Method number:	PV2182
Control number:	T-PV2182-01-8208-CH
Target concentration:	0.05 ppm (0.3 mg/m^3)
Procedure:	Samples are collected by drawing a known volume of air through a silica gel tube. Samples are desorbed with ethanol and analyzed by High Pressure Liquid Chromatography (HPLC) using an ultra violet (UV) detector.
Recommended air volume and sampling rate:	100 minutes at 0.1 Lpm (10 L)
Status of method:	Partially validated method. 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

The OSHA Analytical Laboratory recently received a set of field samples that required analysis for alpha-Chloroacetophenone. The air samples had been collected on charcoal tubes, (SKC, Inc. Lot 107). Desorption studies were done on charcoal tubes using acetone, carbon disulfide, 5% IPA in carbon disulfide, and methylene chloride as desorbing solvents, but no detectable amount of alpha-Chloroacetophenone could be desorbed from the charcoal. This is consistent with NIOSH Failure Report No. S9 which states, "No detectable amount of alpha-Chloroacetophenone could be desorbed from charcoal using 1 mL of carbon disulfide, 5% methanol in carbon disulfide, tetrahydrofuran, methylene chloride, or acetone." The Failure Report went on to state, "Work was also performed to test the desorption efficiency of alpha-Chloroacetophenone from silica gel using ethanol as the desorbing solvent. The desorption efficiencies averaged 98%." The Failure Report further commented, "This method seems promising. However, under humid conditions, silica gel would probably not collect the analyte efficiently." The silica gel tubes were tested by the OSHA Laboratory using 10 liters of air at 85% relative humidity and appear to be a suitable method of collection for alpha-Chloroacetophenone.

1.1.2 Toxic effects

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

alpha-Chloroacetophenone can cause irritation of the eyes and skin upon contact. Vapors may cause a tingling or runny nose, burning, and/or pain of the eyes, blurred vision, and tears. Exposure to high concentrations produces mark conjunctivitis and may cause corneal damage. alpha-Chloroacetophenone, if inhaled, can cause an irritation of the lungs, burning in the chest, difficult breathing, and nausea. Pulmonary edema may occur, often delayed for some 2 hours after exposure. No chronic effects are reported (Ref. 5.1).

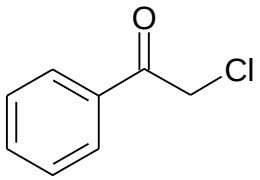
1.1.3 Potential workplace exposure

No workplace exposure level could be found in the literature but alpha-Chloroacetophenone is possibly liberated in the following processes: denaturing of industrial alcohol, as an aerosol for law enforcement and civilian protective devices, and during its manufacture (Ref. 5.1).

1.1.4 Physical properties (Ref. 5.1 and 5.2)

Synonyms:	Phenacyl chloride; Phenyl chloromethyl ketone; tear gas
Molecular weight:	154.59
Density:	1.324
Flash point:	118 ^{0}C (244 ^{0}F)
Boiling point:	247 ^{0}C (477 ^{0}F)
Melting point:	59 ^{0}C (138 ^{0}F)
Solubility:	Insoluble in water, soluble in acetone, benzene, and carbon disulfide.
Molecular formula:	$C_6H_5COCH_2Cl$

Structure:



1.2 Limit defining parameters

1.2.1 Detection limit

Detection limit of the analytical procedure is 4.5 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 Sensitivity

The sensitivity of the analytical procedure over a concentration range of 0.7176 to 3.588 µg/mL is 129646 area units per µg/mL of alpha-Chloroacetophenone. The sensitivity is determined by the slope of the calibration curve (See Figure 2).

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 with the sampler attached.

2.1.2 Silica gel tube: glass tube with ends flame sealed, 7-cm x 6-mm o.d. and 4-mm i.d., containing two sections of 20/40 mesh silica gel separated by a 2-mm portion of urethane foam. The absorbing section contains 100 mg of silica gel, the backup section 50 mg. A 3-mm portion 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

None required.

2.3 Sampling technique

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

2.3.2 Connect the tube to the sampling pump with flexible tubing. The backup section of the silica gel tubes should be positioned closest to the sampling pump.

2.3.3 The tubes should be placed in a vertical position during sampling with the open end down to minimize channeling.

2.3.4 Air being sampled should not pass through any hose or tubing before entering the silica gel tube.

2.3.5 Seal the silica gel tubes with plastic caps immediately after sampling. Seal each sample lengthwise with official Form OSHA-21 seal.

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 ends, 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 put in the same container used for the silica gel tubes.

2.4 Desorption efficiency

The average desorption efficiency from the silica gel tube spiked with 3.2 µg of alpha-Chloroacetophenone was 90.7%. The tubes were desorbed with 1 mL of ethanol and analyzed by HPLC.

Table 2.4.1
alpha-Chloroacetophenone
Desorption Efficiency

sample #	treatment	% recovered	average recovery
1	no air	90.4	
2	no air	92.0	90.7%
3	no air	89.8	

The average desorption efficiency from the silica gel tube spiked with 3.2 µg of alpha-Chloroacetophenone and shaken for one hour was 95.5%.

Table 2.4.2
alpha-Chloroacetophenone
Desorption Efficiency

sample #	treatment	% recovered	average recovery
1	no air - shaken one hour	95.6	95.5%
2		94.8	
3		94.4	
4		97.0	

2.5 Retention efficiency

Ten silica gel tubes were spiked With 3.2 µg of alpha-Chloroacetophenone. Ten liters of dry air were drawn through five of the tubes at 0.1 Lpm. Ten liters of humid air (about 85% relative humidity) were drawn through the other five tubes at 0.1 Lpm. The tubes were desorbed with 1 mL of ethanol and analyzed by HPLC.

Table 2.5
alpha-Chloroacetophenone
Retention Efficiency

sample #	treatment	% recovered	average recovery
1	10 L dry air	92.8	93.7%
2		94.7	
3		94.0	
4		95.6	
5		91.4	
6	10 L humid	88.7	90.9%
7		90.7	
8		93.4	
9		88.9	
10		92.8	

2.6 Sample storage

Four silica gel tubes were spiked with 3.2 µg of alpha-Chloroacetophenone. One tube was stored in a refrigerator for twelve days and the other three tubes were stored at ambient temperature for twelve days.

Table 2.6
alpha-Chloroacetophenone
Storage Study

sample #	days stored	treatment	% recovered	average recovery
1	12	fridge	95.2	95.2%
2	12	ambient	89.8	90.6%
3	12	ambient	92.6	
4	12	ambient	89.5	

2.7 Recommended air volume and sampling rate.

2.7.1 The recommended air volume is 10 liters.

2.7.2 The recommended sampling rate is 0.1 liters per minute.

2.8 Interferences

It is important to be aware of other components in the atmosphere which may interfere with the collection of the analyte. List any possible interference on paperwork.

2.9 Safety precautions

2.9.1 Care must be taken when opening the sealed ends of the silica gel tubes to avoid serious cuts to the hands or glass fragments in the eye.

2.9.2 Safety glasses should be worn when opening the sealed ends of the silica gel 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 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 High pressure liquid chromatograph equipped with UV detector.

3.1.2 HPLC reverse phase C_{18} analytical column. DuPont Zorbax ODS column was used for this study.

3.1.3 An electronic integrator or other suitable method to measure detector response.

3.1.4 Microliter syringe or automatic sampling device for making sample injections.

3.1.5 Volumetric flasks of convenient sizes for preparing standards.

3.1.6 Shaking device for desorption of samples.

3.2 Reagents

3.2.1 alpha-Chloroacetophenone, reagent grade

3.2.2 Ethanol, reagent grade

3.2.3 Methanol, HPLC grade

3.2.4 Water, HPLC grade

3.2.5 Phosphoric Acid, reagent grade

3.2.6 Di-n-butylamine, reagent grade

3.3 Standard preparation

3.3.1 Standard of alpha-Chloroacetophenone is prepared by weighing 16.0 mg of alpha-Chloroacetophenone into a 5-mL volumetric flask and making it to volume with ethanol.

3.3.2 A calibration curve is prepared by making dilutions of the above standard with ethanol.

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 ethanol.

3.4.3 The vials are sealed immediately and allowed to desorb with shaking for one hour.

3.5 Analysis

3.5.1 LC conditions

Column: 25-cm x 4.6-mm DuPont Zorbax ODS

Mobile phase:	60:40:0.1:0.1 Methanol/H_20/Phosphoric acid/Di-n-butylamine
Flow rate:	1.0 mL/minute
Detector wavelength:	254-nm
Injection volume:	25 uL
Retention time:	8.0 min

3.5.2 Chromatogram

See Figure 1.

3.5.3 Peak magnitude is measured by electronic integrator or other means.

3.5.4 An external standard procedure is used to prepare a calibration curve from the analysis of at least three different concentrations from two separate weighings.

3.5.5 Bracket the sample with analytical standards.

3.6 Interferences (Analytical)

3.6.1 Any collected compound that has the same HPLC retention time as alpha-Chloroacetophenone and absorbs at 254-nm is interference.

3.6.2 HPLC parameters may be varied to circumvent most interference.

3.6.3 Retention time alone is not proof of a chemical identity. Confirmation by other means should be sought when possible.

3.7 Calculations

3.7.1 The integrator value in area units for each standard is plotted against its concentration in µg/mL and a calibration curve using the best-fit straight line through the points is obtained.

3.7.2 Sample concentration is calculated from the calibration curve.

3.7.3 The air concentration of alpha-Chloroacetophenone for a sample is calculated by the following equation:

$$mg/m^3 = \frac{(\mu g/mL,\ blank\ corrected)(1\ mL,\ desorption\ volume)}{(10L,\ air\ volume)}$$

3.7.4 The equivalent ppm air concentration of samples, based on 10-liter air sample and 1 mL desorbing solution, is calculated in the following manner:

$$ppm = \frac{(\mu g/mL)(DV)(24.46)}{(L)(DE)(MW)}$$

Where:

µg/mL = concentration of analyte in sample
24.46 = Molar volume (liters/mole) at 25 °C and 760 mmHg
MW = Molecular weight (g/mole)
DV = Desorption volume, 1.0 mL
10 L = Air volume, L
DE = Desorption efficiency, decimal

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.

3.8.3 Wear safety glasses at times in laboratory area.

4 Recommendations for further study

4.1 Further work should be done on breakthrough.

4.2 Longer storage tests should be performed.

4.3 More storage tests should be performed at ambient temperature.

4.4 Desorption studies should be done from 0.5 to 2 times the PEL.

4.5 A retention study should be done at two times the PEL.

5 References

5.1 "NIOSH/OSHA Occupational Health Guidelines," September, 1978; p.1-3.

5.2 "The Condensed Chemical Dictionary," 10th ed.; Hawley, G.G., ed.; Van Norstrand Reinhold Company, New York, 1981; p. 232.

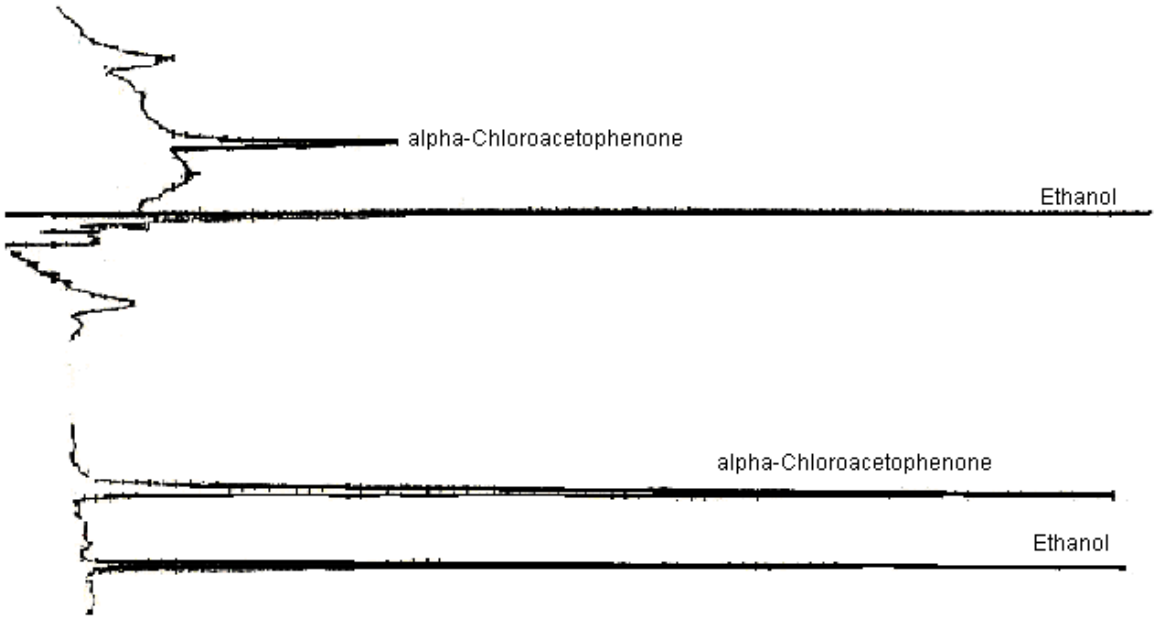


Figure 1. Chromatogram of Detection Limit Standard and a high concentration Standard

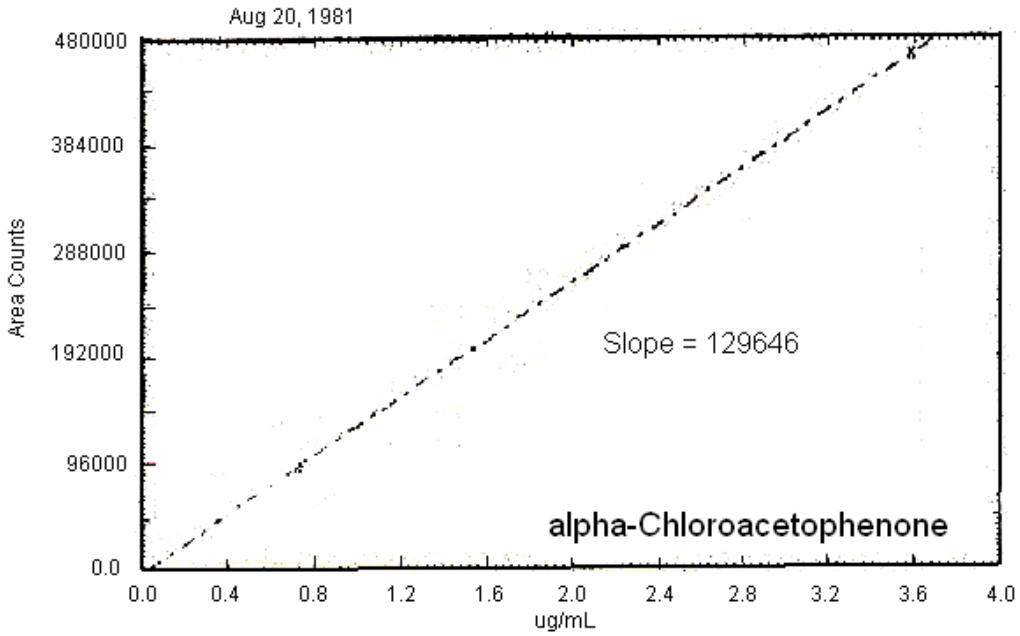


Figure 2. Calibration Curve