ACETOPHENONE

Method no.	PV2003
Target concentration:	100 ppm (491 mg/m^3)
Procedure:	Samples are collected by drawing a known volume of air through a Tenax GC tube. Samples are desorbed with a solvent mixture of (5:95) Isopropanol:Carbon Disulfide (IPA):(CS_2) and analyzed by gas chromatography with a flame ionization detector.
Recommended air volume and sampling rate:	120 minutes at 0.1 L/min (12 L)
Status of Method:	Partially Validated. This method has been only partially evaluated and is presented for information and trial use.

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1 General Discussion

1.1 Background

1.1.1 History of procedure

Recently, the OSHA Analytical Laboratory received a set of field samples that required analysis for acetophenone. The air samples had been collected on charcoal tubes and isopropanol impingers. Desorption studies were done on charcoal tubes using acetone, carbon disulfide, 5:95 isopropanol:carbon disulfide, and methylene chloride as desorbing solvents. The best results were obtained with 5:95 isopropanol:carbon disulfide, but the recovery was only 68%, which indicated that charcoal tubes should not be recommended for the collection of acetophenone air samples. An evaluation of isopropanol impingers was not performed because it was preferable to find an adsorbent procedure for sample collection. NIOSH method 291 for α-chloroacetophenone uses Tenax GC tubes. The Tenax GC tubes were tried for acetophenone, and appeared to be a suitable method of collection.

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

Acetophenone is a narcotic in high concentrations (Ref. 5.1). The oral LD_{50} for acetophenone in rats is 3 g/kg. (Ref. 5.2). Acetophenone is reported to be capable of causing dermatitis to humans following skin contact (Ref. 5.3). Animal data indicates that acetophenone may cause eye irritation and possibly transient corneal injury (Ref. 5.4).

1.1.3 Potential workplace exposure

No workplace exposure level could be found in the literature, but acetophenone is used in the following processes: perfumery, solvent, intermediate for pharmaceuticals, resin, polymerization catalyst, and flavoring (Ref. 5.1)

1.1.4 Physical properties (Ref. 5.1)

Synonyms:	phenyl methyl ketone
molecular weight:	120.15
density:	1.0281
flash point	82.2 °C (180 °F) (COC)
boiling point:	202 °C
freezing point:	19.7 °C
solubility:	Slightly soluble in water, freely soluble in alcohol, chloroform, ether, fatty oils, and glycerol.
description:	Combustible, colorless liquid, with sweet, pungent odor and taste
molecular formula:	$C_6H_5COCH_3$

1.2 Limit defining parameters

1.2.1 Detection limit of the analytical procedure is 20.6 ng/injection. This is the amount of analyte which will give a peak whose height is approximately five times the baseline noise.

1.2.2 The sensitivity of the analytical procedure over a concentration range of 10.28 to 1028.1 Φg/mL is 407297 area units per Φg/mL of acetophenone. The sensitivity is determined by the slope of the calibration curve. (See Figure 1)

2 Sampling Procedure

2.1 Apparatus

2.1.1 A calibrated personal sampling pump whose flow can be determined with ∀5% of the recommended flow.

2.1.2 Tenax GC tubes: glass tube with both ends flame sealed, 7-cm long with a 6-mm o.d. and a 4-mm i.d., containing 2 sections of Tenax GC separated by a 2-mm plug of urethane foam. The absorbing section contains 30 mg of Tenax GC, the backup section 15 mg. A 3-mm plug of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section.

2.2 Reagents

2.2.1 None required.

2.3 Sampling technique

2.3.1 Immediately before sampling, break off the ends of the Tenax GC tubes. All tubes must be from the same lot.

2.3.2 Connect the tube to the sampling pump with flexible tubing. The smaller backup section of the Tenax GC tubes should be positioned nearer the sampling pump.

2.3.3 The tubes should be placed in a vertical position during sampling to minimize channeling.

2.3.4 Air being sampled should not pass through any hose or tubing before entering the Tenax GC tubes.

2.3.5 Immediately after sampling, seal the Tenax GC tubes with plastic caps. Seal each sample lengthwise with an official Form OSHA 21 label.

2.3.6 With each batch of samples, submit at least one blank tube from the same lot used for samples. This tube should be subjected to exactly the same handling as the samples (break, seal, and transport) except that no air is drawn through it.

2.3.7 Transport the samples (and corresponding paperwork) to the laboratory for analysis.

2.3.8 If bulk samples are submitted for analysis, they should be transported in glass containers with PTFE-lined caps. These samples must not be shipped in the same container used for the Tenax GC tubes.

2.4 Desorption efficiency

The average desorption efficiency from the Tenax GC tubes spiked with 1.028 mg of acetophenone was 99.1%.

Sample	Treatment	Recovery	Average Recovery
1	No Air	99.51	
2	No Air	100.99	99.1
3	No Air	99.29	
4	No Air	98.25	
5	No Air	97.68	

2.5 Retention efficiency

Eight Tenax GC tubes were spiked with 1.028 mg of acetophenone. Twelve liters of dry air were drawn through four of the tubes at 0.1 L/min. Twelve liters of humid air (about 85% relative humidity) were drawn through the other four tubes at 0.1 L/min.

Average Sample	Treatment	% Recovery	Average % Recovery
1	12 L Dry Air	100.89	
2	"	99.79	99.3
3	"	95.72	
4	"	99.93	
5	12 L Humid Air	104.5	
6	"	102.08	99.7
7	"	l06.57	
8	"	85.54	

2.6 Sample storage

Four Tenax GC tubes were spiked with 1.028 mg of acetophenone. Two tubes were stored in a refrigerator for six days and two tubes were stored in a closed drawer at ambient temperature for six days.

Sample	Storage Days	Treatment	% Recovery	Average % Recovery
1	6	Refrigerator	97.95	
2	6	"	93.55	95.8
3	6	Ambient	96.13	96.7
4	6	"	97.22	

2.7 Recommended air volume and sampling rate.

2.7.1 The recommended air volume is 12.0 liters.

2.7.2 The recommended sampling rate is 0.1 liter per minute.

2.8 Interferences

2.8.1 It is important to be aware of other components in the atmosphere which may interfere with the collection of the analyte. Report possible interferences with submitted samples.

2.9 Safety precautions

2.9.1 Care must be taken when opening the sealed ends of the Tenax GC tubes to avoid serious cuts to the hands.

2.9.2 Safety glasses should be worn when opening the sealed ends of the Tenax GC tubes to avoid injury to the eyes from glass splinters.

2.9.3 Attach the sampling equipment to the worker in such a manner that it will not interfere with the work performance of the employee.

2.9.4 Follow all safety practices that apply to the work area being sampled.

3 Analytical procedure

3.1 Apparatus

3.1.1 Gas chromatograph equipped with a flame ionization detector (GC/FID).

3.1.2 GC column capable of separating the solvent, acetophenone and the internal standard (n-hexylbenzene). The column used for validation studies was 1/8 inch x 10 ft stainless steel containing 3% SP-2100 on 100/120 Supelcoport.

3.1.3 An electronic integrator or some other suitable method of measuring peak areas.

3.1.4 Two milliliter vials with PTFE-lined caps.

3.1.5 Two microliter syringes for sample injections.

3.1.6 Volumetric flasks, 5-mL, and other convenient sizes for preparing standards.

3.1.7 Pipettes for dispensing desorbing reagent. The Glenco 1-mL dispenser is adequate and convenient.

3.2 Reagents

3.2.1 Carbon disulfide, reagent grade.

3.2.2 Isopropyl alcohol, reagent grade.

3.2.3 n-Hexylbenzene, internal standard, reagent grade.

3.2.4 Desorbing reagent - 1 μL/mL internal standard in 5% IPA:95% CS_2.

3.2.5 Acetophenone, reagent grade.

3.2.6 Chromatographic quality nitrogen, hydrogen, and air.

3.3 Standard preparation

3.3.1 Standard of acetophenone is prepared by injecting 5 µl of acetophenone into a 5-mL volumetric flask of the desorbing reagent and making it to volume.

3.3.2 A calibration curve is prepared by making dilutions with the desorbing reagent. (Figure 1.)

3.4 Sample preparation

3.4.1 The front and back section of each sample are transferred to separate 2-mL vials.

3.4.2 Each sample is desorbed with 1.0 mL of desorbing reagent.

3.4.3 The vials are sealed immediately and allowed to desorb for 30 minutes with occasional shaking.

3.5 Analysis

3.5.1 GC conditions

Flow rates	(mL/min)	Temperature (°C)	
Nitrogen	- 25	Injector	- 200
Hydrogen	- 20	Detector	- 250
Air	- 300	Column	- 150

Injection size - 2.0 μl
Elution time - 1.4 minutes

3.5.2 Chromatogram (See Figure 2)

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

3.5.4 An internal standard procedure is used.

3.6 Interferences

3.6.1 Any compound having the general retention time as the analyte or the internal standard is an interference. Possible interferences should be listed on the sample data sheet. GC parameters should be adjusted, if necessary, so these interferences will pose no problems.

3.6.2 Retention time data on a single column is not considered proof of chemical identity. Samples results greater than 100 ppm should be confirmed by GC/Mass Spectrometry or other suitable means.

3.7 Calculations

3.7.1 The equivalent ppm air concentration of samples is calculated in the following manner:

$$ppm = \frac{X\ {}^{\mu g}/_{mL} \times 24.46 \times 1\,mL}{mw \times air\ vol\ x\ de}$$

Where
X Φg/mL = Concentration of samples
24.45 = Molar volume (liter/mole) at 25 °C and 760 mmHg
mw = Molecular weight = 120.15
1 mL = Desorption volume
air vol = Sample air volume taken (L)
de = Desorption efficiency

3.7.2 This calculation is done for each section of the sampling tube and the results added together. Perform blank corrections when the analyte is detected in blank samples.

3.8 Safety precautions

3.8.1 All handling of solvents should be done in a hood.

3.8.2 Avoid skin contact with all solvents. Use appropriate disposable gloves.

3.8.3 Wear safety glasses at all times.

4 Recommendations for further study

4.1 Further work should be done on breakthrough.

4.2 Longer storage tests should be performed.

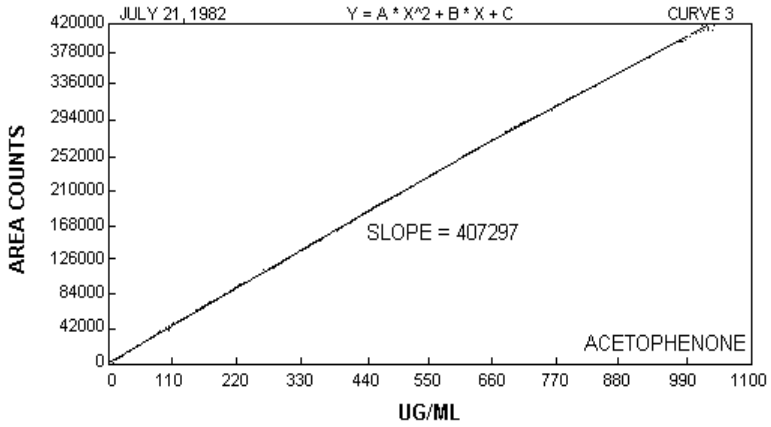

Figure 1. Calibration Curve for determining sample concentration

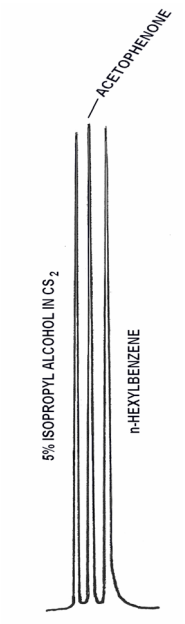

Figure 2. Chromatogram

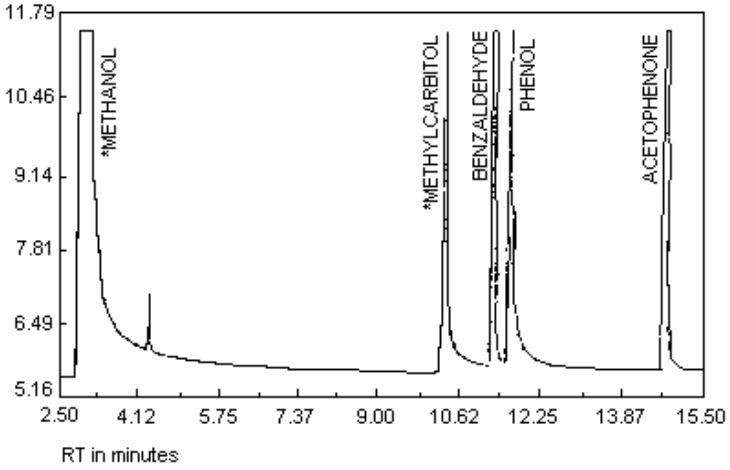

Figure 3. Bulk sample analysis by GC/FID

A bulk sample was analyzed by gas chromatography on a Varian 3400 with a flame ionization detector. The analysis was for % methyl carbitol, benzaldehyde, phenol, and acetophenone, with methanol as the solvent. The column used was a 60 meter, DB-1 capillary column, Temperature = 80 °C for 2 minutes, then increased at 5°/minute to 180 °C. (See Figure 3)

5 References

5.1 "The Condensed Chemical Dictionary", 10th ed.; Hawley, Ed.; Van Norstrand Reinhold Company, New York, 1981; p. 9.

5.2 "The Merck Index", 9th ed.; Windholz, Martha, Ed.; Merck and Company, Inc., New Jersey, 1976; p. 9.

5.3 "Spice Mill"; Katz, A.E.; 69, 1946; p. 46.

5.4 "Journal of Industrial Hygiene Toxicology"; Smyth, H.F. Jr., and Carpenter, C.P.; 30, 1948; p. 63.