Benzophenone

OSHA Method PV2130 | January 2004

For problems with accessibility in using figures and illustrations, please contact the Salt Lake Technical Center 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.

Method no.:	PV2130
Control no.:	T-PV2130-01-0401-M
Target Concentration:	0.5 mg/m^3 (AIHA Workplace Environmental Exposure Level (WEEL))
Procedure:	Samples are collected by drawing a known volume of air through glass sampling tubes containing Chromosorb 106. Samples are extracted with a solution of 99:1 carbon disulfide: N,N-dimethylformamide and analyzed by gas chromatography using a flame ionization detector (GC/FID).
Sampling rate:	240 min at 0.2 L/min (48 L)
Reliable quantitation limit:	18.5 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.

January 2004 Mary E. Eide

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

1. General Discussion
   1.1. Background
      1.1.1. History

Air samples collected on Chromosorb 106 tubes were received at OSHA Salt Lake Technical Center (OSHA SLTC) requesting analysis for benzophenone. In a previous study, samples collected on OVS-7 tubes requesting benzophenone analysis were received at OSHA SLTC, but the extraction study showed a recovery of 81.7% when extracted with methyl alcohol. These samples were analyzed by gas chromatography with a flame ionization detector (GC-FID).[1] That instrumentation was used in this study. The xAD-7 of the OVS-7 tubes is a polar medium, while the Chromosorb 106 is a nonpolar collection media. Carbon disulfide was first tried as the extraction solvent for the Chromosorb 106. While the extraction efficiency for dry tubes was 97.6%, the spiked tubes that had humid air pulled them had a loss of benzophenone in the extracted solution after the samples sat on the autosampler for more than two hours after shaking. Next a solution of 99:1 carbon disulfide:N,N-dimethylformamide (DMF), was tried and found to give good extraction (98.4% recovery) with no loss as the samples waited on the autosampler to be analyzed. The retention efficiency was 98.6% and the storage stability recovery of 98.0% on Day 14 of ambient storage.

      1.1.2. Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy).[2,3,4]

Benzophenone is a naturally occurring compound used in flavorings and perfumes. The FDA allows 0.5 ppm in non-alcoholic beverages, 1.70 ppm in candy, and 0.09-0.3% in perfumes, but recommends that the least amount possible for the effect desired be used in formulations, due to its toxicity. At higher concentrations, benzophenone is a contact irritant affecting eyes, skin, and respiratory system. Benzophenone is moderately toxic by ingestion.

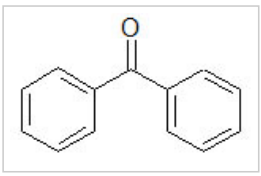
      1.1.3. Workplace exposure[5,6]

Benzophenone is used as a fixative for heavy perfumes in soaps, detergents, and room deodorizers. It is used as a flavoring agent, ultraviolet absorber in inks and coatings, and as a polymerization inhibitor for styrene. It is used in the manufacture of antihistamines, hypnotics, and insecticides.

1.1.4. Physical properties and other descriptive information[7]

synonyms:	benzoylbenzene	diphenylmethanone	diphenyl Ketone	a-oxodiphenyl methane	phenyl ketone
CAS number:	119-61-9	molecular weight:	182.22		
melting point:	48.5 °C	boiling point:	305 °C		
appearance:	white solid	molecular formula:	$C_{13}H_{10}O$		
odor:	rose or geranium-like	flash point:	144°C (291 °F) (cc)		
solubility:	insoluble in water, soluble in organics such as alcohol, ether, chloroform				
IMIS[8]:	B505				

Structural Formula:



This method was evaluated according to the OSHA SLTC "Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis".[9]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 analyte, such that the highest sampler loading was 12.6 µ of benzophenone. This is the amount spiked on a sampler that would produce a peak at least 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 and slope) for the calculation of the DLOP. The slope was 1528 and the SEE was 136. 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 0.27 µg (5.63 µg/m^3) and 0.89 µg (18.5 µg/m^3) respectively. The recovery at the RQL was 95.7%.

Table 1.2
Detection Limit of the Overall Procedure for Benzophenone

mass per sample (µg)	area counts (µV-s)
0.00	0
1.26	2148
2.52	3654
3.78	5789
5.04	7664
6.30	6910
7.56	11506
8.82	13680
10.1	15348
11.3	17168
12.6	19379

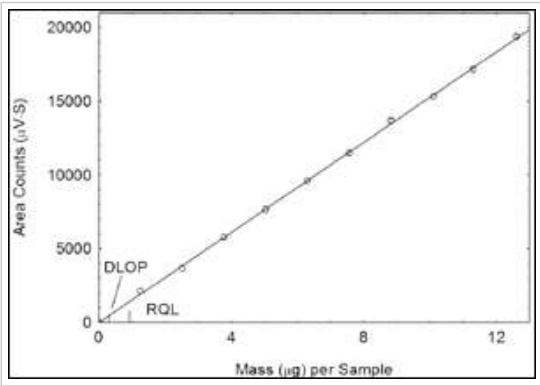


Figure 1.2.1 Plot of data to determine the DLOP/RQL for benozophenone. (y=1528x+5.33)

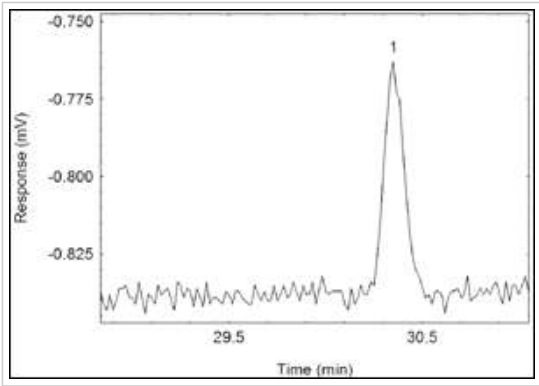


Figure 1.2.2 Chromatogram of the RQL level of benzophenone. (Key: (1) benzophenone)

2. Sampling Procedures

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 x 4-mm i.d. x 7-mm o.d. glass sampling tubes packed with two sections (100/50 mg) of Chromosorb 106. The sections are held in place and separated with a glass wool plug and two urethane foam plugs. For this evaluation, commercially prepared sampling tubes were purchased from SKC, Inc. (catalog no. 226-110 lot 2573).

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 ends. Use tube holders to minimize the hazard of broken glass. All tubes should be from the same lot.

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

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 sampler 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 front sections of Chromosorb 106 tubes with benzophenone at 0.1 to 2 times the target concentration. These samples were stored overnight at ambient temperature and then extracted with 1 mL of extracting solvent for 30 minutes on a shaker, and analyzed by GC-FID. The mean extraction efficiency over the studied range was 98.4%. The wet extraction efficiency was determined at 1 times the target concentration by liquid spiking the analyte onto Chromsorb 106 tubes which had 48-L humid air (absolute humidity of 15.9 mg/L of water, about 80% relative humidity at 22.2 °C) drawn through them immediately before spiking. The mean recovery for the wet samples was 98.5%.

Table 2.4
Extraction Efficiency (%) of Benzophenone

level		sample number						
x target concn	µg per Sample	1	2	3	4	5	6	Mean
0.1	2.42	99.4	99.1	97.0	98.5	97.9	99.1	98.5

0.5	12.1	99.8	99.5	97.7	98.7	97.6	98.4	98.6
1.0	24.2	98.6	97.6	98.5	97.9	98.8	98.5	98.3
1.5	36.3	98.2	98.0	97.5	99.0	97.2	98.8	98.1
2.0	48.4	98.9	98.5	98.7	98.5	98.9	98.6	98.7
1.0 (wet)	24.2	97.9	98.9	98.1	99.0	97.9	98.9	98.5

2.5. Retention efficiency

Six Chromosorb 106 tubes were spiked with 48.4 µ (1.01 mg/m^3) of benzophenone and allowed to equilibrate for 6 h. The tubes had 48-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 98.6%. There was no analyte found on the backup section of any of the tubes.

Table 2.5
Extraction Efficiency (%) of Benzophenone

	sample number						
section	1	2	3	4	5	6	mean
front	98.7	97.6	99.0	99.2	98.8	98.4	98.6
rear	0.0	0.0	0.0	0.0	0.0	0.0	0.0
total	98.7	97.6	99.0	99.2	98.8	98.4	98.6

2.6. Sample storage

Fifteen Chromosorb 106 tubes were each spiked with 24.2 µg (0.50 mg/m^3) of benzophenone. They were allowed to equilibrate for 6 h, then 48 L of air, with an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2 °), was drawn through them. Three samples were analyzed immediately. Six of the remaining samples were sealed and stored at room temperature. The other six samples were sealed and stored in the refrigerator. Three samples from each storage condition were removed after 7 days and analyzed. The remaining three samples of each storage condition were analyzed after 14 days of storage. The amounts recovered indicate good storage stability for the time period studied.

Table 2.6
Storage Test for Benzophenone

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	97.9	98.1	99.0			
7	98.4	98.1	98.8	99.2	98.0	98.9
14	97.5	98.3	98.2	97.7	98.6	98.3

2.7. Recommended air volume and sampling rate

Based on the data collected in this evaluation, 48-L air samples should be collected at a sampling rate of 0.2 L/min for 240 minutes.

2.8. Inferences (sampling)

There is no known compound which will severely interfere with the collection of benzophenone. 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. For this evaluation, an Agilent 6890 Gas Chromatograph equipped with a 7683 Injector was used.

3.1.2. A GC column capable of separating benzophenone from the extraction solvent, internal standard and any potential interferences. A 60-m x 0.32-mm i.d. capillary DB-1 with a 1.0-µm df (J&W Scientific, Folsom, CA) was used in the evaluation.

3.1.3. An electronic integrator or some other suitable means of measuring peak areas. A Waters Millennium^{3}2 Data System was 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 extracting 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 syringe for preparing standards.

3.1.8. Shaker or rotator to agitate samples during extraction. An Eberbach shaker was used in this evaluation.

3.2. Reagents

3.2.1. Benzophenone, Reagent grade. Aldrich 99% (lot 09710TA) was used in this evaluation.

3.2.2. Carbon disulfide, Reagent grade. Omni-Solv®99.99% (lot 43279343) was used for this evaluation.

3.2.3. p-Cymene, Reagent grade. Aldrich 99% (lot 11703TR) was used in this evaluation.

3.2.4. N,N-Dimethylformamide, anhydrous. Aldrich 99.8% (lot 04643LA) was used in this evaluation.

3.2.5. The extraction solvent was a solution of 99:1 carbon disulfide:DMF with 0.25 µ/mL p-cymene internal standard.

3.2.6. GC grade nitrogen, air, and hydrogen.

3.3. Standard preparation

Prepare working analytical standards by weighing microgram amounts of benzophenone into volumetric flasks and diluting up to the mark with the extraction solvent. Weigh out at least two stock standards. Make dilutions of these stock standards with the extraction solvent to bracket the samples. If sample concentrations are higher than the concentration range of prepared standards, either analyze higher standards, or dilute the sample. The higher standards should be at least as high in concentration as the highest sample. Diluted samples should be prepared with extracting solvent to obtain a concentration within the existing standard range. The concentration range of standards used in this study was from 1 to 48.4 µg/mL.

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.

3.4.4. Shake the vials on a shaker for 30 minutes.

3.5. Analysis

3.5.1. Gas chromatograph conditions.

GC conditions

temperatures:	
column:	50°C, hold 1 min, ramp at 10°/min to 170°, hold 21 min
injector:	250°
detector:	250°
run time:	34 min
column gas flow:	3.2 mL/min (hydrogen)
septum purge:	1.9 mL/min (hydrogen)
injection size:	1.0 µ (10:1 split)
column:	60-m x 0.32-mm i.d. capillary DB-1(1.0-µm df)
retention times:	4.0 min (carbon disulfide); 7.0 min (DMF); 11.8 min (p-cymene); 31.0 min (benzophenone)

FID conditions

hydrogen flow:	30 mL/min
air flow:	400 mL/min
makeup flow: (nitrogen)	25 mL/min

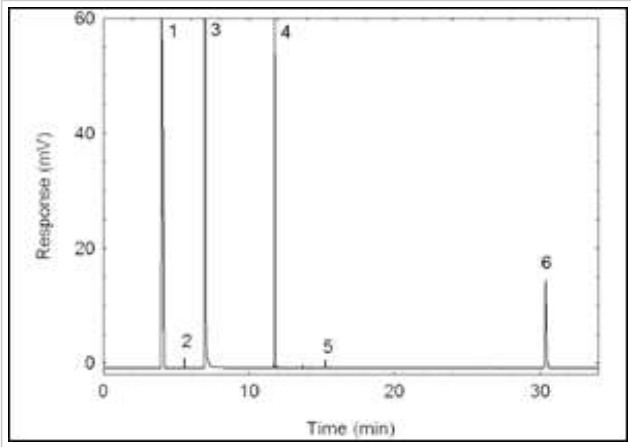


Figure 3.5.1 A chromatogram of 48.8 µ/mL benzophenone in 99:1 carbon disulfide: DMF with 0.25 µg/mLp-cymene internal standard. Key: (1) carbon disulfide; (2) benzene contaminant in the carbon disulfide; (3) DMF; (4)p-cymene; (5) contaminant in solvent; (6) benzophenone

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 ISTD-corrected response of standard injections versus micrograms of analyte per sample. Bracket the samples with freshly prepared analytical standards over a range of concentrations.

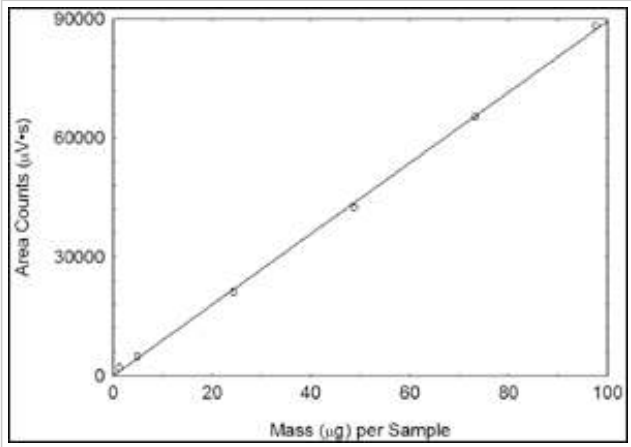


Figure 3.5.3 Calibration curve of benzophenone (y=894x + 113)

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 interference were reported, they should be considered before samples are extracted. Generally, chromatographic conditions can be altered to separate interference from the analyte.

When necessary, the identity or purity of an analyte peak may be confirmed by mass spectrometry or by another analytical procedure. The mass spectrum in Figure 3.6 was from the NIST spectral library.

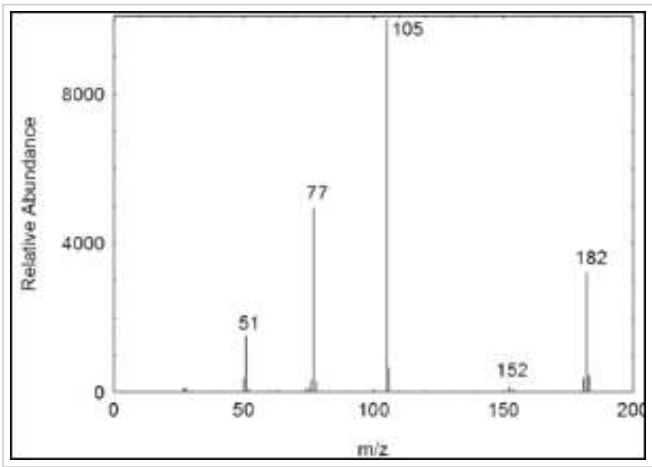


Figure 3.6 The mass spectrum of benzopehone

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 formula.

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

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

4. Recommendations for Further Study
   Collection, reproducibility, and other detection limit studies need to be performed to make this a fully validated method.

References

1. Eide, M., Collection and Analysis of Benzophene from OVS-7 Tubes, 1993, unpublished.
2. Lewis, R., Ed., Sax's Dangerous Properties of Industrial Materials, 10th ed., John Wiley & Sons, New York, 2000, p 390.
3. National Toxicology Program, ntp-server.niehs.nih.gov, (accessed 12/18/03).
4. Material Safety Data Sheet: Benzophenone, Aldrich Chemical Co., Milwaukee, WI, Dec. 2003.
5. Lewis, R., ED., Hawley's Condensed Chemical Dictionary, 14th ed., John Wiley & Sons, New York, 2001, p 126.
6. O'Neil, M., The Merck Index, 13th ed., Merck & Co., Whitehouse Station, NJ 2001, p 188.
7. Lewis, R., ED., Hawley's Condensed Chemical Dictionary, 14th ed., John Wiley & Sons, New York, 2001, p 126.
8. OSHA Chemical sampling information. www.osha.gov (accessed 12/17/03).
9. 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.

UNITED STATES
DEPARTMENT OF LABOR

Occupational Safety and Health Administration
200 Constitution Ave NW
Washington, DC 20210
800-321-6742 (OSHA)
TTY
www.OSHA.gov

FEDERAL GOVERNMENT

White House
Severe Storm and Flood Recovery Assistance
Disaster Recovery Assistance
DisasterAssistance.gov
USA.gov
No Fear Act Data
U.S. Office of Special Counsel

OCCUPATIONAL SAFETY AND HEALTH

Frequently Asked Questions
A - Z Index
Freedom of Information Act
Read the OSHA Newsletter
Subscribe to the OSHA Newsletter
OSHA Publications
Office of Inspector General

ABOUT THE SITE

Freedom of Information Act
Privacy & Security Statement
Disclaimers
Important Website Notices
Plug-Ins Used by DOL
Accessibility Statement