Benzyl Acetate

Method number: PV2124

Target concentration: 10 ppm (61 mg/m^3)
ACGIH TLV: 10 ppm (61 mg/m^3)

Procedure: Samples are collected by drawing a known volume of air through glass sampling tubes containing 4-tert-butylcatechol (TBC) coated charcoal. Samples are extracted with carbon disulfide and analyzed by GC using a flame ionization detector(FID).

Recommended sampling time
and sampling rate: 100 min at 0.1 L/min (10 L)

Reliable quantitation limit: 52.1 ppb
0.009 mg/m^3

Status of method: Partially evaluated method. This method has been subjected to established evaluation procedures of the Method Development Team and is presented for information and trial use.

June 2003   Chromatography Team   Yogi C. Shah
                     Industrial Hygiene Chemistry Division
                     OSHA Salt Lake Technical Center
                     Salt Lake City UT 84115-1802

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1. General Discussion

   1.1 Background

      1.1.1 History

      ACGIH TLV for benzyl acetate is 10 ppm (61 mg/m^3). This work was performed because no method was available. Analysis by gas chromatography with a flame ionization detector was chosen. Charcoal tubes did not give good recovery when 10 L humid air was drawn thru the tubes, TBC charcoal tubes were selected for better recovery. Carbon disulfide was selected for the extraction solvent and was found to give an extraction efficiency of 97.3%. The retention efficiency when 10 L humid air drawn was 94.3% and the storage stability was 98.6% recovery on Day 14.

      1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.) [1]

      If ingested benzyl acetate can cause gastrointestinal (G.I.) irritation with vomiting and diarrhea. It also is irritating to skin, eyes and respiratory tract.

      1.1.3 Workplace exposure[2]

      Benzyl acetate is used in artificial jasmine and other perfumes, soap perfume, flavoring, natural and synthetic resins, oils, lacquers, polishes, printing inks and varnish removers.

      1.1.4 Physical properties and other descriptive information[3,4]

CAS number:	140-11-4	IMIS[4]:	B508
RTECS number:	AF 5075000:1738	molecular weight:	150.17
melting point:	-51 °C	boiling point:	213 °C
appearance:	clear liquid	molecular formula:	$C_9H_{10}O_2$
odor:	pear like	flash point:	102 °C (216 °F)(cc)
autoignition temperature:	460 °C	density:	1.05
synonyms:	Acetic acid phenylmethyl ester; acetic acid benzyl ester		
solubility:	ether, alcohol		
structural formula:			

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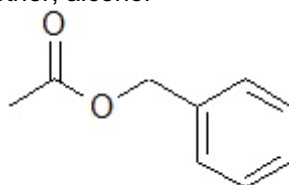
[1] The Merck Index , 11th edition Merck & Co..Inc .Rawhay, N.J. 1989, p 176.

[2] The Condensed Chemical Dictionary, thirteenth Ed. Gessner G. Hawley. Von Nostrand Reinhold : New York, 1997, p 129.

[3] The Condensed Chemical Dictionary, thirteenth Ed. Gessner G. Hawley. Von Nostrand Reinhold: New York, 1997, p 129.

[4] OSHA Chemical Sampling Guide, http://www:osha.gov (01/05/2003 accessed)

This method was evaluated according to the OSHA SLTC "Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis".[5] 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 concentrations, based on the recommended sampling parameters. Ten samplers were spiked with equal descending increments of analyte, such that the highest sampler loading was 3.2 µg benzyl acetate. 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 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 1997 and the SEE was 104.2. 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 0.157µg   and 0.521 µg, respectively.

Table 1.2.
Detection Limit of the Overall Procedure
for benzyl Acetate

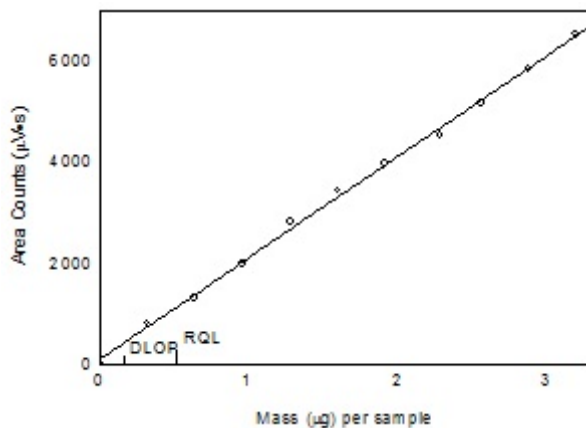| mass per sample (µg)	area counts (µV-s)
0.00	0
0.32	809
0.64	1366
0.96	2189
1.28	2816
1.60	3429
1.92	3969
2.24	4523
2.56	5142
2.88	5836
3.20	6522

Figure 1.2.1 Plot of data to determine the DLOP/RQL for benzyl acetate. (Y = 1997X + 95.8)

Below is chromatogram of the RQL level.

[5] 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.
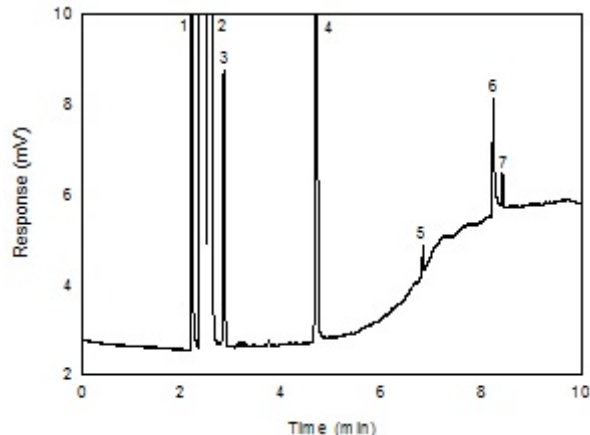
Figure 1.2.2. Chromatogram of the RQL of benzyl acetate. (1, 5, and 6 = impurity; 2 (doublet)= carbon disulfide; 3= benzene (contaminant in the carbon disulfide); 4 = *p*-cymene; and 7 = benzyl acetate)

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

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

2.1.2 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 TBC Coated charcoal. The sections are held in place and separated with glass wool plugs. For this evaluation, commercially prepared sampling tubes were purchased from SKC, Inc. (catalog no. 226-73).

2.2 Reagents

None required.

2.3 Technique

2.3.1 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.

2.3.2 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.

2.3.3 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.

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2.3.4   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.

2.3.5   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.

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

2.3.7   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 liquid-spiking TBC Coated charcoal tube with benzyl acetate at 0.1 to 2 times the target concentration. These samples were stored overnight at ambient temperature and then extracted for 30 minutes with occasional shaking, and analyzed. The mean extraction efficiency over the studied range was 97.3%. The wet extraction efficiency was determined at 1 times the target concentration by liquid spiking the analyte onto TBC Coated charcoal tubes which had 10 L humid air (absolute humidity of 15.9 mg/L of water, about 80% relative humidity at 22.2 °C) drawn through them. The mean recovery for the wet samples was 94.6%.

Table 2.4
Extraction Efficiency (%) of Benzyl Acetate

level		sample number					
× target concn	mg per sample	1	2	3	4	5	mean
0.1	0.06	97.9	99.1	97.9	99,2	96.3	98.1
0.25	0.15	99.1	98.6	99.2	100.2	99.1	99.1
0.5	0.31	97.3	92.7	98.7	98.4	97.3	96.9
1.0	0.61	97.2	95.8	96.5	100.2	97.4	97.4
2.0	1.22	95.8	95.6.	93.2	94.8	96.2	95.1
1.0 (wet)	0.61	97.3	93.9	93.2	94.4	94.2	94.6

2.5   Retention efficiency

Six TBC Coated charcoal tubes were spiked with 1.22 mg (20 ppm) of benzyl acetate and allowed to equilibrate for 6 h. The tubes had 10 L humid air (absolute humidity of 15.9 mg/L of water, about 80% relative humidity at 22.2 °C) pulled through them at 0.1 L/min. The samples were extracted and analyzed. The mean retention recovery was 94.3%. There was no analyte found on the backup section of any of the tubes.

Table 2.5
Retention Efficiency (%) of Benzyl Acetate

section	sample number						mean
	1	2	3	4	5	6	
front	94.3	94.1	96.8	93.7	93.8	93.1	94.3
rear	0.0	0.0	0.0	0.0	0.0	0.0	0.0
total	94.3	94.1	96.8	93.7	93.8	93.1	94.3

2.6   Sample storage

Nine TBC Coated charcoal tubes were each spiked with 0.61 mg (10.0 ppm) of benzyl acetate. They were allowed to equilibrate for 6 h, then 10 L of air, with an absolute humidity of 15.7

milligrams of water per liter of air (about 80% relative humidity at 22.2 °C), was drawn through them. Three samples were analyzed immediately, and the rest were sealed and stored at room temperature. Three more were analyzed after 7 days of storage and the remaining three after 14 days of storage. The amounts recovered, which are corrected for retention efficiency, indicate good storage stability for the time period studied.

Table 2.6
Storage Test for Benzyl Acetate (% Recovery)

| time (days) | sample number | | | mean |
	1	2	3	
0	99.4	96.9	96.2	97.5
7	99.5	98.8	99.7	99.3
14	98.3	98.7	98.8	98.6

2.7   Recommended air volume and sampling rate.

Based on the data collected in this evaluation, 10-L air samples should be collected at a sampling rate of 0.1 L/min for 100 minutes.

2.8   Interferences (sampling)

2.8.1   There are no known compounds that will severely interfere with the collection of benzyl acetate.

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. For this evaluation, a Hewlett-Packard 6890 Series Gas Chromatograph equipped with a 6890 Automatic Sampler was used.

3.1.2   A GC column capable of separating benzyl acetate from the desorption solvent, internal standard and any potential interferences. A 60-m × 0.32-mm i.d. capillary STABILWAX with a 0.5 µm df (Restek Corporation) was used in the evaluation.

3.1.3   An electronic integrator or some other suitable means of measuring peak areas. A Waters Millennium[32] 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 desorbing solvent to prepare standards and samples. If a dispenser is not available, a 1.0-mL volumetric pipet may be used.

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

3.1.8   Calibrated 10-µL syringe for preparing standards.

3.2   Reagents

3.2.1   benzyl acetate, reagent grade. Aldrich 99% (lot 08515DS) was used in this evaluation.

3.2.2 carbon disulfide, reagent grade. Omni-Solv® 99.99% (lot 34279) was used for this evaluation.

3.2.3 *p*-cymene, reagent grade. Aldrich 99% (lot 11703TR) was used in this evaluation.

3.2.4 The extraction solvent was 0.25 µL/mL *p*-cymene in carbon disulfide.

3.2.5 GC grade nitrogen, air, and hydrogen.

3.3 Standard preparation

3.3.1 Prepare working analytical standards by injecting micro liter amounts of benzyl acetate into volumetric flasks containing the extraction solvent. An analytical standard at a concentration of 1.22 mg/mL (1.16 µL/mL) is equivalent to 20.0 ppm based on a 10-liter air volume.

3.3.2 Bracket sample concentrations with working standard concentrations. If sample concentrations are higher than the concentration range of prepared standards, prepare and analyze additional standards, at least as high a concentration as the highest sample, to ascertain the linearity of response, or dilute the sample with extracting solvent to obtain a concentration within the existing standard range. The range of standards used in this study was from 0.00032 to 1.22 mg/mL.

3.4 Sample preparation

3.4.1 Remove the plastic end caps from the sample tubes and carefully transfer the adsorbent sections to separate 2-mL vials. Discard the glass tube 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 vigorously by hand several times during the next 30 minutes.

3.5 Analysis

3.5.1 Analytical conditions

GC conditions
Injector: 250°C
Detector: 250°C
run time: 14 min
column gas flow: 2.5 mL/min (hydrogen)
septum purge: 1.9 mL/min (hydrogen)
injection size: 1.0 µL (15:1 split)
column: 60-m × 0.32-mm i.d. capillary STABILWAX (0.5-µm df)
retention times: 2.53 min (carbon disulfide); 2.81 min (benzene contaminate in the carbon disulfide); 4.68 min (p-cymene); 8.41 min (benzyl acetate)
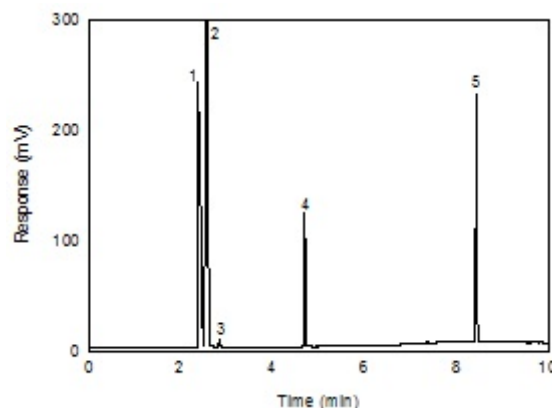

Figure 3.5.1. A chromatogram of 610 µg/mL benzyl acetate in carbon disulfide with 0.25 µL/mL *p*-cymene internal standard. Key: (1) and (2) carbon disulfide; (3) benzene contaminant in the carbon disulfide.(4) *p*-cymene; (5) benzyl acetate.

<u>FID conditions</u>
hydrogen flow   38 mL/min
air flow: 450 mL/min
makeup flow: 50 mL/min (nitrogen)

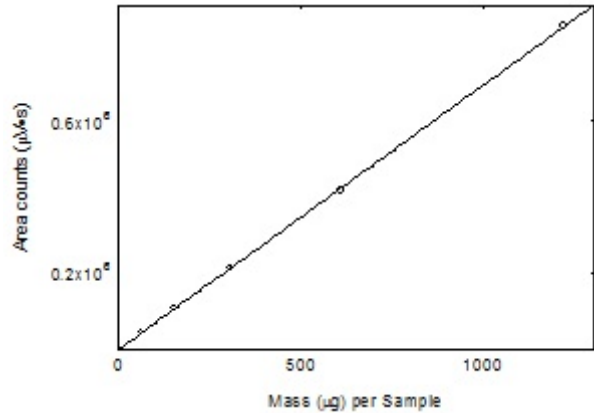3.5.2   Peak areas are measured by an integrator or other suitable means.

Figure 3.5.3 Calibration curve of benzyl acetate. (Y = 694 x - 336)

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 milligrams of analyte per sample. Bracket the samples with freshly prepared analytical standards over a range of concentrations.

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 mass spectrometry or by another analytical procedure. The mass spectrum in Figure 3.6.2 was from the NIST spectral library.
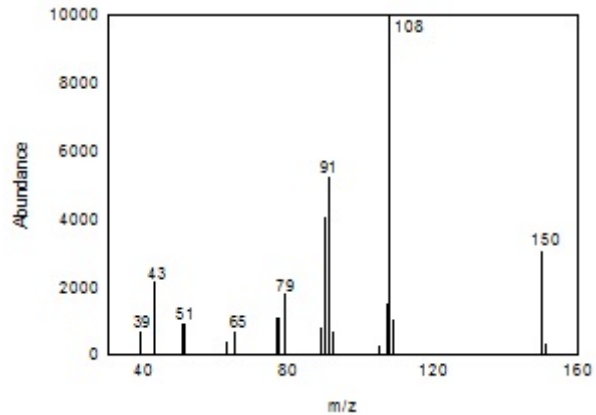
Figure 3.6.1 The mass spectrum of benzyl acetate.

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 °C = 24.46
C_M is concentration by weight
M_r is molecular weight = 150.17

4. Recommendations for Further Study

Several other tests need to be performed to make this a validated method.

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