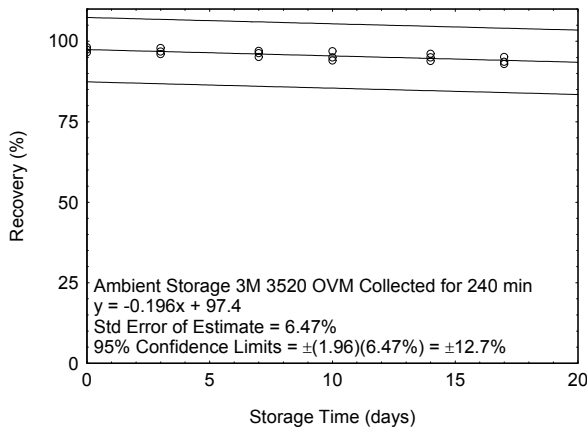


Figure 4.5.1.3. Ambient storage test for styrene at the TWA PEL collected for 240 min on 3M 3520 OVMs.

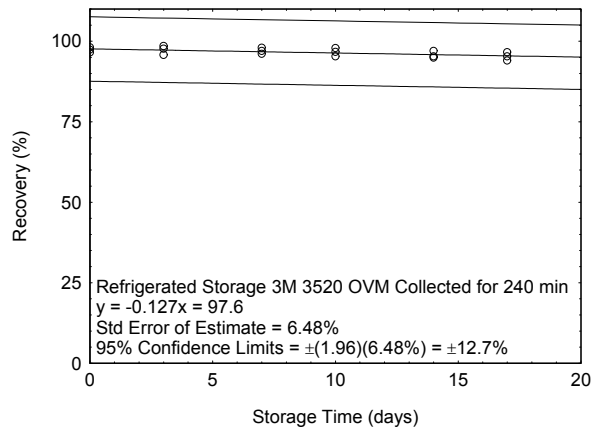


Figure 4.5.1.4. Refrigerated storage test for styrene at the TWA PEL collected for 240 min on 3M 3520 OVMs.

4.5.2 SKC 575-006 Passive Samplers

Storage samples for styrene were prepared by collecting samples from a dynamically generated test atmosphere using the recommended sampling conditions for SKC 575-006 Passive Samplers. Two sets of samples at different loadings were prepared. The first set of samples was collected for 240 min from a test atmosphere at the TWA target concentration (429 mg/m³ or 101 ppm), with an average relative humidity of 80% at 23 °C. The second set of samples was collected for 15 min from a test atmosphere at the ceiling target concentration (858 mg/m³ or 202 ppm), with an average relative humidity of 80% at 23 °C. Each set contained thirty-three storage samples. Three samples were analyzed on the day of generation from each set of samples. In each set, fifteen of the SKC 575-006 Passive Samplers were stored at reduced temperature (4 °C) and the other fifteen were stored in a closed drawer at ambient temperature (about 23 °C). At 3 to 4-day intervals, three samples were selected from each set and analyzed. Sample results are not corrected for extraction efficiency. The recoveries on day 17, calculated from the equation of the storage graph, for samples collected for 15-min ceiling samples were 94.6% for ambient and 96.5% for refrigerated, and for 240-min TWA samples the recoveries were 95.0% for ambient and 96.1% for refrigerated storage.

Table 4.5.2.1
Storage Test for Styrene on SKC 575-006 Passive Samplers
Collected for 15 min at Ceiling PEL

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
	0	98.3	96.9	97.8		
3	96.4	99.1	97.6	99.6	96.9	98.5
7	96.9	96.6	97.8	99.2	98.2	96.0
10	95.1	96.2	95.7	98.9	96.1	97.5
14	95.0	96.1	94.8	97.7	97.0	95.1
17	95.3	94.5	93.3	96.1	98.3	94.5

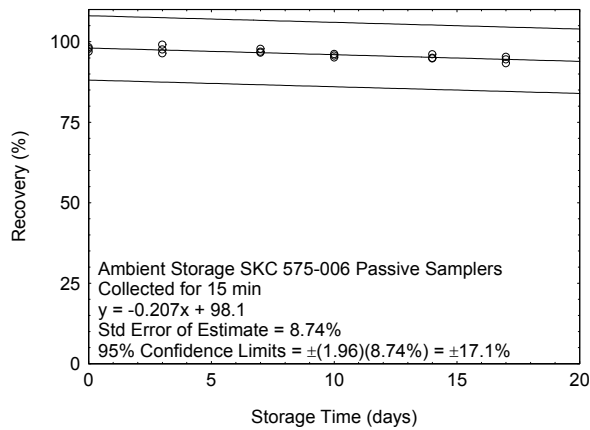


Figure 4.5.2.1. Ambient storage test for styrene at the ceiling PEL collected for 15 min on SKC 575-006 Passive Samplers.

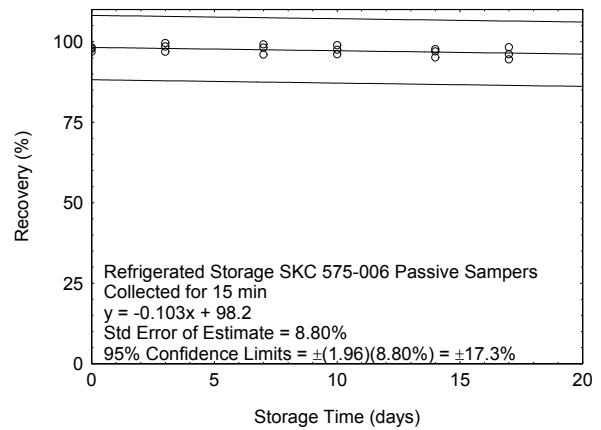


Figure 4.5.2.2. Refrigerated storage test for styrene at the ceiling PEL collected for 15 min on SKC 575-006 Passive Samplers.

Table 4.5.2.2
Storage Test for Styrene on SKC 575-006 Passive Samplers
Collected for 240 min at TWA PEL

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
	0	98.5	96.5	97.9		
3	95.9	98.8	96.2	98.2	96.2	99.1
7	96.3	98.0	95.0	96.6	97.1	98.9
10	98.1	95.5	96.2	97.3	96.2	98.1
14	97.0	94.4	95.4	95.6	97.0	96.7
17	96.1	94.5	93.4	96.1	95.8	95.1

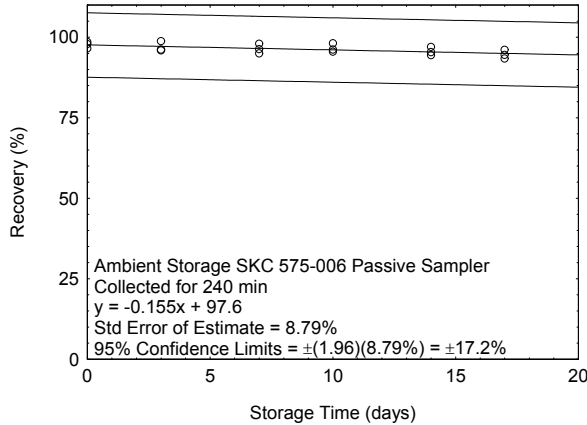


Figure 4.5.2.3. Ambient storage test for styrene at the TWA PEL collected for 240 min on SKC 575-006 Passive Samplers.

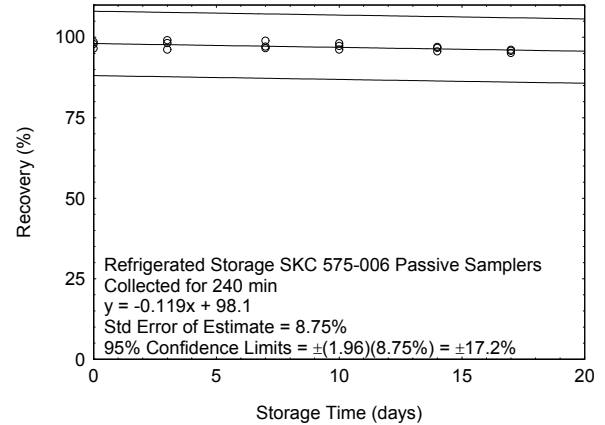


Figure 4.5.2.4. Refrigerated storage test for styrene at the TWA PEL collected for 240 min on SKC 575-006 Passive Samplers.

4.6 Reproducibility

Six samples were taken for 15 min at the ceiling PEL for each of the two types of samplers by collecting them from a controlled test atmosphere similar to those used in the collection of the storage samples, 202 ppm styrene (858 mg/m³), with an average relative humidity of 80% at 23 °C. Six samples were taken for 240 min at the TWA PEL for each of the two types of samplers by collecting them from a controlled test atmosphere similar to those used in the collection of the storage samples, 101 ppm styrene (429 mg/m³), with an average relative humidity of 80% at 23 °C. The samples were submitted to the OSHA Salt Lake Technical Center for analysis, along with a draft copy of this method. The 15-min and 240-min samples were analyzed after being stored at 4 °C for 4 days. Sample results were corrected for extraction efficiency. No sample result had a deviation greater than the precision of the overall procedure determined in Section 4.4.

Table 4.6.1
Reproducibility Data for Ceiling PEL Styrene
Sampled for 15 min on 3M 3520 OVM

theoretical (mg/sample)	recovered (mg/sample)	recovery (%)	deviation (%)
0.193	0.181	93.8	-6.2
0.193	0.180	93.3	-6.7
0.193	0.179	92.7	-7.3
0.193	0.188	97.4	-2.6
0.193	0.186	96.4	-3.6
0.193	0.191	99.0	-1.0

Table 4.6.2
Reproducibility Data for Ceiling PEL Styrene Sampled
for 15 min on SKC 575-006 Passive Samplers

theoretical (mg/sample)	recovered (mg/sample)	recovery (%)	deviation (%)
0.0875	0.0860	98.3	-1.7
0.0875	0.0811	92.7	-7.3
0.0875	0.0809	92.5	-7.5
0.0875	0.0832	95.1	-4.9
0.0875	0.0804	91.9	-8.1
0.0875	0.0819	93.6	-6.4

Table 4.6.3
Reproducibility Data for TWA PEL Styrene
Sampled for 240 min on 3M 3520 OVM

theoretical (mg/sample)	recovered (mg/sample)	recovery (%)	deviation (%)
3.09	2.98	96.4	-3.6
3.09	3.03	98.1	-1.9
3.09	3.10	100.3	+0.3
3.09	3.07	99.4	-0.6
3.09	3.02	97.7	-2.3
3.09	3.05	98.7	-1.3

Table 4.6.4
Reproducibility Data for TWA PEL Styrene Sampled
for 240 min on SKC 575-006 Passive Samplers

theoretical (mg/sample)	recovered (mg/sample)	recovery (%)	deviation (%)
1.40	1.39	99.3	-0.7
1.40	1.32	94.3	-5.7
1.40	1.30	92.9	-7.1
1.40	1.35	96.4	-3.6
1.40	1.37	97.9	-2.1
1.40	1.33	95.0	-5.0

4.7 Sampler capacity

4.7.1 3M 3520 OVMs

The sampling rate and sampler capacity are determined with samples collected for increasing time intervals from a controlled test atmosphere. The concentration of the test atmosphere was two times the TWA PEL target concentration with an average relative humidity of approximately 80% at 23 °C. The atmosphere tested was 858 mg/m³ or 202 ppm. Three samplers were exposed for each test. Sampling rates were determined at ambient temperature and pressure, but were converted to their equivalent at 760 mmHg and 25 °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. The average sampling rate of all values between the lines was 29.93 mL/min. The standard deviation and RSD are 1.01 mL/min and 3.37%. Mass collected was corrected for extraction efficiency. The sampler capacity is exceeded when the sampling rate rapidly decreases (greater than 8 hours). The recommended sampling time is 240 min for TWA samples and 15 min for ceiling samples.

Table 4.7.1
Determination of Sampling Rate and Time of Styrene for 3M 3520 OVMs from a 202-ppm Atmosphere

time (h)	sampling rate (mL/min)		
	first	second	third
0.083	26.72	25.31	26.42
0.167	28.34	28.96	29.06
0.25	30.02	29.78	28.81
0.5	29.29	30.36	29.87
1	30.13	29.05	28.69
2	31.25	29.86	30.87
3	29.24	29.89	30.43
4	30.33	30.78	29.59
6	28.81	28.58	29.93
8	28.27	27.54	26.95
10	24.80	26.05	25.78

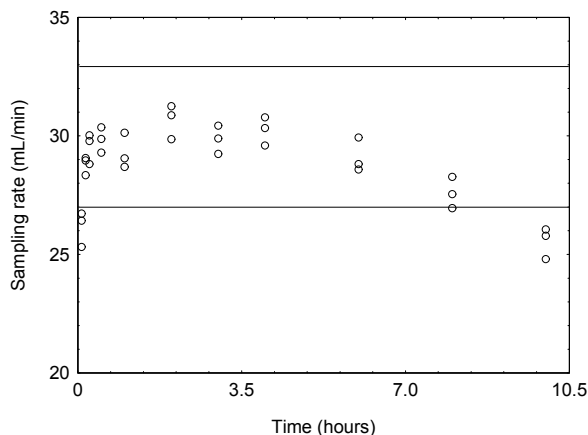


Figure 4.7.1. The 3M 3520 OVM data in Table 4.7.1 plotted to determine the recommended sampling time and sampling rate of styrene from a 202-ppm atmosphere.

4.7.2 SKC 575-006 Passive Samplers

The sampling rate and sampler capacity are determined with samples collected for increasing time intervals from a controlled test atmosphere. The concentration of the test atmosphere was two times the TWA PEL target concentration with an average relative humidity of approximately 80% at 23 °C. The atmosphere tested was 858 mg/m³ or 202 ppm. Three samplers were exposed for each test. Sampling rates were determined at ambient temperature and pressure, but were converted to their equivalent at 760 mmHg and 25 °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. The average sampling rate of all values between the lines was 13.55 mL/min. The standard deviation and RSD are 0.52 mL/min and 3.80%. Mass collected was corrected for extraction efficiency. The sampler capacity is exceeded when the sampling rate rapidly decreases (greater than 8 hours). The recommended sampling time is 240 min for TWA samples and 15 min for ceiling samples.

Table 4.7.2
Determination of Sampling Rate and Time of Styrene for SKC 575-006 Passive Samplers from a 202-ppm Atmosphere

time (h)	sampling rate (mL/min)		
	first	second	third
0.083	12.18	11.59	11.96
0.167	12.76	12.94	12.70
0.25	13.57	13.31	13.99
0.5	14.21	13.66	14.07
1	13.88	13.41	14.16
2	13.39	13.69	14.12
3	13.64	14.27	13.76
4	14.14	13.56	13.99
6	13.16	13.59	13.63
8	13.12	12.68	12.49
10	11.87	12.21	12.38

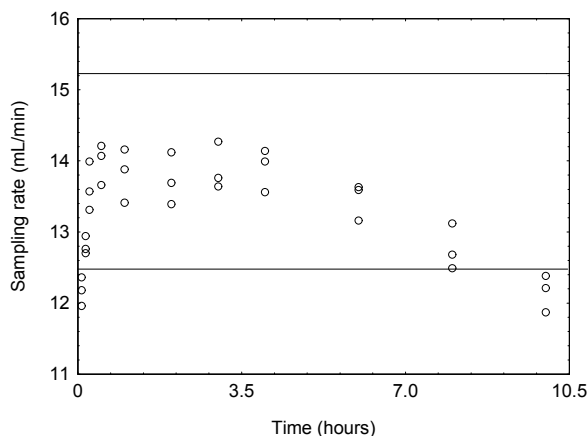


Figure 4.7.2. The SKC 575-006 Passive Sampler data in Table 4.7.2 plotted to determine the recommended sampling time and sampling rate of styrene from a 202-ppm atmosphere.

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 toluene with 1.0 $\mu\text{L/mL}$ *n*-hexylbenzene internal standard. 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 3M 3520 OVMs

Extraction efficiency

The extraction efficiencies of styrene were determined by liquid-spiking four charcoal pads from 3M 3520 OVMs, at each concentration level, with the analyte from the RQL to 2 times the TWA PEL target concentration. These samples were stored overnight at ambient temperature and then analyzed. The mean extraction efficiency over the working range from the RQL to 2 times the TWA PEL target concentration is 97.2%. The 1.0 x the ceiling PEL concentration was not included in this average as it was similar to the 0.1 x the TWA PEL level. 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. Wet samplers were prepared by sampling humid air having an average relative humidity of about 80% at 23 °C for 240 min, then liquid-spiking each with the analyte, storing them overnight, and then analyzing them. The extraction efficiency was not affected by the presence of water.

Table 4.8.1.1
Extraction Efficiency (%) of Styrene from 3M 3520 OVM Using Toluene

level		sample number				mean
× TWA target concn	mg per sample	1	2	3	4	
RQL	0.001	95.9	94.9	96.6	97.0	96.1
0.1	0.31	96.6	96.5	98.2	97.0	97.1
0.25	0.77	95.8	95.6	96.9	97.8	96.5
0.5	1.54	96.9	97.4	95.8	97.0	96.8
1.0	3.08	97.5	98.1	98.9	96.3	97.7
1.5	4.62	97.4	95.4	98.8	97.7	97.3
2.0	6.16	99.1	98.9	97.9	98.6	98.6
1.0 (ceiling)	0.384	98.3	97.5	96.3	98.5	97.6
1.0 (wet)	3.09	95.4	96.7	97.7	96.1	96.5

Stability of extracted samples

The stability of extracted samples was investigated by reanalyzing the target concentration samples 24, 48, and 72 h after initial analysis. After the original analysis was performed, two autosampler vials were recapped with new septa while the remaining two retained their punctured septa, and all samples were allowed to stand in the autosampler tray at ambient temperature. The samples were reanalyzed with fresh standards. Each septum on the vial was punctured 5 times by the autosampler syringe for each analysis. Extracted samples remain stable for at least 72 h. In Tables 4.8.1.2 and 4.8.1.3, diff means the difference between the initial analysis and the subsequent analysis.

Table 4.8.1.2
Stability of Samples for Styrene on 3M 3520 OVMs at 1 x Ceiling PEL Extracted with Toluene

punctured septa replaced							punctured septa retained						
initial (%)	24 h (%)	diff (%)	48 h (%)	diff (%)	72 h (%)	diff (%)	initial (%)	24 h (%)	diff (%)	48 h (%)	diff (%)	72 h (%)	diff (%)
98.3	96.1	-2.2	97.6	-0.7	97.8	-0.5	96.3	97.8	+1.5	98.3	+2.0	98.8	+2.5
97.5	95.0	-2.5	98.0	+0.5	98.4	+0.9	98.5	98.2	-0.3	99.5	+1.0	98.4	-0.1
			(mean)							(mean)			
97.9	95.6	-2.3	97.8	-0.1	98.1	+0.2	97.4	98.0	+0.6	98.9	+1.5	98.6	+1.2

Table 4.8.1.3
Stability of Samples for Styrene on 3M 3520 OVMs at 1 x TWA PEL Extracted with Toluene

punctured septa replaced							punctured septa retained						
initial (%)	24 h (%)	diff (%)	48 h (%)	diff (%)	72 h (%)	diff (%)	initial (%)	24 h (%)	diff (%)	48 h (%)	diff (%)	72 h (%)	diff (%)
97.5	97.1	-0.4	96.8	-0.7	96.3	-1.2	98.9	99.3	+0.4	98.4	-0.5	99.0	+0.1
98.1	97.3	-0.8	97.0	-1.1	96.7	-1.4	96.3	97.5	+1.2	96.6	+0.3	96.8	+0.5
			(mean)							(mean)			
97.8	97.2	-0.6	96.9	-0.9	96.5	-1.3	97.6	98.4	+0.8	97.5	-0.1	97.9	+0.3

An alternative extraction solvent is 99:1 carbon disulfide:DMF with 1 µL/mL *n*-hexylbenzene internal standard. The extraction efficiencies of styrene were determined by liquid-spiking four charcoal pads from 3M 3520 OVMs, at each concentration level, with the analyte from the RQL to 2 times the TWA PEL target concentration. These samples were stored overnight at ambient temperature and then

analyzed. The mean extraction efficiency over the working range from the RQL to 2 times the TWA PEL target concentration is 89.1%. The 1.0 x the ceiling PEL concentration was not included in this average as it was similar to the 0.1 x the TWA PEL level. 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. Wet samplers were prepared by sampling humid air having an average relative humidity of about 80% at 23 °C for 240 min, then liquid-spiking each with the analyte, storing them overnight, and then analyzing them. The extraction efficiency was not affected by the presence of water.

Table 4.8.1.4
Extraction Efficiency (%) of Styrene from
3M OVM Using 99:1 Carbon Disulfide:DMF

level		sample number				mean
× TWA target concn	mg per sample	1	2	3	4	
RQL	0.001	86.7	85.7	87.2	86.3	86.5
0.1	0.31	87.2	86.3	85.8	86.0	86.3
0.25	0.77	87.3	87.6	86.5	88.2	87.4
0.5	1.54	90.9	88.0	89.6	88.7	89.3
1.0	3.08	91.4	88.4	92.0	89.4	90.3
1.5	4.62	91.2	92.4	90.9	91.1	91.4
2.0	6.16	92.6	93.8	91.9	90.5	92.2
1.0 (ceiling)	0.384	90.9	88.1	91.8	88.8	89.9
1.0 (wet)	3.08	90.4	92.1	91.2	89.8	90.8

Stability of extracted samples

The stability of extracted samples using 99:1 carbon disulfide:DMF with 1 µL/mL *n*-hexylbenzene was investigated by reanalyzing the target concentration samples 24, 48, and 72 h after initial analysis. After the original analysis was performed, two autosampler vials were recapped with new septa while the remaining two retained their punctured septa, and all samples were allowed to stand in the autosampler tray at ambient temperature. The samples were reanalyzed with fresh standards. Each septum on the vial was punctured 5 times by the autosampler syringe for each analysis. Extracted samples remain stable for at least 72 h. In Tables 4.8.1.5 and 4.8.1.6, diff means the difference between the initial analysis and the subsequent analysis.

Table 4.8.1.5
Stability of Samples for Styrene on 3M 3520 OVMs at 1 x Ceiling PEL Extracted with 99:1 Carbon Disulfide:DMF

<u>punctured septa replaced</u>							<u>punctured septa retained</u>						
initial (%)	24 h (%)	diff (%)	48 h (%)	diff (%)	72 h (%)	diff (%)	initial (%)	24 h (%)	diff (%)	48 h (%)	diff (%)	72 h (%)	diff (%)
90.9	86.1	-4.8	89.4	-1.5	88.6	-2.3	91.8	87.1	-4.7	91.9	+0.1	92.6	+0.8
88.1	88.4	+0.3	90.2	+2.1	89.4	+1.3	88.8	85.0	-3.8	89.9	+1.1	90.4	+1.6
			(mean)							(mean)			
89.5	87.2	+2.3	89.8	+0.3	89.0	-0.5	90.3	86.1	-4.2	90.9	+0.6	91.5	+1.2

Table 4.8.1.6
Stability of Samples for Styrene on 3M 3520 OVMs at 1 x TWA PEL Extracted with 99:1 Carbon Disulfide:DMF

initial (%)	24 h (%)	punctured septa replaced				diff (%)	initial (%)	24 h (%)	punctured septa retained				diff (%)
		diff (%)	48 h (%)	diff (%)	72 h (%)				diff (%)	48 h (%)	diff (%)	72 h (%)	
91.4	90.3	-1.1	91.7	+0.3	91.0	-0.4	92.0	92.3	+0.3	92.5	+0.5	91.9	-0.1
88.4	87.9	-0.5	88.3	-0.1	87.8	-0.6	89.4	90.1	+0.7	90.3	+0.9	90.9	+1.5
			(mean)							(mean)			
89.9	89.1	-0.8	90.0	-0.1	89.4	-0.5	90.7	91.2	+0.5	91.4	+0.7	91.4	+0.7

4.8.2 SKC 575-006 Passive Samplers

Extraction efficiency

The extraction efficiencies of styrene were determined by liquid-spiking four SKC 575-006 Passive Samplers, at each concentration level, with the analyte from the RQL to 2 times the TWA PEL target concentration. These samples were stored overnight at ambient temperature and then analyzed. The mean extraction efficiency over the working range from the RQL to 2 times the TWA PEL target concentration is 96.7%. The 1.0 x the ceiling PEL concentration was not included in this average as it was similar to the 0.1 x the TWA PEL level. 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. Wet samplers were prepared by sampling humid air having an average relative humidity of about 80% at 23 °C for 240 min, then liquid-spiking each with the analyte, storing them overnight, and then analyzing them. The extraction efficiency was not affected by the presence of water.

Table 4.8.2.1
Extraction Efficiency (%) of Styrene from
SKC 575-006 Passive Samplers Using Toluene

level		sample number				mean
× target concn	mg per sample	1	2	3	4	
RQL	0.001	97.6	95.0	96.9	95.2	96.2
0.1	0.14	97.4	98.0	95.5	97.9	97.2
0.25	0.34	96.3	97.8	95.5	97.3	96.7
0.5	0.68	95.7	95.6	95.9	96.0	95.8
1.0	1.36	97.4	97.8	95.9	96.7	97.0
1.5	2.04	95.9	98.2	96.2	98.1	97.1
2.0	2.72	97.3	96.8	98.5	96.4	97.2
1.0 (ceiling)	0.17	98.3	96.5	96.4	97.8	97.2
1.0 (wet)	1.36	94.3	93.2	93.9	94.7	94.0

Stability of extracted samples

The stability of extracted samples was investigated by reanalyzing the target concentration samples 24, 48, and 72 h after initial analysis. After the original analysis was performed two autosampler vials were recapped with new septa while the remaining two retained their punctured septa, and all samples were allowed to stand in the autosampler tray at ambient temperature. The samples were reanalyzed with fresh standards. Each septum on the vial was punctured 5 times by the autosampler syringe

for each analysis. Extracted samples remain stable for at least 72 h. In Tables 4.8.2.2 and 4.8.2.3, diff means the difference between the initial analysis and the subsequent analysis.

Table 4.8.2.2
Stability of Extracted Samples for Styrene on SKC 575-006 Passive Samplers
at 1 x Ceiling PEL Extracted with Toluene

<u>punctured septa replaced</u>							<u>punctured septa retained</u>						
initial (%)	24 h (%)	diff (%)	48 h (%)	diff (%)	72 h (%)	diff (%)	initial (%)	24 h (%)	diff (%)	48 h (%)	diff (%)	72 h (%)	diff (%)
98.3	95.7	-2.6	98.4	+0.1	97.8	-0.5	96.4	97.4	+1.0	98.4	+2.0	98.7	+2.3
96.5	96.6	+0.1	98.8	+2.3	96.8	+0.3	97.8	97.9	+0.1	98.6	+0.8	99.5	+1.7
			(mean)							(mean)			
97.4	96.2	-1.2	98.6	+1.2	97.3	-0.1	97.1	97.6	+0.5	98.5	+1.4	99.1	+2.0

Table 4.8.2.3
Stability of Extracted Samples for Styrene on SKC 575-006 Passive Samplers
at 1 x TWA PEL Extracted with Toluene

<u>punctured septa replaced</u>							<u>punctured septa retained</u>						
initial (%)	24 h (%)	diff (%)	48 h (%)	diff (%)	72 h (%)	diff (%)	initial (%)	24 h (%)	diff (%)	48 h (%)	diff (%)	72 h (%)	diff (%)
97.4	96.2	-1.2	96.9	-0.5	96.4	-1.0	95.9	95.5	-0.4	96.6	+0.7	96.8	+0.9
97.8	96.8	-1.0	96.3	-1.5	97.0	-0.8	96.7	96.5	-0.2	97.8	+1.1	96.2	-0.5
			(mean)							(mean)			
97.6	96.5	-1.1	96.6	-1.0	96.7	-0.9	96.3	96.0	-0.3	97.0	+0.9	96.5	+0.2

An alternative extraction solvent is a mixture of 99:1 carbon disulfide:DMF with 1 µL/mL *n*-hexylbenzene internal standard. The extraction efficiencies of styrene were determined by liquid-spiking four SKC 575-006 Passive Samplers, at each concentration level, with the analyte from the RQL to 2 times the TWA PEL target concentration. These samples were stored overnight at ambient temperature and then analyzed. The mean extraction efficiency over the working range from the RQL to 2 times the TWA PEL target concentration is 83.7%. The 1.0 x ceiling PEL concentration was not included in this average as it was similar to the 0.1 x TWA PEL level. 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. Wet samplers were prepared by sampling humid air having an average relative humidity of about 80% at 23 °C for 240 min, then liquid-spiking each with the analyte, storing them overnight, and then analyzing them. The extraction efficiency was not affected by the presence of water.

Table 4.8.2.4
Extraction Efficiency (%) of Styrene from
SKC 575-006 Passive Samplers Using 99:1 Carbon Disulfide:DMF

<u>level</u>		<u>sample number</u>				<u>mean</u>
\times target concn	mg per sample	1	2	3	4	
RQL	0.001	80.2	81.4	82.3	83.0	81.7
0.1	0.14	83.1	82.6	81.7	82.9	82.6
0.25	0.34	83.0	82.9	84.4	82.5	83.2
0.5	0.68	85.3	85.1	83.3	83.9	84.4
1.0	1.36	84.2	85.0	83.6	83.2	84.0
1.5	2.04	85.2	86.0	83.9	83.2	84.6
2.0	2.72	83.9	84.8	86.7	85.4	85.2
1.0 (ceiling)	0.17	83.9	84.7	85.2	83.8	84.4
1.0 (wet)	1.36	84.0	83.7	85.2	83.9	84.2

Stability of extracted samples

The stability of extracted samples was investigated by reanalyzing the target concentration samples 24, 48, and 72 h after initial analysis. After the original analysis was performed two autosampler vials were recapped with new septa while the remaining two retained their punctured septa, and all samples were allowed to stand in the autosampler tray at ambient temperature. The samples were reanalyzed with fresh standards. Each septum on the vial was punctured 5 times by the autosampler syringe for each analysis. Extracted samples remain stable for at least 72 h. In Tables 4.8.1.5 and 4.8.1.6, diff means the difference between the initial analysis and the subsequent analysis.

Table 4.8.2.5
Stability of Extracted Samples for Styrene on SKC 575-006 Passive Samplers
at 1 x Ceiling PEL Extracted with 99:1 Carbon Disulfide:DMF

initial (%)	24 h (%)	<u>punctured septa replaced</u>				<u>punctured septa retained</u>							
		diff (%)	48 h (%)	diff (%)	72 h (%)	diff (%)	initial (%)	24 h (%)	diff (%)	48 h (%)	diff (%)	72 h (%)	diff (%)
83.9	82.8	-1.1	83.2	-0.7	84.6	+0.7	85.2	84.0	-1.2	85.4	+0.2	86.7	+1.5
84.7	83.1	-1.6	84.8	+0.1	85.6	+0.9	83.8	82.5	-1.3	85.0	+1.2	85.5	+1.7
			(mean)							(mean)			
84.3	83.0	-1.3	84.0	+0.3	85.1	+0.8	84.5	83.2	-1.3	85.2	+0.7	86.1	+1.6

Table 4.8.2.6
Stability of Extracted Samples for Styrene on SKC 575-006 Passive Samplers
at 1 x TWA PEL Extracted with 99:1 Carbon Disulfide:DMF

initial (%)	24 h (%)	<u>punctured septa replaced</u>				<u>punctured septa retained</u>							
		diff (%)	48 h (%)	diff (%)	72 h (%)	diff (%)	initial (%)	24 h (%)	diff (%)	48 h (%)	diff (%)	72 h (%)	diff (%)
84.2	83.5	-0.7	85.0	+0.8	84.3	+0.1	83.6	84.3	+0.7	84.9	+1.3	85.4	+1.8
85.0	85.3	+0.3	85.8	+0.8	86.1	+1.1	83.2	84.7	+0.5	85.1	+1.9	84.8	+1.6
			(mean)							(mean)			
84.6	84.4	-0.2	85.4	+0.8	85.2	+0.6	83.4	84.5	+0.6	85.0	+1.6	85.1	+1.7

4.9 Interferences (sampling)

4.9.1 3M 3520 OVMs

Reverse diffusion

Reverse diffusion is the measure of the ability of the sorbent within a diffusive sampler to retain styrene after it has been 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. The concentration

of the test atmosphere was 852 mg/m^3 (200 ppm) at an average relative humidity of 80% at 23 °C. The 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 little loss of collected analyte to reverse diffusion (Table 4.9.1.1). The theoretical loading on the samplers was 1476 μg styrene.

Table 4.9.1.1
Reverse Diffusion of Styrene on
3M 3520 OVMs

set	mass (μg)			mean
	1	2	3	
first	1454	1472	1467	1464
second	1445	1459	1468	1457
second/first				99.5%

Low humidity

The ability of 3M 3520 OVMs to collect styrene from a relatively dry atmosphere was tested at 2 x the ceiling PEL by sampling a test atmosphere containing 1704 mg/m^3 (400 ppm) of styrene at an average relative humidity of 20% at 23 °C for 15 min, and at 2 x the TWA PEL by sampling a test atmosphere containing 852 mg/m^3 (200 ppm) of styrene at an average relative humidity of 20% at 23 °C for 240 min. All of the samples were immediately analyzed. The 15-min ceiling samples had collected 99.0%, 97.0%, and 98.3% of theoretical; and the 240-min TWA samples had collected 97.6%, 98.8% and 97.1% of theoretical.

Low concentration

The ability of 3M 3520 OVMs to collect styrene at a low concentration of 0.1 x the ceiling PEL was tested by sampling an atmosphere containing 85.2 mg/m^3 (20 ppm) of styrene at an average relative humidity of 80% at 23 °C for 15 min, and also at 0.1 x the TWA PEL by sampling an atmosphere containing 42.6 mg/m^3 (10 ppm) of styrene at an average relative humidity of 80% at 23 °C for 240 min. All of the samples were immediately analyzed. The 15-min ceiling samples had collected 96.1%, 97.7%, and 98.3% of theoretical; and the 240-min TWA samples had collected 99.2%, 98.5% and 97.6% of theoretical.

Sampling interference

The ability of 3M 3520 OVMs to collect the analyte was tested when other potential interferences are present by sampling individual atmospheres containing styrene and an interfering chemical. The interference test of acetone was performed by exposing the samplers to a test atmosphere at the TWA PEL level of acetone and styrene in humid air having an average relative humidity of 80% at 22 °C. The concentrations of the test atmosphere were: acetone (2400 mg/m^3 or 1000 ppm) and styrene (429 mg/m^3 or 101 ppm). Three 3M 3520 OVMs were collected for 1 hour due to potential capacity

problems with the high concentration of acetone. The recoveries (% of theoretical) were: 102.1%, 100.4%, and 98.9% for styrene. There was no styrene on the backup pad of the sampler for any of the tests, but there was acetone on the back-up pad. Over half of the styrene samples analyzed at OSHA Salt Lake Technical Center in 2005-2008 were from fiberglass operations. To test the ability of 3M 3520 OVMs to collect styrene at the recommended TWA sampling time of 240 min with acetone concentrations at a similar level, as would be found in fiberglass operations where the acetone is present in the mix at a near equal level to the styrene, a test atmosphere was created at the TWA PEL for styrene and 0.1 x the TWA PEL for acetone in humid air having an average relative humidity of 80% at 22 °C. The concentrations of the test atmospheres were: acetone (240 mg/m³ or 100 ppm) and styrene (429 mg/m³ or 101 ppm). To test the ability of 3M 3520 OVMs to collect styrene at the recommended ceiling sampling time of 15 min with acetone concentrations at a similar level a test atmosphere was created at the ceiling PEL for styrene and 0.2 x the TWA PEL for acetone in humid air having an average relative humidity of 80% at 22 °C. The concentrations of the test atmospheres were: acetone (480 mg/m³ or 200 ppm) and styrene (858 mg/m³ or 202 ppm). The styrene recoveries (% of theoretical) were: 98.0%, 97.0%, and 96.1% for the 15-min ceiling samples; and 101.2%, 99.9%, and 98.1% for the 240-min TWA samples. There was no styrene or acetone on the backup pad of the 15-min samplers. There was no styrene on the back-up pad of the 240-min samplers, but there was a small amount of acetone on the back-up pad.

The ability of 3M 3520 OVMs to collect styrene in the presence of an interfering chemical at the same concentration was tested by sampling atmospheres containing styrene and an interference of methyl methacrylate at 1 x the ceiling PEL for 15 min and 1 x the TWA PEL for 240 min. The concentrations of the analytes in the 1 x the ceiling PEL test atmosphere at an average humidity of 80% at 23 °C were: styrene (858 mg/m³ or 202 ppm), and methyl methacrylate (826 mg/m³ or 202 ppm). The concentrations of the analytes in the 1 x the TWA PEL test atmosphere at an average humidity of 79% at 23 °C were: styrene (429 mg/m³ or 101 ppm), and methyl methacrylate (413 mg/m³ or 101 ppm). Thirty three samplers were exposed to contaminated air (air containing the analyte and interferences) for each set of samples collected. Three samples from each set were immediately analyzed. The recoveries of styrene (% of theoretical) on day 0 were: 97.9%, 98.3%, and 96.0% for the 15-min ceiling samples, and 98.7%, 96.1%, and 97.3% for the 240-min TWA samples. Since methyl methacrylate can polymerize with styrene, a storage study was done with the remaining samplers to determine if there was a loss of styrene upon storage. Sample results are not corrected for extraction efficiency. The recoveries, calculated from the equation of the storage graphs, on day 17 for 15-min ceiling samples were 90.2% for ambient and 94.8% for refrigerated storage (Table 4.9.1.2, Figures 4.9.1.1 and 4.9.1.2), and recoveries for 240-min TWA samples were 90.0% for ambient and 94.5% for refrigerated storage (Table 4.9.1.3, Figures 4.9.1.3 and 4.9.1.4).

Table 4.9.1.2
Storage Test for Styrene at Ceiling PEL with Interference of Methyl Methacrylate
Collected on 3M 3520 OVMs for 15 min

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	97.9	98.3	96.0			
3	98.4	96.1	97.3	98.1	97.2	96.2
7	96.7	95.1	94.7	97.4	95.0	96.4
10	93.5	92.2	94.2	96.9	95.1	94.2
14	92.4	90.9	91.9	95.8	94.9	96.3
17	88.9	89.9	90.5	94.0	95.3	94.9

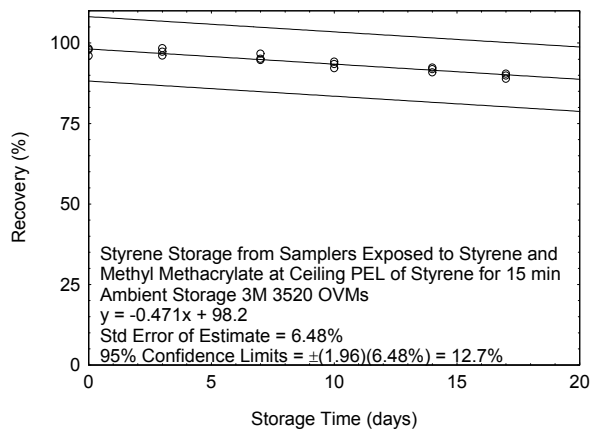


Figure 4.9.1.1. Ambient storage test for styrene collected for 15 min from an atmosphere at ceiling PEL of styrene (202 ppm) and with methyl methacrylate at 202 ppm using 3M 3520 OVMs.

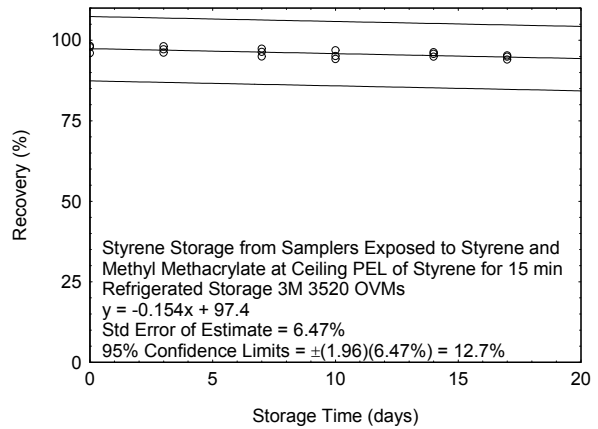


Figure 4.9.1.2. Refrigerated storage test for styrene collected for 15 min from an atmosphere at ceiling PEL of styrene (202 ppm) and with methyl methacrylate at 202 ppm using 3M 3520 OVMs.

Table 4.9.1.3
Storage Test for Styrene at TWA PEL with Interference of Methyl Methacrylate
Collected on 3M 3520 OVMs for 240 min

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	98.7	96.1	97.3			
3	96.9	94.5	95.9	97.9	96.0	98.2
7	95.6	94.4	94.1	95.2	97.2	96.9
10	94.3	93.2	92.7	94.1	96.7	97.1
14	92.1	91.9	90.8	93.2	95.4	96.0
17	88.7	90.1	89.6	93.6	95.0	94.7

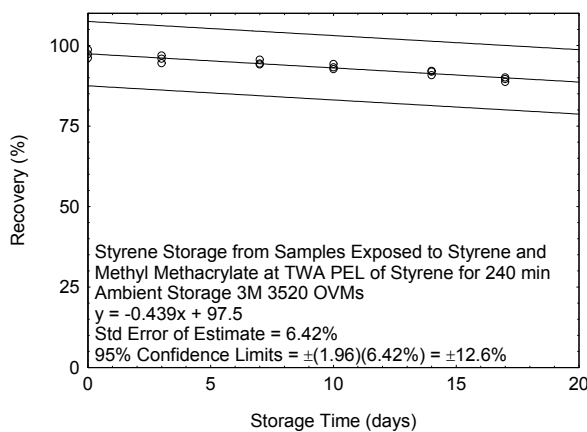


Figure 4.9.1.3. Ambient storage test for styrene collected for 240 min from an atmosphere at TWA PELs of styrene (101 ppm) and methyl methacrylate (101 ppm) using 3M 3520 OVMs.

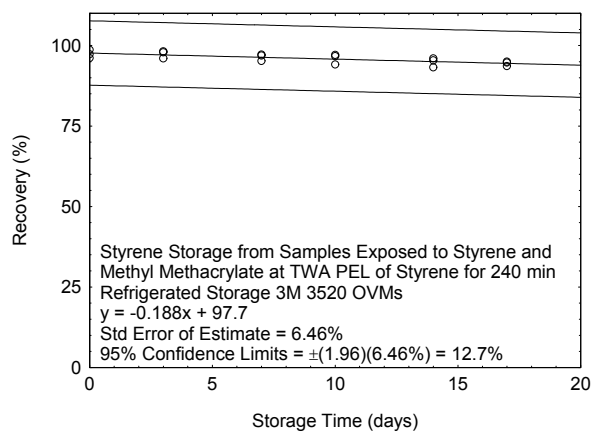


Figure 4.9.1.4. Refrigerated storage test for styrene collected for 240 min from an atmosphere at TWA PELs of styrene (101 ppm) and methyl methacrylate (101 ppm) using 3M 3520 OVMs.

4.9.2 SKC 575-006 Passive Samplers

Reverse diffusion

Reverse diffusion is the measure of the ability of the sorbent within a diffusive sampler to retain styrene after it has been 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. The concentration

Table 4.9.2.1
Reverse Diffusion of Styrene on
SKC 575-006 Passive Samplers

set	mass (μg)			mean
	1	2	3	
first	803	819	806	809
second	791	815	790	799
second/first				98.8%

of the test atmosphere was 852 mg/m^3 (200 ppm) at an average relative humidity of 80% at 23 °C. The 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 575-006 Passive Samplers showed little loss of collected analyte to reverse diffusion (Table 4.9.2.1). The theoretical loading on the samplers was $822 \mu\text{g}$ styrene.

Low humidity

The ability of SKC 575-006 Passive Samplers to collect styrene from a relatively dry atmosphere was tested at 2 x the ceiling PEL by sampling a test atmosphere containing 1704 mg/m^3 (400 ppm) of styrene at an average relative humidity of 20% at 23 °C for 15 min, and at 2 x the TWA PEL by sampling a test atmosphere containing 852 mg/m^3 (200 ppm) of styrene at an average relative humidity of 20% at 23 °C for 240 min. All of the samples were immediately analyzed. The 15-min ceiling samples had collected 97.1%, 96.4%, and 95.9% of theoretical; and the 240-min TWA samples had collected 98.1%, 96.9% and 97.6% of theoretical.

Low concentration

The ability of SKC 575-006 Passive Samplers to collect styrene at a low concentration of 0.1 x the ceiling PEL was tested by sampling an atmosphere containing 85.2 mg/m^3 (20 ppm) of styrene at an average relative humidity of 80% at 23 °C for 15 min, and also at 0.1 x the TWA PEL by sampling an atmosphere containing 42.6 mg/m^3 (10 ppm) of styrene at an average relative humidity of 80% at 23 °C for 240 min. All of the samples were immediately analyzed. The 15-min ceiling samples had collected 97.8%, 98.5%, and 96.9% of theoretical; and the 240-min TWA samples had collected 98.3%, 97.4% and 99.6% of theoretical.

Sampling interference

A test of the ability of SKC 575-006 Passive Samplers to collect the analyte was tested when other potential interferences are present by sampling individual atmospheres containing styrene and an interfering chemical. The interference test of acetone was performed by exposing the samplers to a test atmosphere at the TWA PEL level of acetone and styrene in humid air having an average relative humidity of 80% at 22 °C. The concentrations of the test atmosphere were: acetone (2400 mg/m^3 or 1000 ppm) and styrene (429 mg/m^3 or 101 ppm). Three SKC 575-006 Passive Samplers were collected for 1 hour due to potential capacity problems with the high concentration of acetone. The recoveries (% of theoretical) were: 99.3%, 97.1%, and 98.3% for styrene.

Over half of the styrene samples analyzed at OSHA Salt Lake Technical Center in 2005-2008 were from fiberglass operations. To test the ability of SKC 575-006 Passive Samplers to collect styrene at the recommended sampling time of 240 min with acetone concentrations at a similar level, as would be found in fiberglass operations where the acetone is present in the mix at a near equal level to the styrene, a test atmosphere was created at the TWA PEL for styrene and 0.1 x the TWA PEL acetone in humid air having an average relative humidity of 80% at 22 °C. The concentrations of the test atmosphere were: acetone (240 mg/m³ or 100 ppm) and styrene (429 mg/m³ or 101 ppm). To test the ability of 3M 3520 OVMs to collect styrene at the recommended ceiling sampling time of 15 min with acetone concentrations at a similar level a test atmosphere was created at the ceiling PEL styrene and 0.2 x TWA PEL acetone in humid air having an average relative humidity of 80% at 22 °C. The concentrations of the test atmospheres were: acetone (480 mg/m³ or 200 ppm) and styrene (858 mg/m³ or 202 ppm). The styrene recoveries (% of theoretical) were: 98.4%, 99.0%, and 97.1% for the 15-min ceiling samples; and 99.8%, 98.5%, and 97.2% for the 240-min TWA samples.

The ability of SKC 575-006 Passive Samplers to collect styrene in the presence of an interfering chemical at the same concentration was tested by sampling atmospheres containing styrene and an interference of methyl methacrylate at 1 x the ceiling PEL for 15 min and 1 x the TWA PEL for 240 min. The concentrations of the analytes in the 1 x the ceiling PEL test atmosphere at an average humidity of 80% at 23 °C were: styrene (858 mg/m³ or 202 ppm), and methyl methacrylate (826 mg/m³ or 202 ppm). The concentrations of the analytes in the 1 x TWA PEL test atmosphere at an average humidity of 79% at 23 °C were: styrene (429 mg/m³ or 101 ppm), and methyl methacrylate (413 mg/m³ or 101 ppm). Thirty three samplers were exposed to contaminated air (air containing the analyte and interferences) for each set of samples collected. Three samples from each set were immediately analyzed. The recoveries of styrene (% of theoretical) on day 0 were: 97.1%, 96.8%, and 95.5% for 15-min ceiling samples, and 98.6%, 96.3%, and 97.3% for 240-min TWA samples. Since methyl methacrylate can polymerize with styrene, a storage study was done with the remaining samplers to determine if there was a loss of styrene upon storage. Sample results are not corrected for extraction efficiency. The recoveries, calculated from the equation of the storage graphs, on day 17 for 15-min ceiling samples were 91.5% for ambient and 95.1% for refrigerated storage (Table 4.9.2.2, Figures 4.9.2.1 and 4.9.2.2), and recoveries for 240-min TWA samples were 91.4% for ambient and 94.6% for refrigerated storage (Table 4.9.2.3, Figures 4.9.2.3 and 4.9.2.4).

Table 4.9.2.2
Storage Test for Styrene at Ceiling PEL with Interference of Methyl Methacrylate
Collected on SKC 575-006 Passive Samplers for 15 min

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
	0	97.1	96.8	95.5		
3	97.0	97.9	95.3	98.1	96.3	97.9
7	95.9	96.6	94.4	96.8	98.0	95.9
10	94.7	95.6	93.8	95.2	96.1	97.8
14	93.6	91.5	92.9	94.1	95.7	96.7
17	90.6	89.9	91.8	93.3	95.6	94.8

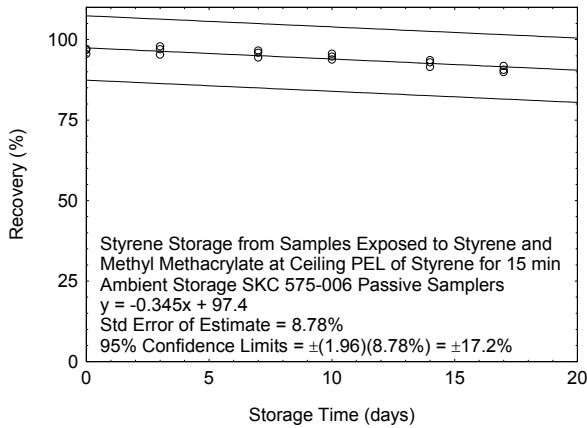


Figure 4.9.2.1. Ambient storage test for styrene collected for 15 min from an atmosphere at ceiling PEL of styrene (202 ppm) and with methyl methacrylate at 202 ppm using SKC 575-006 Passive Samplers.

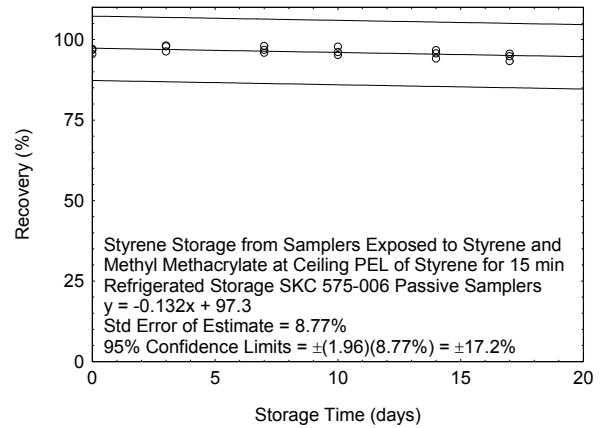


Figure 4.9.2.2. Refrigerated storage test for styrene collected for 15 min from an atmosphere at ceiling PEL of styrene (202 ppm) and with methyl methacrylate at 202 ppm collected on SKC 575-006 Passive Samplers.

Table 4.9.2.3
Storage Test for Styrene at TWA PEL with Interference of Methyl Methacrylate
Collected on SKC 575-006 Passive Samplers for 240 min

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	98.6	96.3	97.3			
3	96.3	98.1	95.6	98.8	96.4	97.7
7	95.7	96.7	94.9	95.3	97.8	96.2
10	93.9	95.3	93.3	94.9	95.7	97.9
14	94.1	91.9	92.4	93.8	95.1	96.8
17	92.2	89.8	90.5	93.7	95.2	94.0

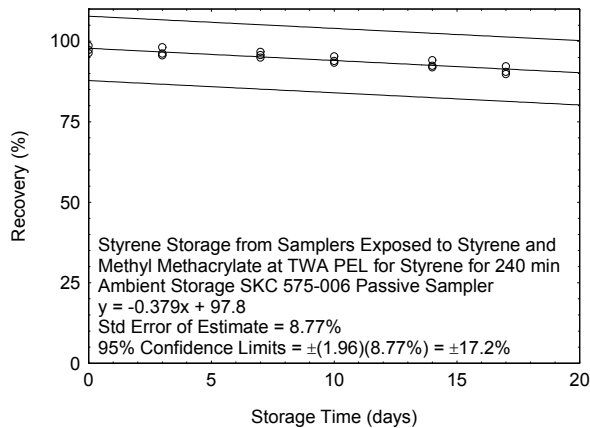


Figure 4.9.2.3. Ambient storage test for styrene collected for 240 min from an atmosphere at TWA PELs of styrene (101 ppm) and methyl methacrylate (101 ppm) using SKC 575-006 Passive Samplers.

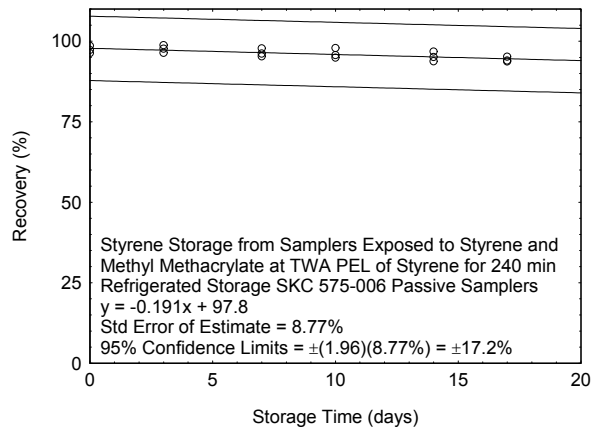


Figure 4.9.2.4. Refrigerated storage test for styrene collected for 240 min from an atmosphere at TWA PELs of styrene (101 ppm) and methyl methacrylate (101 ppm) using SKC 575-006 Passive Samplers.

4.10 Qualitative analysis

When necessary, the identity or purity of an analyte peak can be confirmed by GC-mass spectrometry or by another analytical procedure. The mass spectrum in Figure 4.10.1 was taken from the NIST spectral library.¹⁵

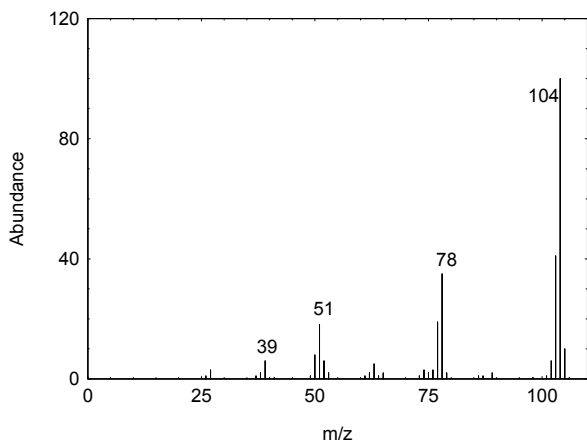


Figure 4.10.1. Mass spectrum of styrene.

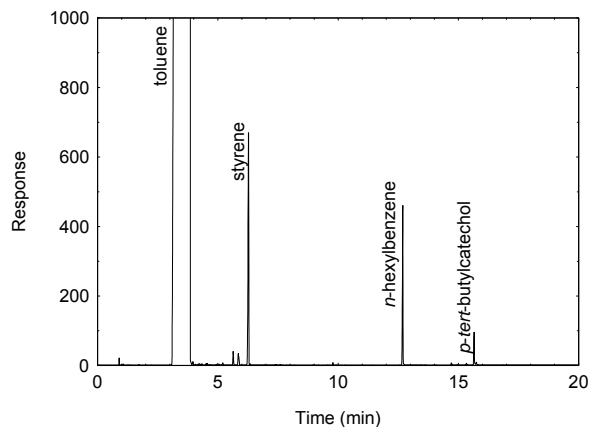


Figure 4.10.2. A total ion chromatogram of a sample analyzed by Agilent 6890 with a 5973 mass selective detector using a DB-1MS Ultra Inert capillary column 15 m x 0.25 mm with 0.25 μm film thickness, by a temperature program of 35 $^{\circ}\text{C}$ hold for 5 min then temperature program at 10 $^{\circ}\text{C}/\text{min}$ to 185 $^{\circ}\text{C}$.

4.11 Generation of test atmospheres

The following apparatus was placed in a walk-in hood. The styrene vapors were generated by pumping the styrene, using the Isco pump, through a short length of 0.53-mm uncoated fused silica capillary tubing into a vapor generator where it was heated and evaporated into the dilution air stream (Figure 4.11). The vapor generator consisted of a 15-cm length of 5-cm diameter glass tubing with a side port for introduction of the capillary tubing. The glass tube of the vapor generator was wrapped with heating tape to evaporate the styrene. The humidity, temperature, and volume of the dilution stream of air were regulated by use of a Miller Nelson Flow-Temperature-Humidity controller. The test atmosphere passed into a glass mixing chamber (76-cm \times 30-cm) from the vapor generator, and then into a glass exposure chamber (76-cm \times 20-cm). Diffusive samplers were placed inside the exposure chamber and active samplers were attached to glass tubes extending from the exposure chamber. The humidity and temperature were measured at the exit of the exposure chamber

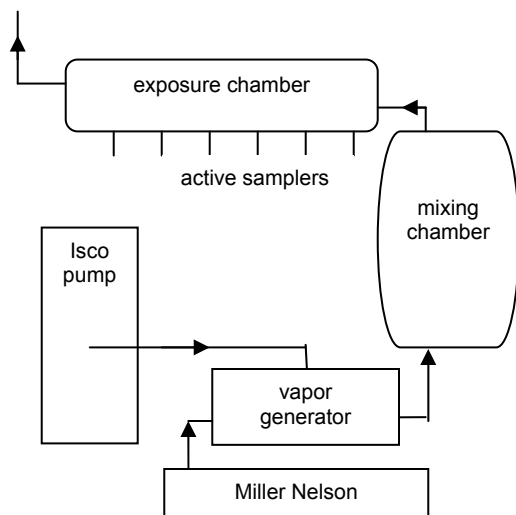


Figure 4.11. The test atmosphere generation and sampling apparatus.

¹⁵ Styrene. NIST Chemistry Webbook. 2009. National Institute of Standards and Technology website. <http://webbook.nist.gov/cgi/cbook.cgi?ID=C100425&Units=SI&Mask=200#Mass-Spec> (accessed 1/22/2009).

with an Omega Digital Thermo-hygrometer. Face velocities of the test atmospheres were calculated by dividing the volumetric flow of each atmosphere by the cross-sectional area available for the air flow in the chamber. The cross-sectional area available for the air flow was the cross-sectional area of the chamber reduced by the cross-sectional areas of the samplers. The face velocity was maintained at 0.4 m/s. The theoretical concentrations for test atmospheres were calculated from ISCO pump flow rates, concentration of the analyte solutions, and air flow rate. Experimental test results were based on theoretical test atmosphere concentrations. The atmospheric concentration for each test was confirmed by use of an active sampler, TBC coated charcoal tubes (SKC catalog no. 226-73), following OSHA Method 89 Divinylbenzene Ethylvinylbenzene Styrene.¹⁶

¹⁶ Burreight, D., OSHA Method 89 Divinylbenzene Ethylvinylbenzene Styrene.
<http://www.osha.gov/dts/sltc/methods/organic/org089/org089.html> (accessed 1/30/09).