

Bisphenol A
Diglycidyl Ether of Bisphenol A



Method number:	1018
Version:	1.0
Target concentration:	5 mg/m ³ for bisphenol A 5 mg/m ³ for diglycidyl ether of bisphenol A
OSHA PEL:	None for bisphenol A None for diglycidyl ether of bisphenol A
ACGIH TLV:	None for bisphenol A None for diglycidyl ether of bisphenol A
Procedure:	Samples are collected by drawing workplace air through a 37-mm glass fiber filter with personal sampling pumps. Samples are extracted with acetonitrile and analyzed by ultra performance liquid chromatography (UPLC) using an ultraviolet (UV) or photodiode array detector (PDA).
Recommended sampling time and sampling rate:	240 min at 1 L/min (240 L)
Reliable quantitation limit:	1.42 µg/m ³ for bisphenol A 3.73 µg/m ³ for diglycidyl ether of bisphenol A
Standard error of estimate at the target concentration:	5.15% bisphenol A 5.17% diglycidyl ether of bisphenol A
Special requirement:	Samples must be shipped cold overnight and stored frozen.
Status of method:	Fully validated method. This method has been subjected to the established evaluation procedures of the Methods Development Team.

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1. General Discussion

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

1.1 Background

1.1.1 History

Due to interest in the exposure to bisphenol A in the community¹ and the workplace, OSHA developed a validated method to collect and analyze bisphenol A and diglycidyl ether of bisphenol A. These chemicals are commonly used to form industrial epoxy resins, plastics, and flame retardants. The method is a modification of NIOSH P&CAM 333² which uses a 37-mm glass fiber filter for sampling and a High Performance Liquid Chromatograph with an UV detector for analysis. The target was chosen based on the German exposure level (MAK) of 5 mg/m³. The MAK was the only available regulatory exposure level available at the time of method development. A fluorescence detector was evaluated for this method but the increase in sensitivity was limited.

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

The primary routes of exposure are inhalation, dermal, and ingestion. Bisphenol A has weak estrogenic effects due to its structural analogies with natural and synthetic estrogens. As a solid it is slightly irritating to the skin and moderately irritating to the eyes. The irritation with bisphenol A increases as it is dissolved in organic solvents.³ The European Commission on the Scientific Committee on Occupational Exposure Limits states the following risks: there is a possible impairment to fertility, respiratory system irritation, serious eye damage, and sensitization by skin contact.⁴ NIOSH has given bisphenol A a skin notation of sensitizer because it is readily absorbed through the skin and there is enough evidence to show it as a skin sensitizer and photoallergen,⁵ but not enough evidence to show systemic toxicity or direct effects on the skin.⁵ Bisphenol A is not currently classified as a teratogen, mutagen, or carcinogen.

Diglycidyl ether of bisphenol A does not have a regulatory target but the German MAK states that it is an irritant and skin sensitizer. Percutaneous absorption of the chemical is significant and further study needs to be completed to determine if it is a carcinogen.⁶ The primary route of exposure is dermal contact resulting in irritation and sensitization.⁶

¹ Ritter, S. Bisphenol A, A rift persists between safety assessments of the man-made estrogen mimic. *Chem. Eng. News* 2011, Vol. 89, No. 23 pp 13-22.

² Taylor, D. Bisphenol A and Diglycidyl Ether of Bisphenol A. NIOSH Manual of Analytical Methods Volume 6 1980. U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Engineering, Division of Physical Sciences and Engineering. Cincinnati, Ohio 1980. pp 333-1 through 333-6.

³ Bisphenol A [MAK Value Documentation, 1999]. The MAK Collection for Occupational Health and Safety. Part 1: MAK Value Documentations (DFG) (Volume 13). WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, Published Online 2012. p 49-87. <http://onlinelibrary.wiley.com/doi/10.1002/3527600418.mb8005e0013/pdf> (accessed Jan 2012).

⁴ Recommendation from the Scientific Committee on Occupational Exposure Limits for Bisphenol-A, 2004. European Commission SCOEL/SUM/113. <http://ec.europa.eu/social/BlobServlet?docId=3873&langId=en> (accessed July 2012).

⁵ NIOSH Skin Notation Profiles: Bisphenol A, 2011. U.S. Department of Health and Human Services, Centers for Disease Control, National Institute for Occupational Safety and Health Web site. <http://www.cdc.gov/niosh/docs/2011-144/pdfs/2011-144.pdf> (accessed Sep 2011).

⁶ Bisphenol A-Diglycidyl ether [MAK Value Documentation 2003]. The MAK Collection for Occupational Health and Safety. Part 1: MAK Value Documentations (DFG) (Volume 19). WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, Published Online 2012. p 43-47. <http://onlinelibrary.wiley.com/doi/10.1002/3527600418.mb167554e0019/pdf> (accessed Jan 2012).

1.1.3 Workplace exposure

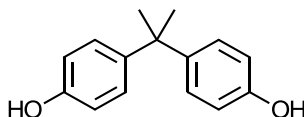
Bisphenol A is used in making epoxy resins and polycarbonate plastics. The epoxy resins are used mainly as protective coatings and adhesives. The polycarbonate plastics are used in eyeglass lenses, medical equipment, water bottles, digital media, consumer electronics, computers, appliances, sports safety equipment, and reusable food and drink containers. Global production capacity was 5.2 million metric tons⁷ in 2008 and according to the EPA Chemical Data Access Tool; United States production was 2.25 billion pounds per year for 2012⁸. Bisphenol A has a low vapor pressure and the main routes of industrial exposures are dust inhalation and dermal absorption during chemical transport, machine maintenance, testing, sampling, and other procedures.

Diglycidyl ether of bisphenol A is used in epoxy surface coatings that provide superior adhesion, flexibility, and corrosion resistance on metal surfaces. Global production was estimated to be 957 thousand metric tons in 2003⁹. A National Library of Medicine report states that "NIOSH (NOES Survey 1981-1983) has statistically estimated that 25,257 workers (4,341 of these are female) are potentially exposed to bisphenol A diglycidyl ether in the US."¹⁰

1.1.4 Physical properties and other descriptive information

Bisphenol A¹¹

synonyms:	4,4'-(1-methylethylidene)-bisphenol, 2,2-bis(4-hydroxyphenyl)propane, 4,4'-isopropylidenediphenol
IMIS ¹² :	0372
CAS number:	80-05-7
boiling point:	220 °C
melting point:	150-155 °C
molecular weight:	228.29
appearance:	crystalline or flakes with mild phenolic odor
molecular formula:	C ₁₅ H ₁₆ O ₂
solubility:	soluble in water 120-300 mg/L, soluble in alcohols, acetone, and dilute alkalies, slightly soluble in carbon tetrachloride
structural formula:	



⁷ Product Safety Assessment, *Bisphenol A (BPA)*, 2010. The Dow Chemical Company Web site.

http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_08b1/0901b803808b19e8.pdf?filepath=productsafety/pdfs/noreg/233-00250.pdf&fromPage=GetDoc (accessed July 2011).

⁸ Chemical Data Access Tool. United States Environmental Protection Agency Web site. http://java.epa.gov/oppt_chemical_search/ (accessed Dec 2013).

⁹ Product Safety Assessment, Diglycidyl ether of *Bisphenol A (BPA)*, 2006. The Dow Chemical Company Web site.

http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_0056/0901b80380056968.pdf?filepath=productsafety/pdfs/noreg/233-00241.pdf&fromPage=GetDoc <http://www.dow.com/> (accessed July 2011).

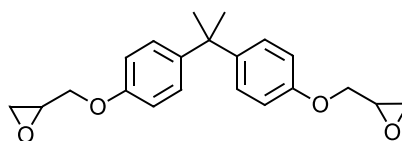
¹⁰ Bisphenol A Diglycidyl Ether. National Library of Medicine Web site. <http://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+331> (accessed Aug 2013).

¹¹ O'Neil, M.; Heckelman, P.; Koch, C.; Roman, K. *The Merck Index*; 14th ed.; Budavari, S., Ed.; Merck & Co. Inc.: Whitehouse Station, NJ, 2006; p 211-212.

¹² Bisphenol A (Chemical Sampling Information), 2011 U.S. Department of Labor, Occupational Safety and Health Administration Web site. http://www.osha.gov/dts/chemicalsampling/data/CH_221000.html (accessed May 2011).

Diglycidyl Ether of Bisphenol A¹³

synonyms:	2,2-bis[4-(glycidyloxy)phenyl]propane, 4,4'-isopropylidenediphenol diglycidyl ether, BADGE ¹⁴
IMIS ¹⁵ :	D709
CAS number:	1675-54-3
melting point:	40 °C
molecular weight:	340.41
appearance:	white solid
molecular formula:	C ₂₁ H ₂₄ O ₄
structural formula:	



¹³ O'Neil, M.; Heckelman, P.; Koch, C.; Roman, K. *The Merck Index*; 14th ed.; Budavari, S., Ed.; Merck & Co. Inc.: Whitehouse Station, NJ, 2006; p 212.

¹⁴ Product Safety Assessment, Diglycidyl Ether of *Bisphenol A* (BPA), 2006. The Dow Chemical Company Web site. http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_0056/0901b80380056968.pdf?filepath=productsafety/pdfs/noreg/233-00241.pdf&fromPage=GetDoc (accessed July 2011).

¹⁵ Diglycidyl Ether of Bisphenol A (Chemical Sampling Information), 2011 U.S. Department of Labor, Occupational Safety and Health Administration Web site. http://www.osha.gov/dts/chemicalsampling/data/CH_235350.html (accessed May 2011).

This method was evaluated according to the OSHA SLTC "Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis"¹⁶. 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).

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 a 37-mm diameter, 2-piece closed-face cassette, containing a Type A/E glass fiber filter (GFF). For this validation, filters were purchased from PALL (catalog no. 61652, lot no. 84875).

Samples are collected using a personal sampling pump calibrated to within $\pm 5\%$ of the recommended flow rate with the sampling device in-line.

2.2 Reagents

None required

2.3 Technique

Remove the plastic end plugs from the filter cassette immediately before sampling.

Attach the cassette to the sampling pump so that it is in an approximately vertical position with the inlet facing down during sampling. Position the sampling pump, cassette, and tubing so it does not impede work performance or safety.

Draw the air to be sampled directly into the inlet of the cassette. The air being sampled is not to be passed through any hose or tubing before entering the cassette.

Sample for up to 240 min at 1 L/min (240 L) to collect TWA (long-term) samples.

After sampling for the appropriate time, remove the cassette and seal with plastic end plugs. Seal each sample end-to-end with a Form OSHA-21 as soon as possible.

Submit at least one blank sample with each set of samples. Handle the blank sample in the same manner as the other samples except do not draw air through it.

Record sample air volume (L), sampling time (min) and sampling rate (L/min) for each sample, along with any potential interferences on the Form OSHA-91A.

Submit the samples to the laboratory for analysis with freezer packs as soon as possible after sampling. If a delay is unavoidable, store the samples in a freezer.

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

¹⁶ Eide, M.; Simmons, M.; Hendricks, W. Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, 2010. United States Department of Labor, Occupational Safety and Health Administration Web site. <http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf> (accessed May 2011).

3. Analytical Procedure

Adhere to the rules set down in your laboratory's Chemical Hygiene Plan¹⁷ (for instance: OSHA SLTC adheres to the rules set down in the OSHA SLTC Chemical Hygiene Plan). Avoid skin contact and inhalation of all chemicals and review all appropriate MSDSs before beginning the analytical procedure. Follow all applicable quality assurance practices established in your laboratory's internal quality system (for instance: OSHA SLTC follows the quality assurance practices established in the OSHA SLTC Quality Assurance Manual).

3.1 Apparatus

A UPLC with a PDA or UV detector. For this evaluation a Waters Acquity UPLC equipped with a Binary Solvent Manager, Sample Manager, Photodiode Array, and Fluorescence Detector was used.

An LC column capable of separating bisphenol A and diglycidyl ether of bisphenol A from the extraction solvent and any potential interferences. A Waters UPLC BEH C18 column (130 Å, 2.1-mm × 50-mm, 1.8-µm) was used in this evaluation (catalog no. 186002350, lot 0178301101).

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

A dispenser capable of delivering 3.0 mL of extraction solvent to prepare standards and samples. If a dispenser is not available, a 3.0-mL volumetric pipet can be used.

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

Calibrated 10-µL and 25-µL syringes for preparing standards.

Water purifier. A Barnstead NANOpure Diamond system was used to produce 18.0 MΩ-cm DI water in this evaluation (model D11901).

A mechanical rotator. A Fisher Roto-Rack was used in this evaluation.

Class A 1-L, 2-mL, and 5-mL volumetric flasks.

Class A 10-mL volumetric pipets.

0.2-µm PTFE Acrodisc CR 13-mm Syringe Filters (catalog no. 4542, lot 21815310 PALL Scientific).

Luer-lock 10-mL glass syringe for filtration of samples.

Type A/E glass fiber filter (GFF) for cassette wipes. For this validation, filters were purchased from PALL (catalog no. 61652, lot no. 84875).

3.2 Reagents and Standards

Bisphenol A, [CAS no. 80-05-7], analytical grade or better. The bisphenol A used in this validation was ≥99% (lot no. MKAA2480V4) purchased from Sigma Aldrich (Milwaukee, WI).

¹⁷ Occupational Exposure to Hazardous Chemicals in Laboratories. *Code of Federal Regulations*, Part 1910.1450, Title 29, 2003.

Diglycidyl ether of bisphenol A, [CAS no 1675-54-3], analytical grade or better. The diglycidyl ether of bisphenol A used in this evaluation was $\geq 95\%$ (lot no. 0001448914) purchased from Fluka (Milwaukee, WI).

DI water, 18.0 M Ω -cm.

Acetonitrile, [CAS no 75-05-8], HPLC grade or better. The acetonitrile used in this evaluation was 99.9% (lot no. PB001803ACN) purchased from Pharmaco-AAPER (Brookfield, CT).

Extraction solvent is 3 mL acetonitrile.

3.3 Standard preparation

Prepare separate concentrated stock standards of bisphenol A and diglycidyl ether of bisphenol A by weighing each powder into acetonitrile and store in separate amber vials or bottles for up to 5 days.

Prepare working analytical standards by injecting microliter amounts of the concentrated stock standard into volumetric flasks containing the extraction solvent. For example, to prepare an approximate target level standard (1188.6 $\mu\text{g}/\text{sample}$ bisphenol A and 1193.4 $\mu\text{g}/\text{sample}$ diglycidyl ether of bisphenol A), inject 7.5 μL of a stock standard containing 105.65 $\mu\text{g}/\mu\text{L}$ bisphenol A and 36 μL of a stock standard containing 22.1 $\mu\text{g}/\mu\text{L}$ diglycidyl ether of bisphenol A into a 2-mL volumetric flask and extraction solvent. Convert $\mu\text{g}/\text{mL}$ to $\mu\text{g}/\text{sample}$ by multiplying the concentration ($\mu\text{g}/\text{mL}$) value by 3, due to the extraction volume. Filter working standards, using 0.2- μm filters, into 2-mL glass autosampler vials.

Bracket the sample concentrations with standard concentrations. If 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

Open the cassette and carefully transfer the glass fiber filter to a 4-mL glass vial so that the filter is flat against the inside surface of the vial, not folded or crumpled, such that the exposed filter surface is facing inside in contact with the extraction solvent and not the glass.

Wet a glass fiber filter with 100 μL of ethanol, wipe the cassette walls, and place in a separate vial as above.

Add 3.0 mL of extraction solvent to each vial and immediately seal with PTFE-lined caps.

Place the 4-mL vials on a mechanical rotator and rotate at 40 rpm for 30 min.

Filter the extraction solution in each 4-mL vial with a 0.2- μm filter into a 2-mL glass autosampler vial and seal with a PTFE-lined cap.

Analyze samples for bisphenol A and diglycidyl ether of bisphenol A as described in Section 3.5.

3.5 Analysis

3.5.1 Analytical conditions

UPLC conditions

eluent: isocratic at 60.3% 18.0 M Ω -cm water and 39.7% acetonitrile
column flow: 0.7 mL/min
column temp: 30 °C
run time: 6.0 min
injection size: 1.0 μ L, partial loop with needle overfill
column: Waters UPLC BEH C18 column, 130 Å, 2.1-mm \times 50-mm, 1.8- μ m

retention times: 0.686 min (bisphenol A)
4.597 min (diglycidyl ether of bisphenol A)

PDA conditions

absorbance: 230 nm, resolution 4.8 nm
sampling rate: 10 point/sec
filter time: 0.1 sec

Sample Manager

temp run: room-temperature
temp storage: 4 °C or place in refrigerator between analytical runs

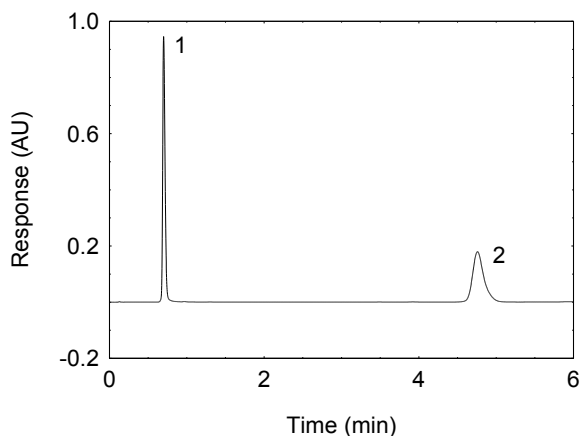


Figure 3.5.1.1. Chromatogram obtained at the target concentration with the recommended analytical conditions (1: bisphenol A; 2: diglycidyl ether of bisphenol A).

3.5.2 Calibration

An external standard 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. These standards cover the range from 0.1 to 2 times the target concentration.

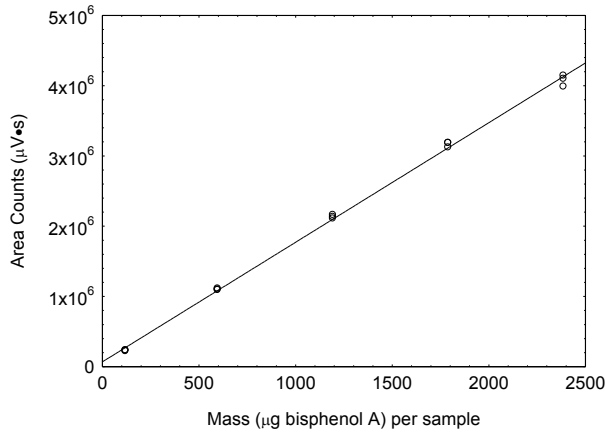


Figure 3.5.2.1. Calibration curve of bisphenol A ($y = 1704x + 56141$).

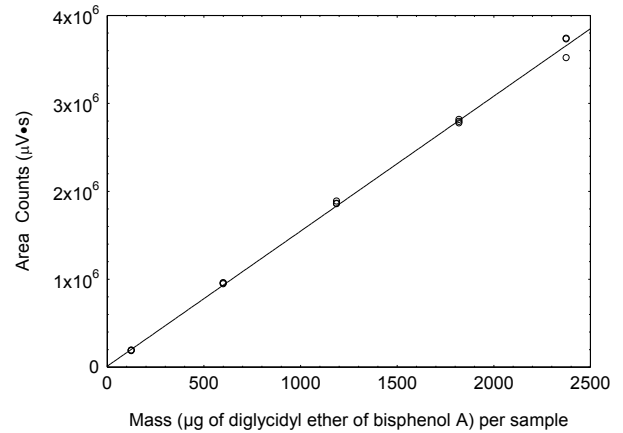


Figure 3.5.2.2. Calibration curve of diglycidyl ether of bisphenol A ($y = 1534x + 23455$).

3.6 Interferences (analytical)

3.6.1 Any compound that produces an ultraviolet detector response and has a similar retention time as the analytes is a potential interference. If any potential interferences were reported, they should be considered before samples are extracted. Generally, chromatographic conditions can be altered to separate an interference from the analyte.

3.6.2 When necessary, the identity of an analyte peak may be confirmed with additional analytical data or procedures (Section 4.11).

3.7 Calculations

The amount of bisphenol A and diglycidyl ether of bisphenol A per sample is obtained from the appropriate calibration curve in terms of micrograms per sample, uncorrected for extraction efficiency. This total amount is then corrected by subtracting the total amount (if any) found on the blank. The air concentration is calculated using the following formula.

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

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

4. Method validation

General instruction for the laboratory validation of OSHA sampling and analytical methods that employ chromatographic analysis is presented in "Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis"¹⁸. These Guidelines detail required validation tests, show examples of statistical calculations, list validation acceptance criteria, and define analytical parameters. Air concentrations listed in ppm are referenced to 25 °C and 760 mmHg (101.3 kPa).

¹⁸ Eide, M.; Simmons, M.; Hendricks, W. Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, 2010. United States Department of Labor, Occupational Safety and Health Administration Web site. <http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf> (accessed May 2011).

SLTC was unable to generate a test atmosphere for bisphenol A and diglycidyl ether of bisphenol A. All tests were liquid spiked and had the corresponding air volume of 240 liters of humid air passed through the sampler. The recommended flow rate for sample collection is 1 L/min for 240 minutes. The tests in Sections 4.6 (Reproducibility) and 4.9 (Interferences) had the flow rate increased to 2 L/min but the volume of the air sampled remained constant at 240 liters.

4.1 Detection limit of the analytical procedure (DLAP)

The DLAP is measured as mass of analyte introduced onto the chromatographic column. Ten analytical standards were prepared with equally descending increments with the highest standard containing 1.34 µg/mL bisphenol A and 1.33 µg/mL of diglycidyl ether of bisphenol A. This is the concentration that would produce a peak approximately 10 times the response of a reagent blank. These standards, and the reagent blank were analyzed with the recommended analytical parameters (1-µL injection), and the data obtained were used to determine the required parameters (standard error of estimate and slope) for the calculation of the DLAP.

For bisphenol A values of 5303 and 73 were obtained for the slope and standard error of estimate respectively. The DLAP for bisphenol A was calculated to be 0.041 ng.

Table 4.1.1
Detection Limit of Analytical Procedure
for Bisphenol A

concentration (µg/mL)	mass on column (ng)	area counts (µV·s)
0.000	0.000	0
0.134	0.134	912
0.268	0.268	1547
0.401	0.401	2333
0.535	0.535	2867
0.669	0.669	3592
0.803	0.803	4329
0.937	0.937	5025
1.07	1.07	5769
1.20	1.20	6533
1.34	1.34	7202

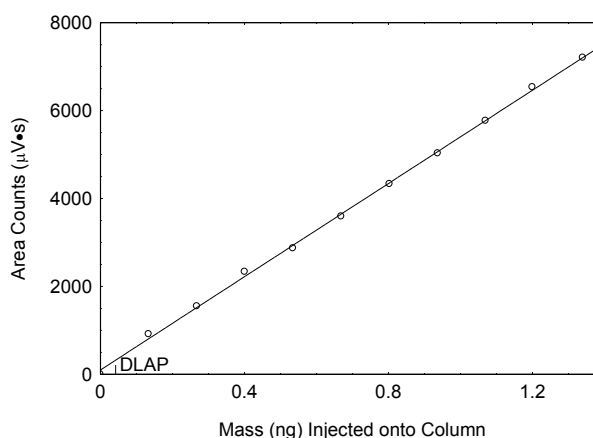


Figure 4.1.1. Plot of data to determine the DLAP for bisphenol A ($y = 5303x + 99.7$).

For diglycidyl ether of bisphenol A values of 4226 and 166 were obtained for the slope and standard error of estimate respectively. The DLAP for diglycidyl ether of bisphenol A was calculated to be 0.118 ng.

Table 4.1.2
Detection Limit of the Analytical Procedure
for Diglycidyl Ether of Bisphenol A

concentration (µg/mL)	mass on column (ng)	area counts (µV·s)
0.000	0.000	0
0.133	0.133	440
0.265	0.265	1083
0.398	0.398	1475
0.530	0.530	2065
0.663	0.663	2392
0.796	0.796	3298
0.928	0.928	3872
1.06	1.06	4345
1.19	1.19	5223
1.33	1.33	5343

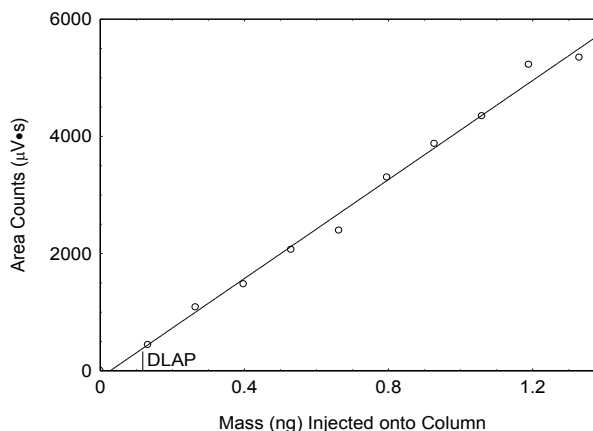


Figure 4.1.2. Plot of data to determine the DLAP for diglycidyl ether of bisphenol A ($y = 4226x - 116.5$).

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

The 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, such that the highest sampler loading was 4.07 µg/sample for bisphenol A and 4.18 µg/sample for diglycidyl ether of bisphenol A. This is the amount spiked on a sampler that would produce a peak approximately 10 times the response for a sample blank. These spiked samplers and the sample blank were analyzed with the recommended analytical parameters, and the data obtained were used to calculate the DLOP. Values for bisphenol A of 1673.7 and 57.3 were obtained for the slope and standard error of estimate respectively. DLOP was calculated to be 0.103 µg/sample (0.00043 mg/m³ for a TWA) for bisphenol A.

Table 4.2.1
Detection Limit of the Overall
Procedure
for Bisphenol A

mass per sample (µg/sample)	area counts (µV·s)
0.000	0
0.407	727
0.814	1466
1.22	2113
1.63	2750
2.03	3551
2.44	4173
2.85	4747
3.25	5430
3.66	6169
4.07	6906

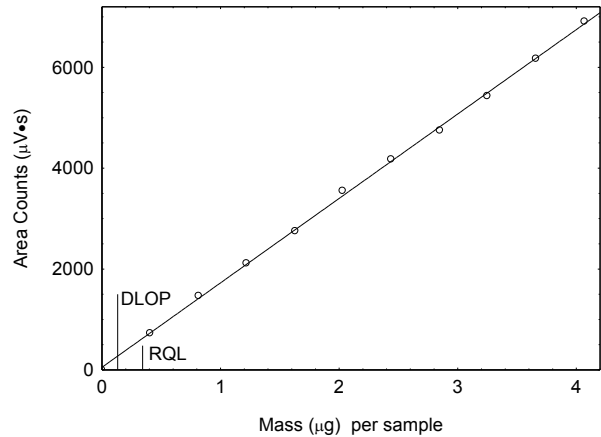


Figure 4.2.1. Plot of data to determine the DLOP and RQL for analysis of bisphenol A ($y = 1673.7x + 53.7$).

For diglycidyl ether of bisphenol A values of 1548.3 and 138.7 were obtained for the slope and standard error of estimate respectively. The DLOP was calculated to be 0.269 µg/sample of diglycidyl ether of bisphenol A (0.00112 mg/m³ for a TWA sample).

Table 4.2.2
Detection Limit of the Overall
Procedure
for Diglycidyl Ether of Bisphenol A

mass per sample (µg/sample)	area counts (µV·s)
0.000	0
0.418	441
0.836	902
1.25	1611
1.67	2380
2.09	3236
2.51	3702
2.93	4521
3.34	5046
3.76	5600
4.18	6196

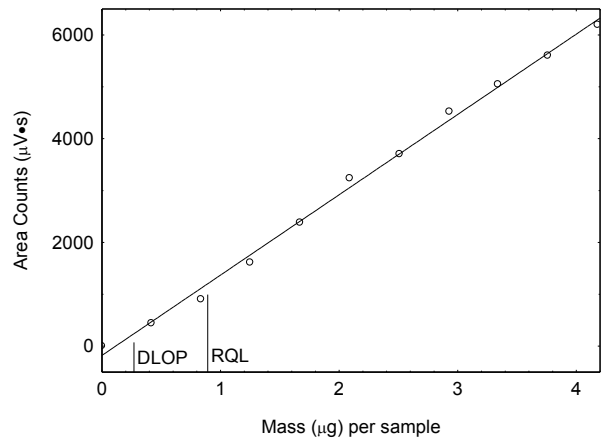


Figure 4.2.2. Plot of data to determine the DLOP and RQL for analysis of diglycidyl ether of bisphenol A ($y = 1548.3x - 177.5$).

The RQL is the lower limit for precise quantitative measurements. It is determined from the regression line parameters obtained from the calculation of the DLQP, providing 75% to 125% of the analyte is recovered. The RQL for bisphenol A is 0.342 μg per sample (0.00143 mg/m^3) and for diglycidyl ether of bisphenol A is 0.896 μg per sample (0.00373 mg/m^3). Recovery at this concentration for bisphenol A is 98.8% and diglycidyl ether of bisphenol A is 83.4%.

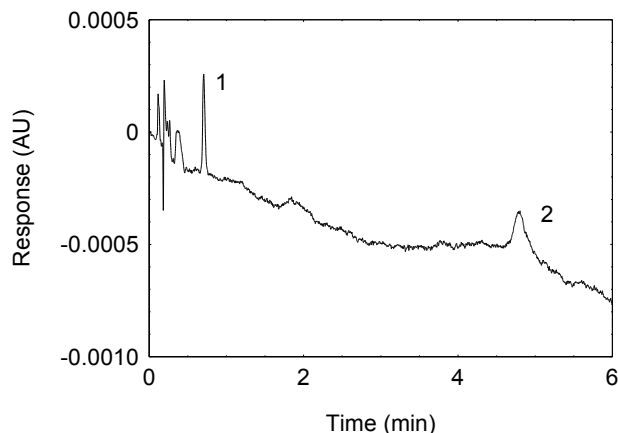


Figure 4.2.3. Chromatogram of the RQL (1: bisphenol A, 2: diglycidyl ether of bisphenol A).

4.3 Precision of the analytical method

The standard error of estimate was determined from the linear regression of data points from standards over a range that covers approximately 0.1 to 2 times the target concentration. Calibration curves for bisphenol A and diglycidyl ether of bisphenol A were constructed and are shown in Section 3.5.2 from the three injections of five standards. The standard errors of estimates are $-2.3 \mu\text{g/sample}$ for bisphenol A and $20.1 \mu\text{g/sample}$ for diglycidyl ether of bisphenol A.

Table 4.3.1
Bisphenol A Instrument Calibration

\times target concn	0.1 \times	0.5 \times	1.0 \times	1.5 \times	2.0 \times
($\mu\text{g/sample}$)	126.8	602.2	1188.6	1822.5	2377.1
area counts	221076	1113361	2110374	3121368	4143908
($\mu\text{V}\cdot\text{s}$)	235793	1092297	2161185	3185263	3987625
	229437	1098462	2132483	3187875	4097865

Table 4.3.2
Diglycidyl Ether of Bisphenol A Instrument Calibration

\times target concn	0.1 \times	0.5 \times	1.0 \times	1.5 \times	2.0 \times
($\mu\text{g/sample}$)	119.3	596.7	1193.4	1790.1	2386.8
area counts	182101	955473	1853174	2772805	3735865
($\mu\text{V}\cdot\text{s}$)	186317	942063	1883312	2811414	3514419
	188970	950616	1859145	2789579	3727763

4.4 Storage test

Storage samples for bisphenol A and diglycidyl ether of bisphenol A were prepared by liquid spiking samplers at the target concentration. After spiking, the samplers had 79.7% humid air at 20.5°C drawn through the cassettes for 4 hrs at a flow rate of 1 L/min for a total volume of 240 liters. Frozen storage was chosen after ambient and refrigerated storage test failed. Eighteen storage samples were prepared for ambient and frozen storage. Three samples were analyzed

on the day of spiking. Fifteen of the samples were stored at reduced temperature (-14 °C) and the other fifteen were stored in a closed drawer at ambient temperature (about 21 °C). At 3-4 day intervals, three samples were selected from each of the two storage sets and analyzed. Sample results were not corrected for extraction efficiency.

Table 4.4.1
Storage Test for Bisphenol A

time (days)	ambient storage recovery (%)			frozen storage recovery (%)		
	0	96.4	97.3	97.0	96.4	97.3
3	94.1	94.1	94.5	95.4	94.6	96.2
7	92.0	90.0	92.4	97.2	95.2	95.9
10	NA	NA	NA	97.8	97.3	96.4
14	NA	NA	NA	97.2	96.1	97.2
17	NA	NA	NA	94.0	94.3	97.8

Table 4.4.2
Storage for Diglycidyl Ether of Bisphenol A

time (days)	ambient storage recovery (%)			frozen storage recovery (%)		
	0	98.5	100.0	100.0	98.5	100.0
3	97.3	96.7	95.6	100.7	100.2	100.9
7	87.5	89.4	88.1	98.3	96.5	96.3
10	NA	NA	NA	98.3	96.7	98.1
14	NA	NA	NA	99.1	98.0	99.4
17	NA	NA	NA	97.4	96.9	98.7

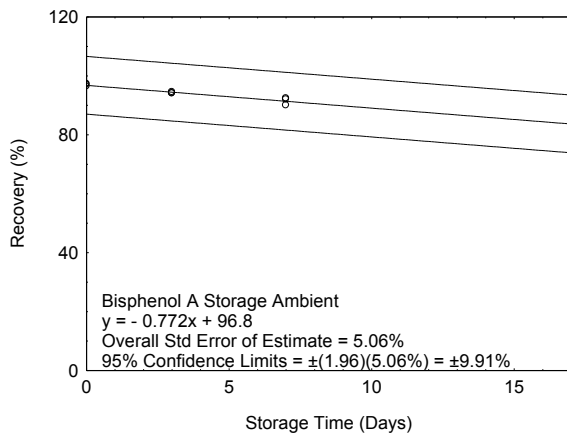


Figure 4.4.1. Ambient storage for bisphenol A.

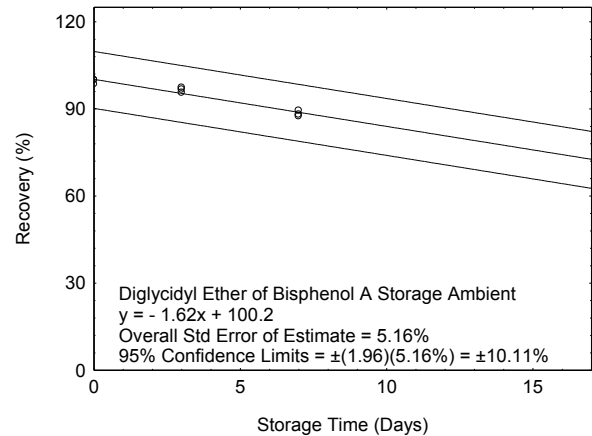


Figure 4.4.2. Ambient storage for diglycidyl ether of bisphenol A.

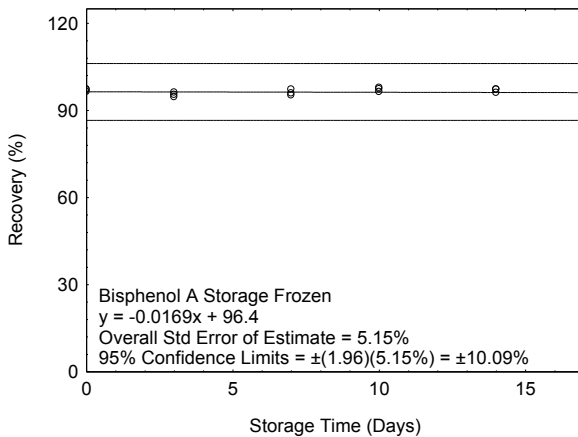


Figure 4.4.3. Frozen storage for bisphenol A.

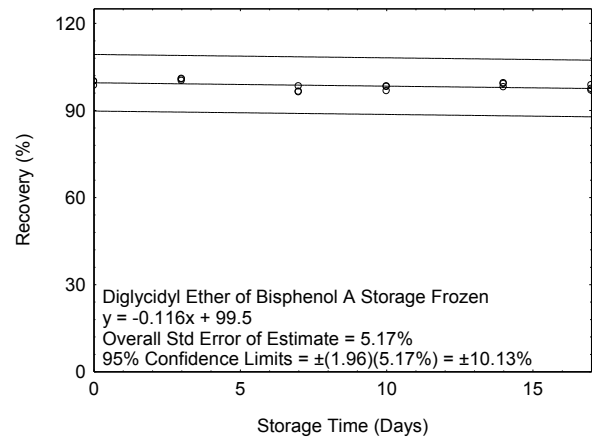


Figure 4.4.4. Frozen storage of diglycidyl ether of bisphenol A.

4.5 Precision (overall procedure)

The precision of the overall procedure at the 95% confidence level is obtained by multiplying the overall standard error of estimate by 1.96 (the z-statistic from the standard normal distribution at the 95% confidence level). Ninety-five percent confidence intervals are drawn about the regression lines in the storage stability figures shown in Section 4.4.

The precision of the overall procedure at the 95% confidence level for the frozen temperature -14 °C 17-day storage test at the target concentration is ±10.09% for both bisphenol A and ±10.13% diglycidyl ether of bisphenol A. It was obtained from the overall standard error of estimate of 5.15% for bisphenol A and 5.17% for diglycidyl ether of bisphenol A of the data shown in Figures 4.4.3 and 4.4.4. It contains an additional 5% for sampling pump error.

The recovery of bisphenol A from samples used in a 17-day storage test remained above 96.1% for bisphenol A and 97.5% for diglycidyl ether of bisphenol A when the samples were stored at -14 °C.

4.6 Reproducibility

Six glass fiber filters were spiked with the target concentrations (5.02 mg/m³ for bisphenol A and 5.05 mg/m³ for diglycidyl ether of bisphenol A). The spiked samplers were then used to sample 240 L of humid air at 2 L/min with 80.2% relative humidity and 21.2 °C. The samples were submitted to the OSHA Salt Lake Technical Center for analysis. The samples were analyzed after being stored for 7 days at -14 °C. Sample results were corrected for extraction efficiency. No sample result for bisphenol A and diglycidyl ether of bisphenol A had a deviation greater than the precision of the overall procedure determined in Section 4.5.

Table 4.6.1
Reproducibility Data for Bisphenol A
Collected on 37-mm GFF

theoretical (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
1204.7	1198.1	99.5	-0.5
1204.7	1195.0	99.2	-0.8
1204.7	1211.5	100.6	+0.6
1204.7	1205.5	100.1	+0.1
1204.7	1205.6	100.1	+0.1
1204.7	1213.4	100.7	+0.7

Table 4.6.2
Reproducibility Data for Diglycidyl Ether of Bisphenol A
Collected on 37-mm GFF

theoretical (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
1212.9	1173.5	96.8	-3.2
1212.9	1179.2	97.2	-2.8
1212.9	1175.3	96.9	-3.1
1212.9	1192.9	98.4	-1.6
1212.9	1189.4	98.1	-1.9
1212.9	1181.5	97.4	-2.6

4.7 Sampler capacity

SLTC was unable to generate an atmosphere for these analytes. Therefore this test was not performed. See Section 4.9 for retention data that supports the recommended air volume.

4.8 Extraction efficiency and stability of extracted samples

The extraction efficiency is affected by the extraction solvent, the internal standard, the sampling medium, and the technique used to extract the samples. Other reagents and techniques than described in this method can be used provided they are tested as specified in the validation guidelines.¹⁹

Extraction efficiency

The extraction efficiency of bisphenol A and diglycidyl ether of bisphenol A was determined by liquid spiking four glass fiber filters at each concentration level. These samples were stored overnight at ambient temperature and then analyzed. The mean extraction efficiency over the working range of the 0.1 to 2 times the target concentration is 98.5% for bisphenol A. The

¹⁹ Eide, M.; Simmons, M.; Hendricks, W. Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, 2010. United States Department of Labor, Occupational Safety and Health Administration Web site. <http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf> (accessed May 2011).

extraction efficiencies for the RQL and wet samplers were not included in the overall mean because it would bias the results. Wet filters were also spiked at the target concentration but, immediately before spiking, the samplers had 80.3% humid air at 21.6 °C drawn through the cassettes for 4 hrs at a flow rate of 1 L/min for a total volume of 240 liters.

Table 4.8.1
Extraction Efficiency (%) of Bisphenol A

x target concn	level	1	2	sample number		mean
	µg per sample			3	4	
0.1	115	94.3	94.8	95.0	95.1	94.8
0.25	297	97.2	98.1	97.8	97.3	97.6
0.5	624	100.6	100.4	99.5	100.3	100.2
1.0	1219	99.6	100.1	97.3	98.9	99.0
1.5	1779	98.3	101.3	101	101.2	100.4
2.0	2391	98.3	99.1	99.3	99.3	99.0
RQL	0.463	86.8	90.6	91.3	96.9	91.4
1.0 (wet)	1232	101.7	100.9	100.6	100.1	100.8

The mean extraction efficiency over the working range of 0.1 to 2 times the target concentration is 99.1% for diglycidyl ether of bisphenol A. The extraction efficiency for the RQL and wet RQL samplers were not included in the overall mean because it would bias the results.

Table 4.8.2
Extraction Efficiency (%) of Diglycidyl Ether of Bisphenol A

x target concn	level	1	2	sample number		mean
	µg per sample			3	4	
0.1	147	97.8	97.8	98.2	97.1	97.7
0.25	313	95.5	99.4	97.8	96.8	97.4
0.5	630	99.7	99.3	99.1	98.1	99.1
1.0	1165	100.1	99.8	97.4	98.6	99.0
1.5	1680	100.3	103.1	102.4	102.0	102.0
2.0	2264	99.1	99.6	99.6	99.1	99.4
RQL	0.806	92.8	92.8	93.1	90.0	92.2
1.0 (wet)	1179	100.7	99.2	99.1	99.2	99.6

Stability of extracted samples

The stability of extracted samples was examined by reanalyzing the target concentration samples 24, 48, and 72 hours after the initial analysis. After the original analysis was performed two vials were recapped with new septa which were replaced after each reanalysis. The remaining two vials retained their punctured septa throughout the test. All samples were allowed to stand in the autosampler tray at 4 °C. The samples were reanalyzed with freshly prepared standards. Diff is the difference between the initial analysis and the subsequent analysis. Each septum was punctured once for each injection. The data obtained are shown in Table 4.8.3 and Table 4.8.4.

Table 4.8.3
Stability of Extracted Samples for Bisphenol A

initial	punctured septa replaced						punctured septa retained						
	24 h	diff	48 h	diff	72 h	diff	initial	24 h	diff	48 h	diff	72 h	diff
99.59	101.1	+1.5	99.42	-0.2	98.40	-1.2	97.34	103.2	+5.9	99.88	+2.5	99.86	+2.5
100.5	100.5	+0.0	99.39	-1.1	100.5	+0.0	98.88	102.2	+3.3	99.30	+0.4	99.55	+0.7
			mean							mean			
100.0	100.8	+0.8	99.41	-0.6	99.45	-0.6	98.11	102.7	+4.6	99.59	+1.5	99.71	+1.6

Table 4.8.4
Stability of Extracted Samples (%) for Diglycidyl Ether of Bisphenol A

initial	punctured septa replaced						initial	punctured septa retained					
	24 h	diff	48 h	diff	72 h	diff		24 h	diff	48 h	diff	72 h	diff
100.1	101.2	+1.1	99.70	-0.4	99.47	-0.6	97.40	103.9	+6.5	100.6	+3.2	99.34	+1.9
99.85	100.6	+0.8	99.82	-0.0	100.0	+0.2	98.60	102.5	+3.9	99.74	+1.1	99.01	+0.4
			mean							mean			
99.98	100.9	+0.9	99.76	-0.2	99.74	-0.2	98.00	103.2	+5.2	100.2	+2.2	99.2	+1.2

4.9 Interferences (sampling)

The tested sampling interferences had no significant effect on the ability of 37-mm glass fiber filters to collect or retain bisphenol A or diglycidyl ether of bisphenol A.

Retention

Six glass fiber filters were spiked with 2430 µg of bisphenol A and 2409 µg of diglycidyl ether of bisphenol A. The samples were loaded into a 3-piece cassette with a spacer and a rear filter. The spiked samplers were then used to sample 300 L of humid air at 2 L/min with 80.0% relative humidity and 22.5 °C. The average retention of bisphenol A is 95.6% and diglycidyl ether of bisphenol A is 99.4%. The data obtained are shown in Tables 4.9.1 and 4.9.2.

Table 4.9.1 Retention Efficiency of Bisphenol A

set	recovery (%)						mean
	1	2	3	4	5	6	
front	95.8	95.5	95.3	95.9	95.4	95.6	95.6
rear	0	0	0	0	0	0	0
total	95.8	95.5	95.3	95.9	95.4	95.6	95.6

Table 4.9.2 Retention Efficiency of Diglycidyl Ether of Bisphenol A

set	recovery (%)						mean
	1	2	3	4	5	6	
front	99.4	99.5	99.0	99.9	98.9	99.4	99.4
rear	0	0	0	0	0	0	0
total	99.4	99.5	99.0	99.9	98.9	99.4	99.4

Low humidity

Three glass fiber filters were spiked with 2366 µg of bisphenol A and 2376 µg of diglycidyl ether of bisphenol A. The spiked samplers were then used to sample 240 L of humid air at 2 L/min with 20.3% relative humidity and 20.9 °C. The samples were immediately analyzed. Sample results were 93.9%, 93.9%, and 93.7% of theoretical for bisphenol A and 101.2%, 100.8%, and 101.4% of theoretical for diglycidyl ether of bisphenol A.

Low concentration

Three glass fiber filters were spiked with 149 µg of bisphenol A and 132 µg of diglycidyl ether of bisphenol A. The spiked samplers were then used to sample 240 L of humid air at 2 L/min with 80.1% relative humidity and 20.1 °C. The samples were immediately analyzed. Sample results were 98.6%, 97.7%, and 96.6% of theoretical for bisphenol A and 102.0%, 101.6%, and 101.1% of theoretical for diglycidyl ether of bisphenol A.

Interferences

Three glass fiber filters were spiked at the target concentration with 1183 µg of bisphenol A and 1188 µg of diglycidyl ether of bisphenol A along with 2 µL (2.6 ppm) of epichlorohydrin and placed in cassettes. The spiked samplers were then used to sample 240 L of humid air at 2

L/min with 80.1% relative humidity and 20.1 °C. The samples were immediately analyzed. Sample results were 92.8%, 92.9%, and 93.7% of theoretical for bisphenol A and 98.2%, 97.7%, and 99.8% of theoretical for diglycidyl ether of bisphenol A.

4.10 Cassette wipes

Blank cassette walls were spiked with solutions of bisphenol A and diglycidyl ether of bisphenol A in ethanol at the target concentration and approximately 10 times the RQL. The cassettes were allowed to air dry overnight and then were wiped with 37-mm glass fiber filters that had been moistened with 0.1 mL of ethanol. Cassette walls were wiped multiple times to determine how many wipes would be needed to get a recovery of 75% of the material.

Table 4.10.1
Recovery of Bisphenol A from Spiked Cassette Walls

pass	mass per cassette (µg)	recovery (%)				mean recovery (%)
wipe 1	1197	80.0	72.3	78.6	79.0	77.5
wipe 2	1197	3.6	14.6	6.5	4.5	7.3
wipe 3	1197	1.7	1.7	0.2	1.7	1.3
wipe 1	5.56	76.9	76.3	76.8	72.8	75.7
wipe 2	5.56	0	0	0	0	0

Table 4.10.2
Recovery of Diglycidyl Ether of Bisphenol A from Spiked Cassette Walls

pass	mass per cassette (µg)	recovery (%)				mean recovery (%)
wipe 1	1204	80.5	71.6	76.0	72.7	75.2
wipe 2	1204	3.3	15.0	5.9	6.7	7.7
wipe 3	1204	1.7	1.6	0.5	2.4	1.6
wipe 1	5.56	79.3	77.2	82.4	78.8	79.4
wipe 2	5.56	0	0	0	0	0

4.11 Qualitative analysis

When necessary, the identity or purity of an analyte peak can be confirmed by spectral library matching using a PDA. The absorbance spectra in Figure 4.11.1 and 4.11.2 are from the target level.

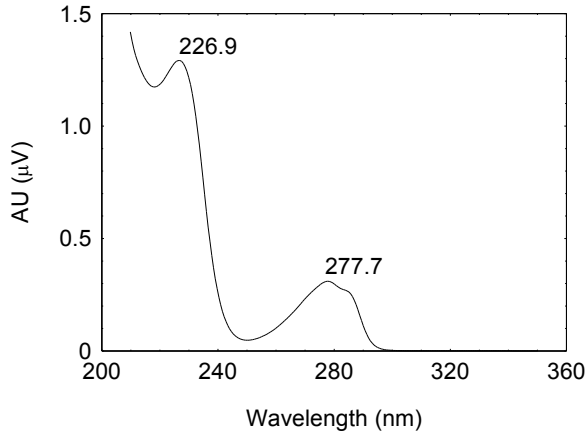


Figure 4.11.1. Absorbance spectra of bisphenol A.

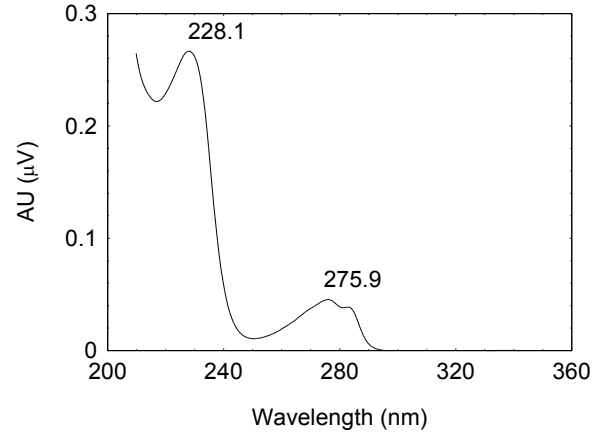


Figure 4.11.2. Absorbance spectra of diglycidyl ether of bisphenol A.

Another option to confirm the analyte peak is by using a fluorescence detector with the same analytical conditions as in section 3.5.1.

Fluorescence conditions

excitation: 285 nm
emission: 300 nm
PMT gain: 1
sensitivity: 10000

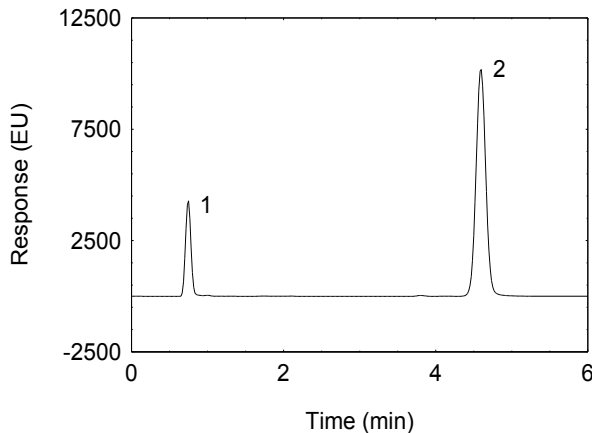


Figure 4.11.3. Chromatogram obtained at the target concentration with the recommended analytical conditions for fluorescence detection (1: bisphenol A; 2: diglycidyl ether of bisphenol A).

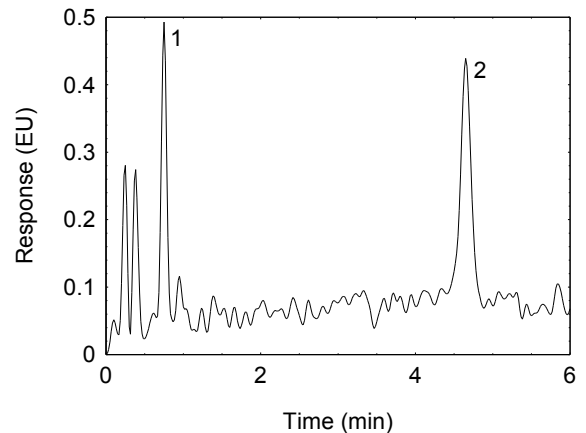


Figure 4.11.4. Chromatogram obtained at the RQL concentration with the recommended analytical conditions for fluorescence detection (1: bisphenol A; 2: diglycidyl ether of bisphenol A).