# Cumene

| | |
|---|---|
| Method no: | PV2137 |
| Control no. | T-PV2137-01-0403-CH |
| OSHA PEL: | 50 ppm (245 mg/m$^3$) |
| Procedure: | Samples are collected by drawing a known volume of air through glass sampling tubes containing coconut shell charcoal. Samples are extracted with 1 mL of a solution of carbon disulfide: *N*,*N*-dimethylformamide (99:1) and analyzed by GC using a flame ionization detector (FID). |
| Recommended sampling time and sampling rate: | 120 min at 0.2 L/min (24 L) |
| Reliable quantitation limit: | 8.4 ppb (41 μg/m$^3$) |
| Status of method: | Partially evaluated method. This method has been subjected to established evaluation procedures of the Methods Development Team and is presented for information and trial use. |

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Uyen Bui

Chromatography Team
Industrial Hygiene Chemistry Division
OSHA Salt Lake Technical Center
Sandy UT 84070-6424

1. General Discussion

1.1 Background

1.1.1 History

Cumene has a PEL of 50 ppm. OSHA desires a partially validated method or validated method for each chemical that has a PEL. A partially validated method was evaluated for cumene, due to limited time and resources available. Other OSHA validated methods collect similar compounds such as xylene[1] on coconut shell charcoal, so this medium was tried and it worked well for cumene.

The samples were extracted with 1 mL of carbon disulfide: *N,N*-dimethylformamide (99:1) ($CS_2$:DMF) with an extraction efficiency of 100.3%. The retention efficiency study showed no cumene present on the back-up section of tubes that had been spiked with 11.75 mg cumene and that had 24 L of humid air drawn through them. The storage study showed 6% loss under refrigerated conditions and 7% loss under ambient conditions for samples stored for up to 14 days.

1.1.2 Toxic effects[2] (This section is for information only and should not be taken as the basis of OSHA policy.)

Cumene is a mucous membrane, skin and eye irritant. It can cause headaches, dermatitis and narcosis. It has a central nervous system depressant action. It is toxic by ingestion, inhalation and skin contact.

1.1.3 Workplace exposure[2,3]

Most exposures to cumene occur in the production of acetone, phenol, acetophenone and α-methyl-styrene. Cumene is also used as a thinner for paints and as a constituent of some petroleum-based solvents. In 2002, U.S. industrial capacity for cumene production was 3503 thousand metric tons.

1.1.4 Physical properties and other descriptive information[2,4]

| | | | |
|---|---|---|---|
| synonyms: | isopropyl benzene; 2-phenylpropane | IMIS[5]: | 0780 |
| | | vapor density: | 4.1 |
| CAS number: | 98-82-8 | boiling point: | 152°C (306°F) |
| molecular weight: | 120.19 | vapor pressure: | 1.33 KPa @38.3°C |
| melting point: | -96°C (-141°F) | flash point: | 39°C (102°F) (closed cup) |
| appearance: | colorless liquid | molecular formula: | $C_9H_{12}$ |
| odor: | sharp, penetrating, aromatic odor | density (g/mL): | 0.864 |
| | | solubility: | insoluble in water, soluble in most organic solvents |
| autoignition temperature: | 424°C (795°F) | | |

[1] OSHA Method 1002. www.osha.gov (accessed 11/15/03).

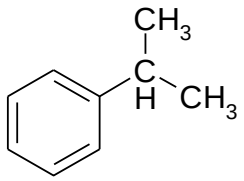
[2] *Documentation of the Threshold Limit Values for Chemical Substances,* 7th ed., American Conference of Governmental Industrial Hygienists Inc., Cincinnati, OH, 2001, vol. 1, p Cumene 1-4.

[3] Chem. Eng. News, 2003, 81 (27), p 53.

[4] Lewis, R., *Hazardous Chemicals Desk Reference,* 3rd ed., Van Nostrand Reinhold, New York, 1993, p 357.

[5] OSHA Chemical Sampling Information. www.osha.gov (accessed 11/15/03).

structural formula:




This method was evaluated according to the OSHA SLTC "Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis"[6]. 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.

1.2 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 concentration, based on the recommended sampling parameters. Ten samplers were spiked with equally descending increments of cumene, such that the highest sampler loading was 10.37 μg of cumene. This is the amount spiked on a sampler that would produce a peak about 10 times the response for a sample blank. These spiked samplers were analyzed with the recommended analytical parameters, and the data obtained used to calculate the required parameters (standard error of estimate (SEE) and slope) for the calculation of the DLOP. The slope was 594.3 and the SEE was 58.7. 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 DLOP and RQL were 0.296 μg (2.5 ppb) and 0.988 μg (8.4 ppb), respectively.

Table 1.2
Detection Limit of the Overall Procedure for Cumene

| mass per sample (μg) | area counts (μV•s) |
|---|---|
| 0.00 | 0 |
| 1.04 | 783 |
| 2.07 | 1308 |
| 3.11 | 1968 |
| 4.15 | 2464 |
| 5.18 | 3093 |
| 6.22 | 3764 |
| 7.26 | 4350 |
| 8.29 | 4967 |
| 9.33 | 5681 |
| 10.4 | 6229 |

[6] Burright, D.; Chan, Y.; Eide, M.; Elskamp, C.; Hendricks, W.; Rose, M. C. Evaluation Guidelines For Air Sampling Methods Utilizing Chromatographic Analysis; OSHA Salt Lake Technical Center, U.S. Department of Labor, Salt Lake City, UT, 1999.

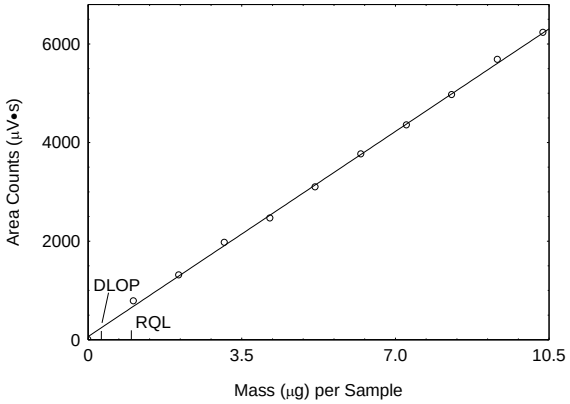



Figure 1.2.1 Plot of data to determine the DLOP/RQL for cumene.
(y = 594x + 65.3; SEE = 58.7)

Below is a chromatogram of cumene at the RQL. The recovery at the RQL was 89.2%.

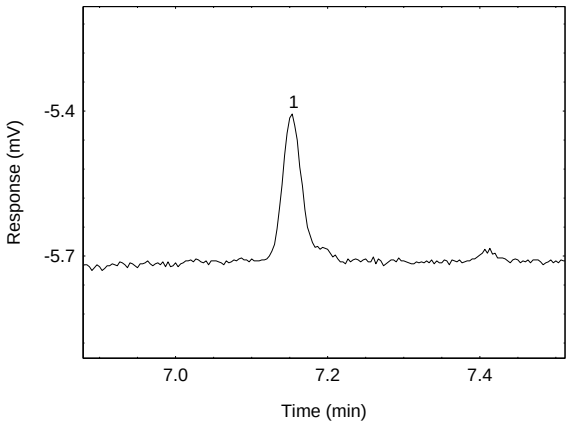



Figure 1.2.2 Chromatogram of the cumene standard near the RQL.
(Key: (1) cumene)

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

Samples are collected with 7-cm × 4-mm i.d. × 7-mm o.d. glass sampling tubes packed with two sections (100/50 mg) of coconut shell charcoal. The sections are held in place with foam

plugs and with a glass wool plug at the front. For this evaluation, commercially prepared sampling tubes were purchased from SKC, Inc. (Catalog no. 226-01, lot 2000).

2.2 Reagents

None required.

2.3 Technique

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

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

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

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

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

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

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

2.4 Extraction efficiency

The extraction efficiency was determined by spiking 16 tubes with cumene at 0.1 to 2 times the target concentration. These samples were stored overnight at ambient temperature and then extracted for 30 minutes using a lab shaker, and analyzed. The mean extraction efficiency over the studied range was 100.3%.

Table 2.4
Extraction Efficiency (%) of Cumene

| level | | sample number | | | | mean |
|---|---|---|---|---|---|---|
| × target concn | mg per sample | 1 | 2 | 3 | 4 | |
| 0.1 | 0.59 | 98.3 | 100.2 | 99.9 | 99.9 | 99.6 |
| 0.5 | 2.94 | 99.9 | 99.5 | 99.3 | 100.9 | 99.9 |
| 1.0 | 5.88 | 100.7 | 99.5 | 101.7 | 100.6 | 100.6 |
| 2.0 | 11.75 | 100.7 | 100.5 | 101.2 | 101.3 | 100.9 |

2.5 Retention efficiency

Six charcoal tubes were spiked with 11.75 mg (100 ppm) of cumene in the front sections, then they had 24-L humid air (absolute humidity of 15.9 mg/L of water, about 80% relative humidity

at 22.2 °C) pulled through them at 0.2 L/min. The samples were extracted and analyzed. The mean recovery was 98.3%. There was no analyte found on the back-up section of any of the tubes.

Table 2.5
Retention Efficiency (%) of Cumene

| section | sample number | | | | | | mean |
|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | |
| front of spiked tube | 97.3 | 98.3 | 98.0 | 99.5 | 97.9 | 99.1 | 98.3 |
| rear of spiked tube | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| total | 97.3 | 98.3 | 98.0 | 99.5 | 97.9 | 99.1 | 98.3 |

2.6 Sample storage

Fifteen charcoal tubes were each spiked with 5.88 mg (50 ppm) of cumene, then they had 24 L of air, with an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 23 °C), drawn through them. Three samples were analyzed immediately, and the rest were sealed. Six were stored at room temperature (23°C), while the other six were stored at refrigerated temperature (4°C). Three samples stored at room temperature and three samples stored at refrigerated temperature were analyzed after 8 days and the remaining six after 14 days. The amounts recovered indicate good storage stability for the time period studied.

Table 2.6
Storage Test for Cumene

| time (days) | ambient storage recovery (%) | | | refrigerated storage recovery (%) | | |
|---|---|---|---|---|---|---|
| 0 | 99.5 | 100 | 98.0 | | | |
| 8 | 94.9 | 95.7 | 97.2 | 98.1 | 97.1 | 96.5 |
| 14 | 91.6 | 95.2 | 92.1 | 93.3 | 93.9 | 93.5 |

2.7 Recommended air volume and sampling rate

Based on the data collected in this evaluation, 24-L air samples should be collected at a sampling rate of 0.2 L/min for 120 minutes.

2.8 Interferences (sampling)

2.8.1 There are no known compounds which will severely interfere with the collection of cumene.

2.8.2 Suspected interferences should be reported to the laboratory with submitted samples.

3. Analytical Procedure

Adhere to the rules set down in your Chemical Hygiene Plan. Avoid skin contact and inhalation of all chemicals and review all appropriate MSDSs.

3.1 Apparatus

3.1.1 A gas chromatograph equipped with an FID detector. For this evaluation, an Agilent 6890 GC was used.

3.1.2 A GC column capable of separating cumene from the extraction solvent, internal standard, and any potential interferences. A 60-m × 0.32-mm i.d. ZB Wax (1-μm df) capillary column was used in this evaluation.

3.1.3 An electronic integrator or some other suitable means of measuring peak areas. A Waters Millennium[32] Data System and an Agilent integrator 3396 were used in this evaluation.

3.1.4 Glass vials with poly(tetrafluoroethylene)-lined caps. For this evaluation, 2-mL vials were used.

3.1.5 A dispenser capable of delivering 1.0 mL of extraction solvent to prepare standards and samples. If a dispenser is not available, a 1.0-mL volumetric pipet may be used.

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

3.1.7 Calibrated 10-μL or 20-μL syringe for preparing standards.

3.1.8 A mechanical shaker. An Eberbach mechanical shaker was used in this evaluation.

3.2 Reagents

3.2.1 Cumene, reagent grade. ChemService lot 229-122C, 99.9% was used in this evaluation.

3.2.2 Carbon disulfide, reagent grade. EM Science lot 40298103, 99.9% was used in this evaluation.

3.2.3 *N,N*-Dimethylformamide, reagent grade. Sigma-Aldrich lot 01340AB, 99.8% was used in this evaluation.

3.2.4 *p*-Cymene, reagent grade. Aldrich lot 11703TR, 99% was used in this evaluation.

3.2.5 The extraction solvent solution was carbon disulfide: *N,N*-dimethylformamide (99:1) with 0.25μL/mL of *p*-cymene as internal standard.

3.3 Standard preparation

3.3.1 Prepare standards by spiking microliter quantities of cumene from a microliter syringe into 2-mL vials, each containing 1 mL of the extraction solution. For example, 6.8 μL of cumene in 1 mL $CS_2$:DMF is equivalent to 5.88 mg/mL. For this evaluation, standards in the range of 0.001 to 11.75 mg/mL were used. A check standard from a second source should be prepared to check the calibration.

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

3.4 Sample preparation

3.4.1 Remove the plastic end caps from the sample tubes and carefully transfer each adsorbent section to separate 2-mL vials. Discard the glass tube, urethane foam plug and glass wool plug.

3.4.2 Add 1.0 mL of extraction solvent to each vial using the same dispenser as used for preparation of standards.

3.4.3 Immediately seal the vials with poly(tetrafluoroethylene)-lined caps, and shake the vials on a shaker for 30 minutes.

3.5 Analysis

3.5.1 Gas chromatographic conditions

GC conditions

| | |
|---|---|
| Temperatures: | |
| Column: | initial 70°C, hold 2 min, program at 15°C/min to 180°C, hold 2 min |
| Injector: | 225°C |
| Detector: | 250°C |
| run time: | 10.3 min |
| column gas flow: | 3.1 mL/min (hydrogen) |
| injection size: | 1.0 μL (10:1 split) |
| column: | 60-m × 0.32-mm i.d. capillary ZB Wax (df = 1 μm) |
| retention times: | 2.8 min (carbon disulfide)<br>8.8 min (*N,N*-dimethylformamide)<br>7.1 min (cumene)<br>8.1 min (*p*-cymene) |
| Chromatogram: | Figure 3.5.1 |

FID conditions

| | |
|---|---|
| hydrogen flow: | 30 mL/min |
| air flow: | 400 mL/min |
| nitrogen makeup flow: | 25 mL/min |

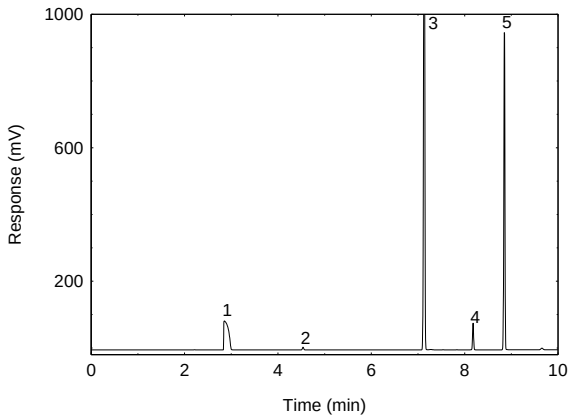



Figure 3.5.1 A chromatogram of 5.88 mg/mL cumene in the extraction solution.
(Key: (1) $CS_2$; (2) benzene, a contaminant in $CS_2$; (3) cumene; (4) *p*-cymene; and (5) DMF).

3.5.2 Peak areas are measured by an integrator or other suitable means.

3.5.3 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.

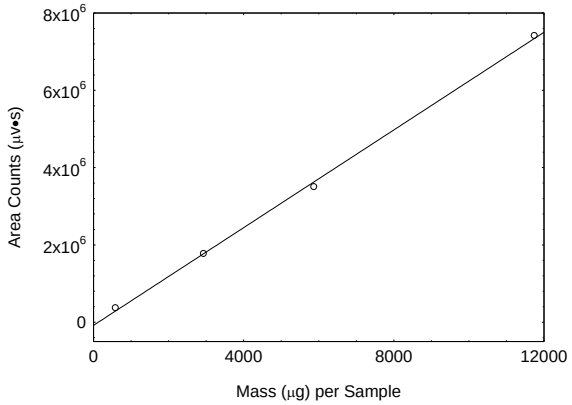



Figure 3.5.3 Calibration curve of cumene. (y = 632x - 8.10E4)

3.6 Interferences (analytical)

3.6.1 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 an interference from the analyte.

3.6.2 When necessary, the identity or purity of an analyte peak may be confirmed by GC-mass spectrometry.

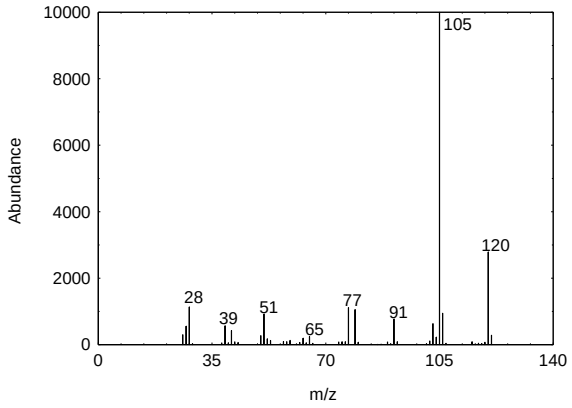



Figure 3.6.2. Mass spectrum of cumene.

3.7 Calculations

The amount of analyte per sampler 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 formulas.

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

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

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

where $C_V$ is concentration by volume (ppm)
$V_M$ is molar volume at 25 $^o$C and 1 atm = 24.46
$C_M$ is concentration by weight
$M_r$ is molecular weight = 120.19

4. Recommendations for Further Study

Collection, reproducibility, and other detection limit studies need to be performed to make this a fully validated method.