ACETONE

Method no.:	69
Matrix:	Air
Target concentration:	1000 ppm (2375 mg/m^3) (OSHA PEL)
Procedure:	Air samples are collected by drawing known volumes of air through standard size sampling tubes containing 130 mg of Carbosieve S-III (carbon based molecular sieve) adsorbent in the front section and 65 mg in the back section. The samples are desorbed with 1% dimethylformamide in carbon disulfide, in the presence of magnesium sulfate, and analyzed by GC with FID detection.
Recommended air volume and sampling rate:	3 L and 0.05 L/min
Reliable quantitation limit:	2.0 ppm (4.7 mg/m^3)
Standard error of estimate at the target concentration: (Section 4.7)	8.16%
Status of method:	Evaluated method. This method has been subjected to the established evaluation procedures of the Organic Methods Evaluation Branch.

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1. General Discussion

1.1 Background

1.1.1 History

The previous OSHA method for sampling acetone is essentially the NIOSH method for sampling organic vapors (Ref. 5.1). In that method air samples are collected on coconut shell charcoal and analyzed by GC/FID following desorption with carbon disulfide. One of the major limitations of the NIOSH method is the poor stability of acetone and other ketones on charcoal (Refs. 5.2 - 5.6). Catalytic oxidation and irreversible adsorption (chemisorption) of ketones on the surface of charcoal is thought to account for the low recovery (Ref. 5.3). This effect is most pronounced for samples collected at high relative humidity (Ref. 5.2).

Alternative sampling methods have been employed to improve the storage stability of ketones collected on an adsorbent surface. Sample tubes packed with either silica gel (Ref. 5.5) or Ambersorb XE-347 (Rohm & Haas, Philadelphia, PA) (Ref. 5.6), a synthetic, carbonaceous molecular sieve adsorbent, have been used to collect 2-butanone with improved sample stability. Collection of air samples on Ambersorb XE-348, a slightly polar type of carbonaceous molecular sieve material, results in improved storage stability of acetone, 2-butanone, methyl isobutyl ketone, cyclohexanone, and isophorone (Ref. 5.2). Pretreatment of coconut shell charcoal with hydroquinone has been shown to slightly improve the stability of cyclohexanone upon storage (Ref. 5.3).

Carbosieve S-III (Supelco, Inc., Bellefonte, PA) was used in this evaluation for the collection of acetone. This material is a carbonaceous molecular sieve adsorbent similar to the Ambersorb XE-347 and XE-348. The stability of acetone collected on this adsorbent is superior to that observed with coconut shell charcoal (Section 4.5) and comparable with Ambersorb XE-348 (Ref. 5.2). The sampling capacity of Carbosieve S-III for acetone is greater than both coconut shell or petroleum-based charcoal. It is also greater than that of Ambersorb XE-347, Ambersorb XE-348, and Purasieve, which is a synthetic carbon-based material manufactured by Union Carbide (Section 4.10).

Occupational exposures to acetone alone are uncommon. Typically acetone is used with other solvents. It would be advantageous if Carbosieve S-III could be used to collect a variety of other solvents simultaneously with acetone. The sample capacities of Carbosieve S-III for some common solvents have been found to equal or exceed that of coconut shell charcoal (Section 4.10). Common ketones and some esters which are known to be unstable when collected on charcoal are also excellent candidates for evaluation with Carbosieve S-III (Ref. 5.3.).

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

Acetone is a relatively non-toxic solvent. An oral LD_{50} of 10.7 mL/kg in the rat has been reported. Inhalation of the vapor may produce headaches, fatigue, excitement, and bronchial irritation. (Ref. 5.8) High vapor concentrations will produce anesthesia. There are no confirmed reports of serious effects produced from chronic exposure to low levels of acetone. Prolonged or repeated skin exposure can dry and defat the skin and lead to dermatitis. Direct contact of acetone with the eye may produce temporary corneal injury. (Ref. 5.9)

1.1.3 Workplace exposure

Acetone is used as a chemical intermediate and solvent. In 1986, approximately 1.94 billion pounds of acetone were produced in the United States (Ref. 5.10). Approximately one-third of the total amount produced in the United States is used as an intermediate in the production of methacrylates via the acetone cyanohydrin process (Ref. 5.9). Another 15% is used as a solvent for vinyl or acrylic resins, alkyd paints, varnishes and lacquers, oils, waxes, plastics, and rubber cements. Approximately 20% of the total U.S. acetone production is used to produce a variety of common solvents. Methyl isobutyl ketone, methyl isobutyl carbinol, mesityl oxide, hexylene glycol, and isophorone are all derived from reactions in which the initial step involves the self condensation of acetone (Ref. 5.9). Acetone is also used as a chemical intermediate in the production of Bisphenol A, as a

solvent and chemical intermediate in the pharmaceutical industry, and as a solvent in the processing of cellulose acetate.

1.1.4 Physical properties (Ref. 5.9 unless otherwise noted)

CAS no.:	67-64-1
molecular weight:	58.08
appearance:	colorless liquid
odor:	pungent, aromatic-like
melting point:	-123.5°C
boiling point at 1 atm:	56.1°C
vapor pressure at 20°C:	24.7 kPa (185 mm Hg)
specific gravity: (at 20°C relative to water at 4°C)	0.783
solubility:	miscible with water, alcohols, chloroform, ether, and most oils (Ref. 5.8)
flash point (closed cup):	-18°C
autoignition temperature:	538°C
flammable (explosive) limits: (% by volume in air)	lower 2.1 upper 13
synonyms:	2-propanone, dimethyl-ketone, beta-keto-propane, pyroacetic acid
formula:	CH_3COCH_3

The analyte air concentrations throughout this method are based on the recommended sampling and analytical parameters. Air concentrations listed in ppm are referenced to 25°C and 760 mm Hg.

1.2 Limit defining parameters

1.2.1 Detection limit of the analytical procedure

The detection limit of the analytical procedure is 0.71 ng per injection. This is the amount of analyte which is readily detectable in the presence of the solvent front. (Section 4.1.)

1.2.2 Detection limit of the overall procedure

The detection limit of the overall procedure is 14.1 µg per sample (2.0 ppm or 4.7 mg/m^3). This is the amount of acetone spiked on the sampling device which allows recovery of an amount of analyte equivalent to the detection limit of the analytical procedure. (Section 4.2)

1.2.3 Reliable quantitation limit

The reliable quantitation limit is 14.1 µg per sample (2.0 ppm or 4.7 mg/m^3). This is the smallest amount of analyte which can be quantitated within the requirements of a recovery of at least 75% and a precision (±1.96 SD) of ±25% or better. (Section 4.3)

The reliable quantitation limit and detection limits reported in the method are based upon optimization of the instrument for the smallest possible amount of the analyte. When the target concentration of the analyte is exceptionally higher than these limits, they may not be attainable at the routine operating parameters.

1.2.4 Instrument response to the analyte

The instrument response over the concentration range of 0.5 to 2 times the target concentration is linear. (Section 4.4)

1.2.5 Recovery

The recovery of acetone from samples used in a storage test was equal to or greater than 86.7% when the samples were stored at about 23°C over a 17-day storage period. This value is determined from the equation of the regression line of the graphed storage data, at the 17th day, for ambient storage of samples collected at high relative humidity (Section 4.5). The recovery of the analyte from the collection medium during storage must be 75% or greater.

1.2.6 Precision (analytical procedure)

The pooled coefficient of variation obtained from replicate determinations of analytical standards at 0.5, 1 and 2 times the target concentration is 0.018. (Section 4.6)

1.2.7 Precision (overall procedure)

The precision at the 95% confidence level for the 17-day ambient temperature storage test is ±14.6% (Section 4.7). This includes an additional ±5% for sampling error. The overall procedure must provide results at the target concentration that are ±25% or better at the 95% confidence level.

1.2.8 Reproducibility

Six samples collected from a test atmosphere and a draft copy of this procedure were given to a chemist with this evaluation. The samples were analyzed after 59 days of storage at 5°C. No sample deviated from its theoretical value by more than the precision reported in Section 1.2.7. (Section 4.8)

1.3 Advantages

This sampling method has a higher sampling capacity and results in improved storage stability for acetone over the existing coconut shell charcoal method.

1.4 Disadvantages

1.4.1 The Carbosieve S-III sampling tubes are slightly more expensive than coconut shell charcoal sampling tubes.

1.4.2 The fine mesh size of Carbosieve S-III (60/80) results in a greater pressure drop across the sample tube than occurs with the conventional coconut shell charcoal sampling tube. At a sampling rate of 0.2 L/min the pressure drop across the tube is 10 in. of water.

2. Sampling Procedure

2.1 Apparatus

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

2.1.2 Samples are collected on 4-mm i.d. x 6-mm o.d. × 45-mm sampling tubes packed with two sections of 60/80 mesh Carbosieve S-III (Supelco Inc., Bellefonte, PA). Empty, clean glass tubes are packed with 130 and 65 mg of adsorbent in the front and back sections respectively. Silanized glass wool plugs are used in the middle and at both ends of the tube to separate and contain the two sections. The sampling tubes are sealed with 7/32-in. plastic caps.

2.1.3 Commercially produced sampling tubes are expected to be available by the spring of 1988.

2.2 Reagents

No sampling reagents are required.

2.3 Sampling technique

2.3.1 Attach the sampling tube to the sampling pump with flexible, plastic tubing such that the large, front section of the sampling tube is exposed directly to the atmosphere. Do not place any tubing in front of the sampler. The sampler should be attached vertically in the worker's breathing zone in such a manner that it does not impede work performance or safety.

2.3.2 After sampling for the appropriate time, remove the sampling device and seal the tube with plastic end caps. Wrap the tube lengthwise with an official OSHA seal (Form 21).

2.3.3 Submit at least one blank with each set of samples. The blank should be handled in the same manner as the other samples except that no air is drawn through it.

2.3.4 List any potential interferences on the sample data sheet.

2.4 Sampler capacity

The sampling capacity of the front section of a Carbosieve S-III sampling tube was determined by sampling a test atmosphere of 3920 mg/m^3 (1650 ppm) acetone at ambient temperature at both low (<5% R.H.), and at high relative humidity (80% R.H.). The sampling rate was approximately 0.05 L/min. The 5% breakthrough air volume was 4.6 L at 80% R.H., and 13.1 L at low humidity (<5% R.H.). These are the air volumes sampled that result in a concentration downstream from the sampling tube which is 5% of the upstream concentration. (Section 4.10)

2.5 Desorption efficiency

2.5.1 No significant difference in desorption efficiency was observed for acetone spiked onto "dry" or "wet" adsorbent when the samples were desorbed as prescribed in the method using anhydrous magnesium sulfate. The average desorption efficiency for acetone from "dry" Carbosieve S-III over the range of 0.5 to 2.0 times the target concentration was 97.5%. The average desorption efficiency from Carbosieve S-III which was first conditioned with 3.0 L of 80% R.H. air prior to spiking with acetone was 99.4% at the target concentration. Because these values do not differ significantly, the desorption efficiency correction factor determined from spiking dry Carbosieve S-III, 97.5%, is used for this method.

The necessity of desorbing samples in the presence of anhydrous magnesium sulfate is evidenced by the desorption efficiency value for acetone from "wet" Carbosieve S-III obtained without the addition of anhydrous magnesium sulfate. The average desorption efficiency under these conditions was only 88.0%. (Section 4.11)

2.5.2 Desorbed samples remain stable for at least 24 h. (Section 4.9)

2.6 Recommended air volume and sampling rate

The recommended air volume is 3 L and the recommended sampling rate is 0.05 L/min.

2.7 Interferences (sampling)

Substances present in the work atmosphere which are capable of reacting with acetone can affect the recovery. The presence of other solvents in the work atmosphere will affect the capacity of the sampling medium for acetone. Suspected interferences should be reported to the laboratory with submitted samples.

2.8 Safety precaution (sampling)

2.8.1 The sampling equipment should be attached to the worker in such a manner that it will not interfere with work performance or safety.

2.8.2 All safety practices that apply to the work area being sampled should be followed.

3. Analytical Procedure

3.1 Apparatus

3.1.1 A GC equipped with an FID detector. A Hewlett-Packard Model 5840A GC and a Varian Model 3400 GC were used in this evaluation. Both instruments were equipped with autosamplers. A Spectra-Physics Model 4290 Integrator (Spectra-Physics, San Jose, CA) was used to integrate data from the Varian GC.

3.1.2 A GC column capable of separating acetone from the solvent and from any interferences. A 10-f t × 1/8-in. stainless steel column packed with 20% SP-2100/0.1% Carbowax 1500 on 100/120 Supelcoport (Supelco Inc., Bellefonte, PA) was used with the HP Model 5840A GC. A 60-m × 0.32-mm i.d. fused silica capillary column, DX-4, 0.25-µm film thickness (J & W Scientific, Folsom, CA), was used with the Varian GC.

3.1.3 Autosampler vials with a minimum internal volume of 1.8 mL. Glass crimp-top vials for use with Hewlett-Packard autosamplers were used in this evaluation.

3.1.4 Volumetric flasks, pipets, and syringes for preparing desorbing solution and standards were used in this evaluation.

3.1.5 A 1-mL dispenser for adding desorbing solution to the sample vials was used in this evaluation.

3.2 Reagents

3.2.1 Reagent grade solvents or better were used in this evaluation. Burdick and Jackson (Muskegon, MI) acetone and dimethylformamide (DMF) were used.

3.2.2 Desorbing solution. One percent DMF in carbon disulfide containing 1 µL/mL ethylbenzene as an internal standard was used in this evaluation. The DMF acts as a polar modifier to improve the recovery of polar molecules.

3.2.3 Magnesium sulfate, anhydrous powder, for use as a drying agent. Baker analyzed reagent (Baker Chemical Co., Phillipsburg, NJ).

3.3 Standard preparation

3.3.1 Prepare standards in the PEL range by spiking microliter quantities of acetone from a microliter syringe directly into autosampler vials which contain 1 mL of the desorbing solution. Seal each vial with a crimp cap seal.

3.3.2 Prepare low level standards by making serial dilutions of a higher standard into the desorbing solution.

3.3.3 Prepare at least three standards to generate a calibration curve. Ensure that the amount of acetone found in the samples is within the range of the standards. Prepare additional standards if necessary.

3.4 Sample preparation

3.4.1 Remove the plastic caps from the sample tube and carefully transfer each section of the adsorbent to separate auto-sampler vials. Include the front glass wool plug with the front adsorbent section and the middle glass wool plug with the back sample section. Discard the rear glass wool plug.

3.4.2 Add approximately 100 mg of anhydrous magnesium sulfate powder to each sample. The use of this drying agent dramatically improves the recoveries of water soluble substances which apparently partition in the water phase and result in low recoveries (Ref. 5.7). The desorption efficiency of acetone on "wet" Carbosieve S-III at the target concentration is 88% without magnesium sulfate and 99% with magnesium sulfate added (Section 4.11).

3.4.3 Carefully add 1.0 mL of desorbing solution to each vial and seal with a crimp top.

3.4.4 Place the sample vials on a mechanical shaker and shake for 15 min prior to analysis.

3.5 Analysis

3.5.1 GC Conditions (HP Model 5840A)

column temperatures:	60°C for 4 min, then program to 150°C at 15°C/min, hold at 150°C for 4 min
injector temperature:	200°C
detector temperature:	220°C
carrier flow rate:	25 mL/min (nitrogen)
detector gas flow rates:	25 mL/min (hydrogen) 250 mL/min (air)
injection volume:	1.0 µL
GC column:	10 ft × 1/8 in. stainless steel column packed with 20% SP-2100/0.1% Carbowax 1500 on 100/120 Supelcoport
retention time:	3.0 min
chromatogram:	Figure 3.5.1

3.5.2 GC Conditions (Varian Model 3400):

column temperatures:	40°C for 4 min, then program to 150°C at 20°C/min
injector temperature:	175°C
detector temperature:	200°C
carrier flow rate:	2.2 mL/min (hydrogen)
Detector gas flow rates:	30 mL/min (hydrogen) 300 mL/min (air)
detector make-up gas:	30 mL/min (nitrogen)
injection volume:	1.0 µL
split ratio:	20 to 1
GC column:	60-m × 0.32-mm i.d. fused silica capillary column, DX-4, 0.25-µm film
retention time:	2.67 min
chromatogram:	Figure 3.5.2

3.5.3. Use a suitable method, such as electronic integration to measure detector response. Prepare an internal standard procedure on the integrator using ethylbenzene as the internal standard.

3.6 Interferences (analytical)

3.6.1 Ensure that potential interferences reported by the industrial hygienist do not interfere with the analysis.

3.6.2 Modify GC parameters to circumvent these interferences if possible.

3.6.3 Retention time on a single column is not proof of chemical identity. GC/MS is a useful means of structure determination. It is recommended that this procedure be used to confirm samples whenever necessary.

3.7 Calculations

3.7.1 Prepare a calibration curve by plotting concentration of acetone determined versus actual concentration for each standard value. A linear least squares fit is used to determine the concentration of acetone in each sample. Use this curve to determine the concentration of acetone in each sample.

3.7.2 If acetone is detected in the back section, sum the concentrations of the front and back sections and subtract any significant amounts found in the blank from this total.

3.7.3 Calculate the air concentration for each sample using the following equation:

$$mg/m^3 = (A)(B)/(C)(D)$$

where A = µg/L from 3.7.2
B = desorption volume (1 mL)
C = liters of air sampled
D = desorption efficiency (97.5%)

3.7.4 Convert acetone results in mg/m^3 to ppm using the following equation:

$$ppm = (mg/m^3)(24.46)/(58.08)$$

where mg/m^3 = result from 3.7.3
24.46 = molar volume at 760 mm Hg and 25°C
58.08 = molecular weight of acetone

3.8 Safety precautions (analytical)

3.8.1 Avoid skin contact and inhalation of all chemicals.

3.8.2 Restrict the use of all chemicals to a fume hood.

3.8.3 Wear safety glasses and a lab coat in all laboratory areas.

4. Backup Data

4.1 Detection limit of the analytical procedure

The detection limit of the analytical procedure was 0.71 ng based on a 1-µL injection of a 14.1 ng/µL standard with a 20 to 1 split ratio. This was the amount of acetone which gave a peak that was readily detectable in the presence of the solvent. A chromatogram of the detection limit of the analytical procedure is shown in Figure 4.1.

4.2 Detection limit of the overall procedure

The detection limit of the overall procedure was determined by analyzing the front sections of sample tubes placed in separate autosampler vials and spiked with 14.1 µg of acetone (4 µL of 3532 µg/mL acetone in carbon disulfide). The samples were desorbed and analyzed approximately 1 h after having been spiked. The injection size recommended in the analytical procedure (1.0 µL) was used in the determination of the detection limit of the overall procedure.

Table 4.2
Detection Limit Data

sample no.	amount spiked (µg)	amount recovered (µg)
1	14.1	11.8
2	14.1	14.1
3	14.1	14.4
4	14.1	14.2
5	14.1	13.7
6	14.1	13.0

4.3 Reliable quantitation limit

The reliable quantitation limit is equal to the overall detection limit. This is the smallest amount of acetone which can be spiked onto the sample tube and result in a recovery of at least 75% and a precision (±1.96 SD) of 25% or better.

Table 4.3
Reliable Quantitation Limit Data
(Based on Samples and Data of Table 4.2)

sample no.	% recovered	statistics
1	83.7	
2	100.0	$\bar{X}$=96.0
3	102.1	SD=7.0
4	100.7	Precision=(1.96)(SD)
5	97.2	Precision=13.9
6	92.2	

4.4 Instrument response to the analyte

The instrument response data reported in this section was determined with the Varian Model 3400; however, a linear response was observed with both instruments used in this evaluation. Analytical conditions were as described in Section 3.5.2. The data presented in Table 4.4. was determined from replicate injections of acetone standards at the 0.5, 1, and 2 times the target concentration. This data is presented graphically in Figure 4.4.

Table 4.4
Acetone Response Data

× target conc	0.5×	1×	2×
µg/sample	3564	7128	14256
ppm	500	1000	2000
area counts	167215	325560	641727
	169948	326024	644136
	169919	324601	660824
	168368	335219	661558
	173239	331389	644165
	176433	325590	673745
$\bar{X}$	170854	328064	654359

4.5 Storage test

The stability of acetone collected on Carbosieve S-III sample tubes from a 1000 ppm test atmosphere at both low (5%) and high (80%) relative humidity was determined. Acetone stability on coconut shell charcoal tubes (Lot 120, SKC Inc., Eighty-four, PA) was also evaluated at 80% R.H. Test atmospheres were generated with a vapor generation system which consisted of a source of clean, dry dilution air, a mixing chamber, and a six port sampling manifold. The interior surfaces of the system consisted entirely of glass and Teflon with the exception of rubber 0-rings at the valve positions. Acetone was metered into the dilution stream with a Sage Instruments Inc. Model 355 syringe pump (Orion Research Inc., Cambridge, MA) which had been gravimetrically calibrated.

High humidity conditions were prepared by passing the dilution air through a water bubbler before combining it with acetone. For low humidity sampling, the water bubbler was bypassed and the dry dilution air mixed directly with the acetone vapor. Air flow was measured with rotameters and mass flow meters which were calibrated with a Gilibrator bubble meter (Gilian Instrument Corp., Wayne, NJ). The relative humidity was monitored with a Model 911 Dew-All Digital Analyzer (EG&G, Waltham, MA).

For each storage test a total of 36 samples were collected under each set of conditions by sampling approximately 3 L of air at a flow rate of approximately 0.05 L/min from the test atmosphere. Six of these samples were analyzed on the day of collection. The remaining 30 samples were split into two groups of fifteen samples for storage. One group was stored in a laboratory drawer at ambient temperature (21-23°C), and the other group was stored in a refrigerator at 5°C. At three- or four-day intervals, three samples were selected from each group of storage samples for analysis. The percentage recovery with time for each sample is reported in Tables 4.5.1 through 4.5.3. These results are presented graphically in Figures 4.5.1.1 through 4.5.3.2. The reported recoveries are based on the theoretical concentration of the acetone test atmosphere determined by gravimetric and volumetric means. No desorption efficiency correction was applied to these results.

Table 4.5.1
Storage Test on Carbosieve S-III (5% RH)

storage time (days)	% recovery (ambient)			% recovery (refrigerated)		
0	94.4	94.7	93.6	93.3	93.9	93.2
3	91.3	95.7	91.3	91.1	91.7	92.6
7	92.7	94.1	94.3	94.9	93.0	93.0
10	89.4	91.6	91.4	90.8	91.6	91.4
14	93.9	94.5	91.8	95.9	92.1	93.1
17	89.6	88.0	94.6	90.9	94.5	90.0

Table 4.5.2
Storage Test on Carbosieve S-III (80% RH)

storage time (days)	% recovery (ambient)			% recovery (refrigerated)		
0	101.3	104.4	107.5	110.0	107.2	103.5
3	92.8	100.4	102.7	94.7	104.5	101.9
7	88.1	88.2	90.9	98.7	99.6	97.5
10	80.9	96.9	88.7	97.0	91.4	99.9
14	91.6	100.3	86.9	78.4	94.0	94.2
17	98.9	82.8	86.6	96.2	92.8	86.0

Table 4.5.3
Storage Test on Coconut Shell Charcoal (80% RH)

storage time (days)	% recovery (ambient)			% recovery (refrigerated)		
0	100.0	96.2	98.1	96.8	96.2	95.9
3	77.3	73.4	76.1	96.9	97.8	85.7
7	70.9	79.0	74.1	89.9	88.1	85.7
10	66.3	69.5	70.4	85.8	86.4	90.4
14	55.2	59.5	72.6	79.8	89.9	84.5
17	52.5	55.3	56.6	83.1	83.7	80.9

4.6 Precision (analytical method only)

The data reported in Table 4.4 were used to calculate analytical precision.

Table 4.6
Precision of the Analytical Method
(Based on the Data of Table 4.4)

× target concn	0.5×	1×	2×
µg/sample	3564	7128	14256
ppm	500	1000	2000
SD[1]	3404	4261	12942
CV	0.020	0.013	0.020
$\overline{CV}$	0.018		

[1]standard deviation is in area counts

4.7 Precision (overall procedure)

The precision of the overall procedure is determined from the storage data. The determination of the standard error of estimate (SEE) for a regression line plotted through the graphed storage data allows the inclusion of storage time as one of the factors affecting overall precision. The SEE is similar to the standard deviation, except it is a measure of dispersion of data about a regression line instead of about a mean. It is determined with the following equation:

$$SEE = \sqrt{\frac{\sum(Y_{obs} - Y_{est})^2}{n - k}}$$

where

n = total number of data points
k = 2 for linear regression
k = 3 for quadratic regression
Y_{obs} = observed % recovery at a given time
Y_{est} = estimated % recovery from the regression line at the same given time

An additional 5% for pump error is added to the SEE by the addition of variances. The precision at the 95% confidence level is obtained by multiplying the SEE (with pump error included) by 1.96 (the z-statistic from the standard normal distribution at the 95% confidence level). The 95% confidence intervals are drawn about their respective regression lines in the storage graphs. The 95% confidence limits for this method are ±16% as shown in Figure 4.5.2.1. This value is determined from the ambient storage data for samples collected at high relative humidity.

4.8 Reproducibility data

Reproducibility samples were prepared from test samples collected from the vapor generation system. The samples and a draft copy of this evaluation were given to a chemist unassociated with this evaluation. The samples were analyzed after 59 days of storage at refrigerated temperature. No sample deviated from its theoretical value by more than the precision (±16.0%) for the method at the 95% confidence level for the 17-day storage test (Section 4.5).

Table 4.8
Reproducibility Results

sample number	µg expected	% of expected	% deviation
1	3297	105.9	36.2
2	3401	105.2	
3	5085	106.4	
4	5220	115.8	
5	6783	95.0	
6	6892	107.9	

4.9 Stability of desorbed samples

The stability of desorbed samples was investigated by reanalyzing samples 24 h after initial analysis. The sample vials were resealed with new septa and reanalyzed with fresh standards. The average recovery, relative to the average recovery of the original analysis, was 93.4%.

Table 4.9
The Stability of Desorbed Samples

sample number	initial recovery (percent)	recovery after 24 h (percent)	percent change
1	101.5	89.0	-11.5
2	91.9	84.5	-7.5
3	82.1	76.3	-5.8
4	85.9	82.0	-3.9
5	97.8	91.2	-6.6
6	92.6	92.8	+0.2
$\overline{X}$	92.0	86.0	
SD	7.2	6.2	

4.10 Sampler capacity

The capacity of Carbosieve S-III for acetone was compared to the capacity of other adsorbents by sampling from an atmosphere of 1650 ppm (3920 mg/m^3) acetone. Sample capacity was determined by sampling with the front section of an adsorbent tube at a sampling rate of 0.05 L/min. Breakthrough was detected by monitoring the concentration of acetone downstream from the sampling tube with a gas chromatograph equipped with a gas sampling valve. The GC was equipped with a 10-ft × 1/8-in. o.d. stainless steel column packed with 10% SP-1000 on 80/100 mesh Supelcoport. The injector, oven, and detector temperatures were 150°C, 100°C, and 200°C respectively. Nitrogen carrier gas was 20 mL/min, hydrogen and air detector gases were 30 mL/min and 250 mL/min respectively.

Five-percent breakthrough air volumes from the 1650 ppm acetone test atmosphere at both low and high relative humidity are reported in Table 4.10.1 for a variety of adsorbents. The 5% breakthrough air volumes for acetone on Carbosieve S-III at high and low relative humidity are 4.6 and 13 L respectively. Coconut shell charcoal has a lower capacity for acetone. The 5% breakthrough air volumes for coconut shell charcoal at high and low relative humidity are 2.4 and 4.5 L respectively.

Breakthrough air volumes for acetone and eight other solvents were determined simultaneously at a sampling rate of 0.05 L/min with both Carbosieve S-III and with coconut shell charcoal at high relative humidity from a test atmosphere mixture and are reported in Table 4.10.2. The total concentration of the mixture was 4420 mg/m^3 of which the concentration of the acetone component was 400 mg/m^3 (170 ppm). Using the chromatography conditions described above for acetone, all nine components in the test atmosphere were resolved on the column and their 5% breakthrough air volumes determined. The sampling capacity of Carbosieve S-III for xylene, perchloroethlylene, toluene, n-butanol, butyl acetate, and methyl isobutyl ketone is approximately equal to or greater than that of coconut shell charcoal. Carbosieve S-III has a higher sampling capacity for the volatile solvents acetone, methylene chloride, and isopropanol. Surprisingly, isophorone (3,5,5-trimethyl-2-cyclohexene-1-one) did not collect on Carbosieve S-III. This relatively high-molecular-weight solvent was apparently excluded from the micropores of Carbosieve S-III because of its size and was therefore not collected.

Table 4.10.1
Sampling Capacity of Various Adsorbents
for Acetone at a Concentration of 1650 ppm (3920 mg/m^3)

adsorbent (mass used)	description	% relative humidity	5% break-through (L)
Puraseive (130 mg)	Union Carbide, carbon-based polymer	80	3.2
coconut shell charcoal (100 mg)	SKC Inc., lot 120	<5	4.5
coconut shell charcoal (100 mg)	SKC Inc., lot 120	80	2.4
petroleum base charcoal (100 mg)	SKC Inc., lot 104	80	1.7
Ambersorb XE-348 (130 mg)	Rohm&Haas, carbon-based molecular sieve	80	2.9
Carboxen 564 (130 mg)	Rohm&Haas, carbon-based molecular sieve	80	2.4
Carbosieve S-III (130 mg)	Rohm&Haas, carbon-based molecular sieve	<5	13
Carbosieve S-III (130 mg)	Rohm&Haas, carbon-based molecular sieve	80	4.6

Table 4.10.2
Sampling Capacity of Carbosieve S-III (130 mg) and Coconut Shell Charcoal (100 mg) from Test Atmosphere Containing Nine Solvents at 80% RH

		air	5% breaktrough volume, (L)	
solvent	PEL (ppm)	concentration (ppm)	lot 120 charcoal	Carbosieve S-III
acetone	1000	170	4.7	8.6
isopropanol	400	160	6.8	9.5
methylene chloride	500	190	3.0	4.6
meethyl isobutyl ketone	100	85	10.2	10.4
perchloroethylene	100	120	10.2	12.7
toluene	200	120	10.3	13.0
xylene	100	100	21.5	>22.5
butyl acetate	150	100	14.8	12.9
n-butanol	100	140	10.6	11.1

4.11 Desorption efficiency

The average desorption efficiency of acetone from Carbosieve S-III evaluated at both low and high relative humidity conditions was determined. To represent low humidity conditions, the desorption efficiency of acetone on Carbosieve S-III was determined with "dry" adsorbent at 0.5, 1, and 2 times the target concentration. Six samples were prepared at each level and each 130-mg section of adsorbent was spiked with either 4.5, 9.0, or 18.0 µL of acetone and allowed to sit for approximately 1 h prior to desorption. The results for the "dry" Carbosieve S-III are given in Table 4.11.1.

To represent high humidity conditions, the desorption efficiency of "wet" adsorbent was determined at the target concentration alone with adsorbent which had been conditioned with approximately 3 L of 80% R.H. prior to spiking with acetone. The average desorption efficiencies of "wet" Carbosieve S-III desorbed with and without 100-mg portions of magnesium sulfate are given in Table 4.11.2. The necessity of using magnesium sulfate to desorb "wet" adsorbent is indicated by the low desorption efficiency result (88.0%) obtained by desorbing the samples without magnesium sulfate.

Table 4.11.1
Desorption Efficiency of Acetone on “Dry” Carbosieve S-III

× target concn µg/sample	0.5× 3548	1× 7064	2× 14004
desorption effeciency, %	99.6	97.9	95.7
	101.8	94.9	96.9
	100.8	101.4	96.8
	99.7	94.8	98.9
	98.2	92.3	98.6
	99.4	93.7	92.8
$\overline{X}$	99.9	95.8	96.6
overall ave	97.5		

Table 4.11.2
Desorption Efficiency of Acetone[1] from “Wet” Carbosieve S-III

magnesium sulfate	absent	present
desorption efficiency, %	87.0	98.6
	88.7	100.6
	88.7	98.3
	89.0	101.0
	87.2	98.8
	87.3	98.5
$\overline{X}$	88.0	99.3

[1] at 1× the target concn (7064 µg)

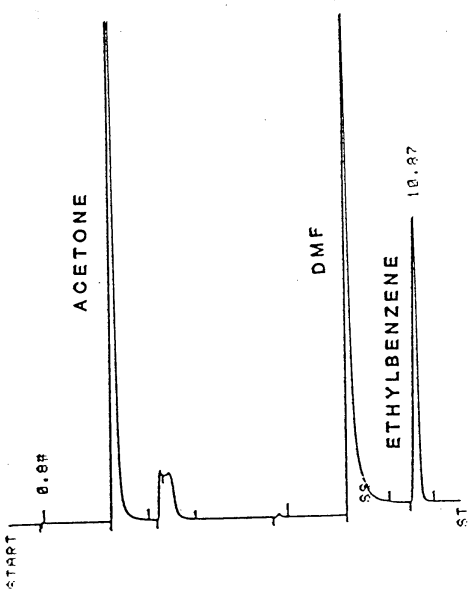

Figure 3.5.1. Chromatogram of acetone at the target level on packed column. Conditions are as described in Section 3.5.1.

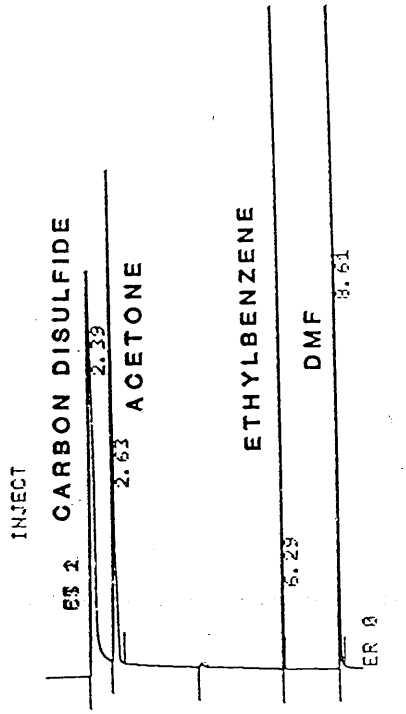

Figure 3.5.2. Chromatogram of acetone at the target level on a capillary column. Conditions are described in Section 3.5.2.

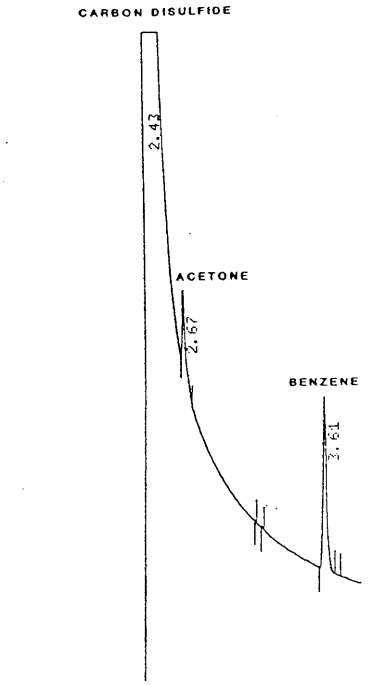

Figure 4.1. Chromatogram of acetone at the detection limit on a capillary column. Conditions are as described in Section 3.5.2.

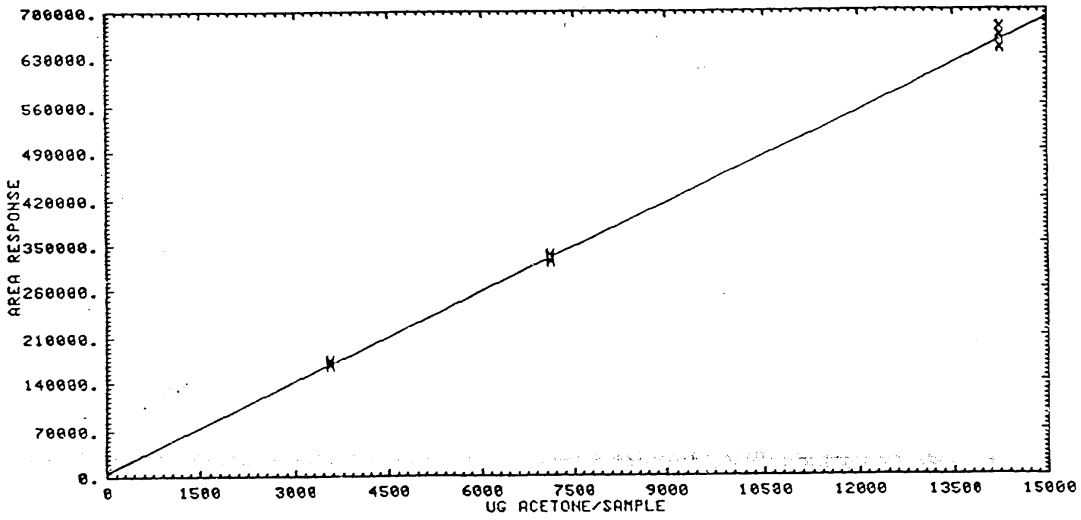

Figure 4.4. Instrument response (FID) to acetone.

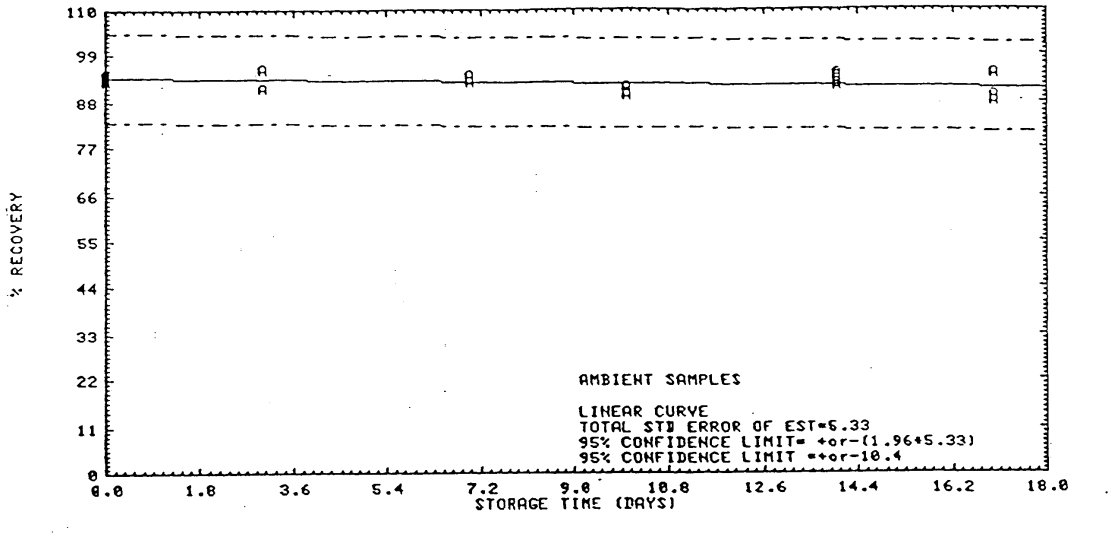

Figure 4.5.1.1. Acetone collected on Carbosieve S-III at 5% R.H. and stored at ambient temperature.

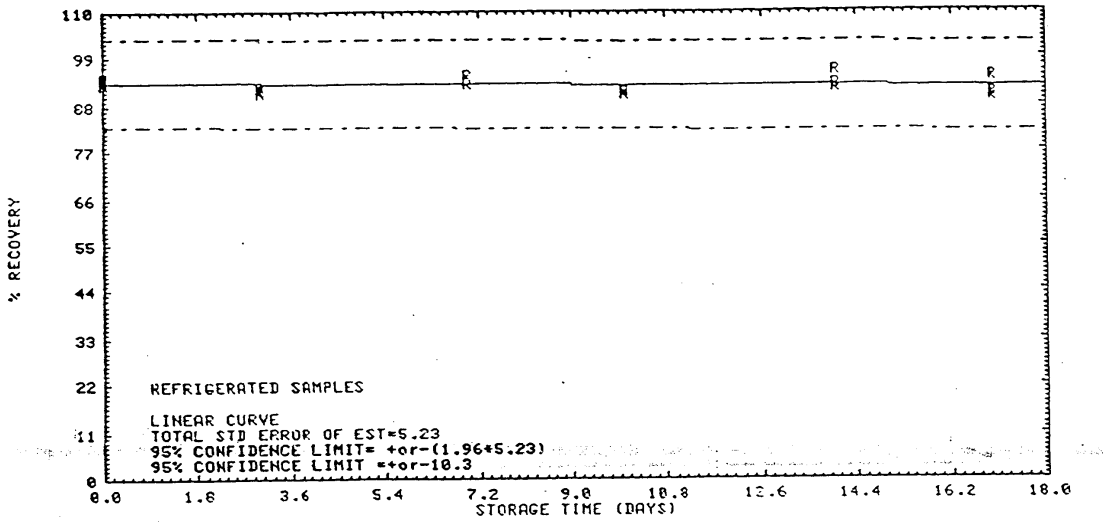

Figure 4.5.1.2. Acetone collected on Carbosieve S-III at 5% R.H. and stored at refrigerated temperature.

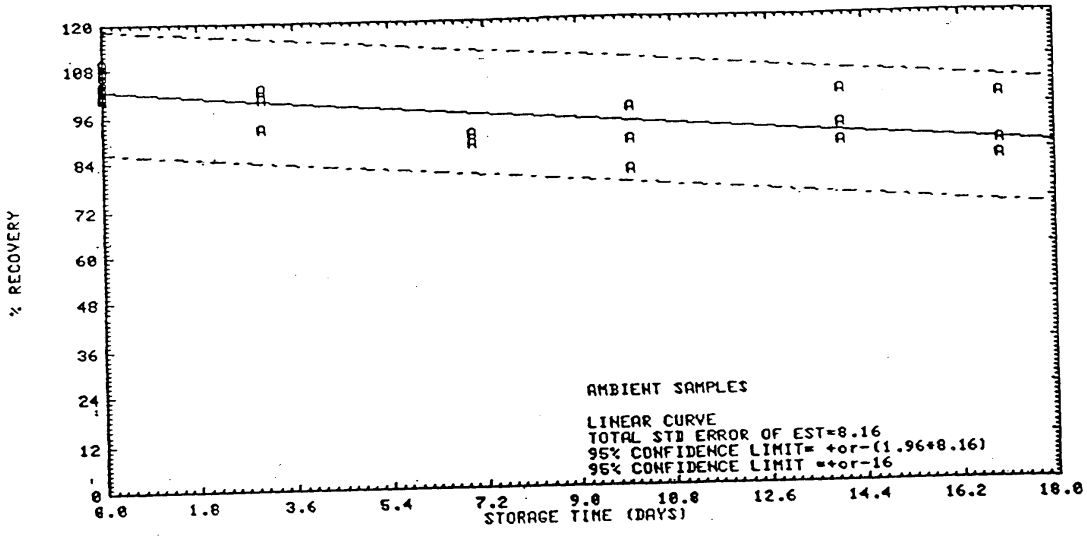

Figure 4.5.2.1. Acetone collected on Carbosieve S-III at 80% R.H. and stored at ambient temperature.

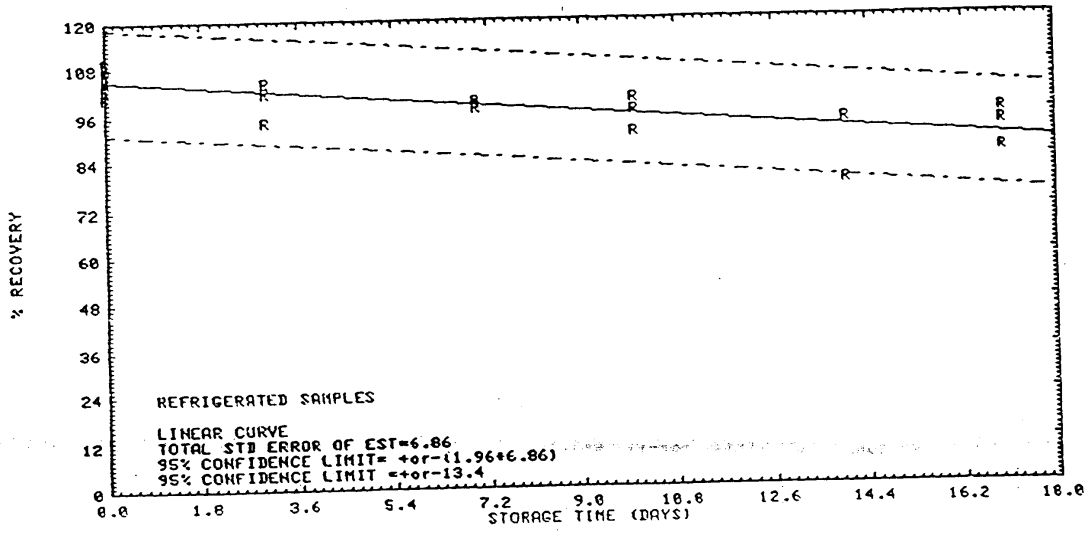

Figure 4.5.2.2. Acetone collected on Carbosieve S-III at 80% R.H. and stored at refrigerated temperature.

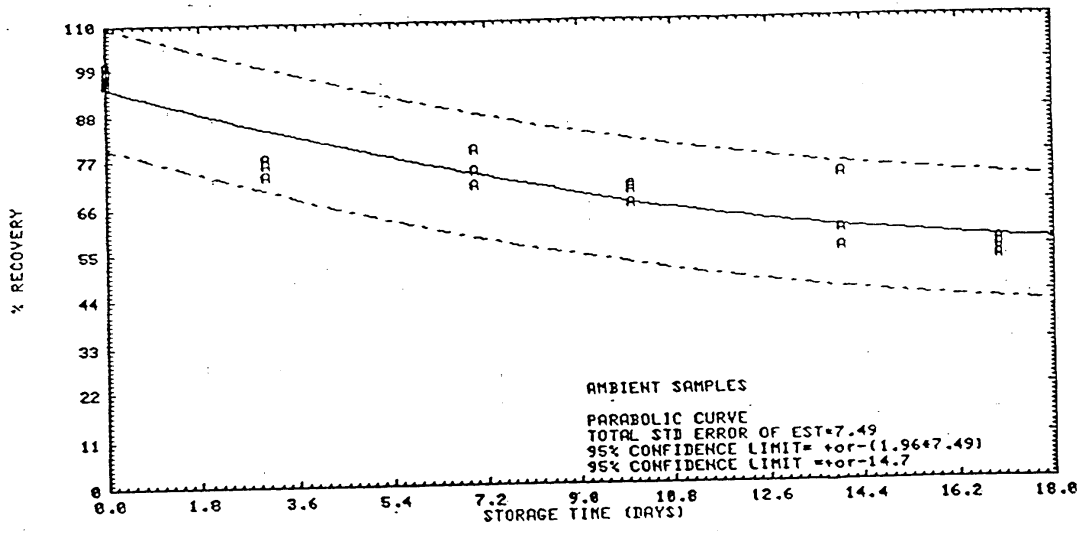

Figure 4.5.3.1. Acetone collected on coconut shell charcoal at 80% R.H. and stored at ambient temperature.

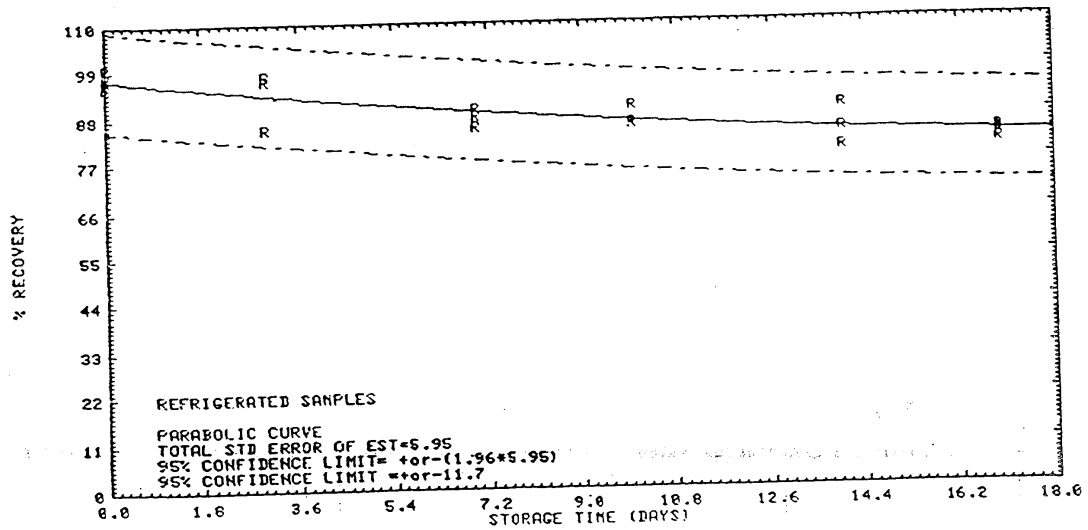

Figure 4.5.3.2. Acetone collected on coconut shell charcoal at 80% R.B. and stored at refrigerated temperature.

5. References

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