METHOD TO-6 Revision 1.0
September, 1986

METHOD FOR THE DETERMINATION OF PHOSGENE IN AMBIENT AIR USING HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

1. Scope

1.1 This document describes a method for determination of phosgene in ambient air, in which phosgene is collected by passage of the air through a solution of aniline, forming carbanilide. The carbanilide is determined by HPLC. The method can be used to detect phosgene at the 0.1 ppbv level.

1.2 Precision for phosgene spiked into a clean air stream is ±15-20% relative standard deviation. Recovery is quantitative within that precision, down to less than 3 ppbv. This method has been developed and tested by a single laboratory (1), and, consequently, each laboratory desiring to use the method should acquire sufficient precision and recovery data to verify performance under those particular conditions. This method is more sensitive, and probably more selective, than the standard colorimetric procedure currently in widespread use for workplace monitoring (2).

2. Applicable Documents

2.1 ASTM Standards

D1356 - Definitions of Terms Related to Atmospheric Sampling and Analysis (3).

2.2 Other Documents

Standard NIOSH Procedure for Phosgene (2).
U.S. EPA Technical Assistance Document (4).

3. Summary of Method

3.1 Ambient air is drawn through a midget impinger containing 10 mL of 2/98 aniline/toluene (by volume). Phosgene readily reacts with aniline to form carbanilide (1,3-diphenylurea), which is stable indefinitely.

3.2 After sampling, the impinger contents are transferred to a screw-capped vial having a Teflon-lined cap and returned to the laboratory for analysis.

3.3 The solution is taken to dryness by heating to 60°C on an aluminum heating block under a gentle stream of pure nitrogen gas. The residue is dissolved in 1 mL of acetonitrile.

3.4 Carbanilide is determined in the acetonitrile solution using reverse-phase HPLC with an ultraviolet absorbance (UV) detector operating at 254 nm.

4. Significance

4.1 Phosgene is widely used in industrial operations, primarily in the synthetic organic chemicals industry. In addition, phosgene is produced by photochemical degradation of chlorinated hydrocarbons (e.g., trichloroethylene) emitted from various sources. Although phosgene is acutely toxic, its effects at low levels (i.e., 1 ppbv and below) are unknown. Nonetheless, its emission into and/or formation in ambient air is of potential concern.

4.2 The conventional method for phosgene has utilized a colorimetric procedure involving reaction with 4,4'-nitrobenzyl pyridine in diethyl phthalate. This method cannot detect phosgene levels below 10 ppbv and is subject to numerous interferences. The method described herein is more sensitive (0.1 ppbv detection limit) and is believed to be more selective due to the chromatographic separation step. However, the method needs to be more rigorously tested for interferences before its degree of selectivity can be firmly established.

5. Definitions

Definitions used in this document and in any user-prepared SOPs should be consistent with ASTM D1356 (3). All abbreviations and symbols are defined within this document at the point of use.

6. Interferences

6.1 There are very few interferences in the method, although this aspect of the method needs to be more thoroughly investigated. Ambient levels of nitrogen oxides, ozone, water vapor, and SO_2 are known not to interfere. Chloroformates can cause interferences by

reacting with the aniline to form urea, which produces a peak that overlies the carbanilide peak in the HPLC trace. Presence of chloroformates should be documented before use of this method. However, the inclusion of a HPLC step overcomes most potential interferences from other organic compounds. High concentrations of acidic materials can cause precipitation of aniline salts in the impinger, thus reducing the amount of available reagent.

6.2 Purity of the aniline reagent is a critical factor, since traces of carbanilide have been found in reagent-grade aniline. This problem can be overcome by vacuum distillation of aniline in an all-glass apparatus.

7. Apparatus

7.1 Isocratic high performance liquid chromatography (HPLC) system consisting of a mobile-phase reservoir, a high-pressure pump, an injection valve, a Zorbax ODS or C-18 reverse-phase column, or equivalent (25 cm x 4.6 mm ID), a variable-wavelength UV detector operating at 254 nm, and a data system or strip-chart recorder (Figure 1).

7.2 Sampling system - capable of accurately and precisely sampling 100-1000 mL/minute of ambient air (Figure 2).

7.3 Stopwatch.

7.4 Friction-top metal can, e.g., one-gallon (paint can) - to hold sampling reagent and samples.

7.5 Thermometer - to record ambient temperature.

7.6 Barometer (optional).

7.7 Analytical balance - 0.1 mg sensitivity.

7.8 Midget impingers - jet inlet type, 25 mL.

7.9 Nitrogen evaporator with heating block - for concentrating samples.

7.10 Suction filtration apparatus - for filtering HPLC mobile phase.

7.11 Volumetric flasks - 100 mL and 500 mL.

7.12 Pipettes - various sizes, 1-10 mL.

7.13 Helium purge line (optional) - for degassing HPLC mobile phase.

7.14 Erlenmeyer flask, 1-L - for preparing HPLC mobile phase.

7.15 Graduated cylinder, 1 L - for preparing HPLC mobile phase.

7.16 Microliter syringe, 10-25 uL - for HPLC injection.

8. Reagents and Materials

8.1 Bottles, 16 oz. glass, with Teflon-lined screw cap - for storing sampling reagent.
8.2 Vials, 20 mL, with Teflon-lined screw cap - for holding samples and extracts.
8.3 Granular charcoal.
8.4 Acetonitrile, toluene, and methanol - distilled in glass or pesticide grade.
8.5 Aniline - 99+%, gold label from Aldrich Chemical Co., or equivalent.
8.6 Carbanilide - highest purity available; Aldrich Chemical Co., or equivalent.
8.7 Nitrogen, compressed gas cylinder - 99.99% purity for sample evaporation.
8.8 Polyester filters, 0.22 um - Nuclepore, or equiv.

9. Preparation of Sampling Reagent

9.1 Sampling reagent is prepared by placing 5.0 mL of aniline in a 250-mL volumetric flask and diluting to the mark with toluene. The flask is inverted 10-20 times to mix the reagent. The reagent is then placed in a clear 16-ounce bottle with a Teflon-lined screw cap. The reagent is refrigerated until use.
9.2 Before use, each batch of reagent is checked for purity by analyzing a 10-mL portion according to the procedure described in Section 11. If acceptable purity (<50 ng of carbanilide per 10 mL of reagent) is not obtained, the aniline or toluene is probably contaminated.

10. Sampling

10.1 The sampling apparatus is assembled and should be similar to that shown in Figure 2. EPA Method 6 uses essentially the same sampling system (5). All glassware (e.g., impingers, sampling bottles, etc.) must be thoroughly rinsed with methanol and oven-dried before use.
10.2 Before sample collection, the entire assembly (including empty sample impingers) is installed and the flow rate checked at a value near the desired rate. Flow rates greater than 1000 mL/minute (±2%) should not be used because impinger

collection efficiency may decrease. Generally, calibration is accomplished using a soap bubble flow meter or calibrated wet test meter connected to the flow exit, assuming that the entire system is sealed. ASTM Method D3686 describes an appropriate calibration scheme that does not require a sealed-flow system downstream of the pump (3).

10.3 Ideally, a dry gas meter is included in the system to record total flow, if the flow rate is sufficient for its use. If a dry gas meter is not available, the operator must measure and record the sampling flow rate at the beginning and end of the sampling period to determine sample volume. If the sampling time exceeds two hours, the flow rate should be measured at intermediate points during the sampling period. Ideally, a rotameter should be included to allow observation of the flow rate without interruption of the sampling process.

10.4 To collect an air sample, the midget impingers are loaded with 10 mL each of sampling reagent. The impingers are installed in the sampling system and sample flow is started. The following parameters are recorded on the data sheet (see Figure 3 for an example): date, sampling location, time, ambient temperature, barometric pressure (if available), relative humidity (if available), dry gas meter reading (if appropriate), flow rate, rotameter setting, sampling reagent batch number, and dry gas meter and pump identification numbers.

10.5 The sampler is allowed to operate for the desired period, with periodic recording of the variables listed above. The total flow should not exceed 50 L. If it does, the operator must use a second impinger.

10.6 At the end of the sampling period, the parameters listed in Section 10.4 are recorded and the sample flow is stopped. If a dry gas meter is not used, the flow rate must be checked at the end of the sampling interval. If the flow rates at the beginning and end of the sampling period differ by more than 15%, the sample should be marked as suspect.

10.7 Immediately after sampling, the impinger is removed from the sampling system. The contents of the impinger are emptied into a clean 20-mL glass vial with a Teflon-lined screw cap. The impinger is then rinsed with 2-3 mL of toluene and the rinse solution is added to the vial. The vial is then capped, sealed with Teflon tape, and placed in a friction-top can containing 1-2

inches of granular charcoal. The samples are stored in the can and refrigerated until analysis.

10.8 If a dry gas meter or equivalent total flow indicator is not used, the average sample flow rate must be calculated according to the following equation:

$$Q_A = \frac{Q_1 + Q_2 \ldots . Q_N}{N}$$

where

Q_A = average flow rate (mL/minute).

$Q_1, Q_2 \ldots . Q_N$ = flow rates determined at the beginning, end, and intermediate points during sampling.

N = number of points averaged.

10.9 The total flow is then calculated using the following equation:

$$V_m = \frac{(T_2 - T_1)Q_A}{1000}$$

where

V_m = total sample volume (L) at measured temperature and pressure.

T_2 = stop time.

T_1 = start time.

T_1-T_2 = total sampling time (minutes).

Q_a = average flow rate (mL/minute).

11. Sample Analysis

11.1 Sample Preparation

11.1.1 The samples are returned to the laboratory in 20-ml screw-capped vials and refrigerated in charcoal containing cans until analysis.

11.1.2 The sample vial is placed in an aluminum heating block maintained at 60°C and a gentle stream of pure nitrogen gas is directed across the sample.

11.1.3 When the sample reaches complete dryness, the vial is removed from the heating block, capped, and cooled to near room temperature. A 1-mL volume of HPLC mobile phase (50/50 acetonitrile/water) is placed in the vial.

The vial is then capped and gently shaken to dissolve the residue.

11.1.4 The concentrated sample is then refrigerated until HPLC analysis, as described in Section 11.2.

11.2 HPLC Analysis

11.2.1 The HPLC system is assembled and calibrated as described in Section 12. The operating parameters are as follows:

Column: C-18 RP
Mobile Phase: 30% acetonitrile/70% distilled water
Detector: ultraviolet, operating at 254 nm
Flow Rate: 1 mL/min

Before each analysis, the detector baseline is checked to ensure stable operation.

11.2.2 A 25-uL aliquot of the sample, dissolved in HPLC mobile phase, is drawn into a clean HPLC injection syringe. The sample injection loop is loaded and an injection is made. The data system is activated simultaneously with the injection and the point of injection is marked on the strip-chart recorder.

11.2.3 After approximately one minute, the injection valve is returned to the "load" position and the syringe and valve are flushed with mobile phase in preparation for the next sample analysis.

11.2.4 After elution of carbanilide, data acquisition is terminated and the component concentrations are calculated as described in Section 13.

11.2.5 Once a stable baseline is achieved, the system can be used for further sample analyses as described above.

11.2.6 If the concentration of carbanilide exceeds the linear range of the instruments, the sample should be diluted with mobile phase, or a smaller volume can be injected into the HPLC.

11.2.7 If the retention time is not duplicated, as determined by the calibration curve, you may increase or decrease the acetonitrile/water ratio to obtain the correct elution time, as specified in Figure 4. If the elution time is too long, increase the ratio; if it is too short, decrease the ratio.

11.2.8 If a dirty column causes improper detection of carbanilide, you may reactivate the column by reverse solvent flushing utilizing the following sequence: water, methanol, acetonitrile, dichloromethane, hexane, acetonitrile, then 50/50 acetonitrile in water.

12. HPLC Assembly and Calibration

12.1 The HPLC system is assembled and operated according to the parameters outlined in Section 11.2.1. An example of a typical chromatogram obtained using the above parameters is shown in Figure 4.

12.2 The mobile phase is prepared by mixing 500 mL of acetonitrile and 500 mL of reagent water. This mixture is filtered through a 0.22-um polyester membrane filter in an all-glass and Teflon suction filtration. A constant back pressure restrictor (50 psi) or short length (6-12 inches) of 0.01-inch I.D. Teflon tubing should be placed after the detector to eliminate further mobile phase outgassing.

12.3 The mobile phase is placed in the HPLC solvent reservoir and the pump is set at a flow rate of 1 mL/minute and allowed to pump for 20-30 minutes before the first analysis. The detector is switched on at least 30 minutes before the first analysis and the detector output is displayed on a strip-chart recorder or similar output device at a sensitivity of ca 0.008 absorbance units full scale (AUFS). Once a stable baseline is achieved, the system is ready for calibration.

12.4 Carbanilide standards are prepared in HPLC mobile phase. A concentrated stock solution of 100 mg/L is prepared by dissolving 10 mg of carbanilide in 100 mL of mobile phase. This solution is used to prepare calibration standards containing concentrations of 0.05-5 mg/L.

12.5 Each calibration standard (at least five levels) is analyzed three times and area response is tabulated against mass injected. All calibration runs are performed as described for sample analyses in Section 11. Using the UV detector, a linear response range (Figures 5a through 5e) of approximately 0.1 to 10 mg/L should be achieved for a 25-uL injection volumes. The results may be used to prepare a calibration curve, as illustrated in Figure 6. Linear response is indicated where a correlation coefficient of at least 0.999 for a linear least-squares fit of data (concentration versus area response) is obtained.

12.6 Once linear response has been documented, an intermediate concentration standard near the anticipated levels for ambient air, but at least 10 times the detection limit, should be chosen for daily calibration. The response for carbanilide should be within 10% day to day. If greater variability is observed, more frequent calibration may be required to ensure that valid results are obtained or a new calibration curve must be developed from fresh standards.

12.7 The response for carbanilide in the daily calibration standard is used to calculate a response factor according to the following equation:

$$RF_c = \frac{C_c \; X \; V_I}{R_c}$$

where

RF_c = response factor (usually area counts) for carbanilide in nanograms injected/response unit.

C_c = concentration (mg/L) of carbanilide in the daily calibration standard.

V_I = volume (uL) of calibration standard injected.

R_c = response (area counts) for carbanilide in calibration standard.

13. Calculations

13.1 The volume of air sampled is often reported uncorrected for atmospheric conditions (i.e., under ambient conditions). The value should be adjusted to standard conditions (25°C and 760 mm pressure) using the following equation:

$$V_s = V_m \times \frac{P_A}{760} \times \frac{298}{273 + T_A}$$

where

V_s = total sample volume (L) at 25°C and 760 mm Hg pressure.

V_m = total sample volume (L) under ambient conditions, calculated as in Section 10.9 or from dry gas meter reading.

P_A = ambient pressure (mm Hg).

T_A = ambient temperature (°C).

13.2 The concentration of carbanilide is calculated for each sample using the following equation:

$$W_d = RF_c \; X \; R_d \; X \frac{V_E}{V_I}$$

where

W_d = total quantity of carbanilide (ug) in the sample.
RF_c = response factor calculated in Section 12.7.
R_d = response (area counts or other response units) for carbanilide in sample extract.
V_E = final volume (mL) of sample extract.
V_I = volume (uL) of extract injected into the HPLC system.

13.3 The concentration of phosgene in the original sample is calculated from the following equation:

$$C_A = \frac{W_d}{V_m \; (or \; V_s)} \times \frac{99}{212} \times 1000$$

where

C_A = concentration of phosgene (ng/L) in the original sample.
W_d = total quantity of carbanilide (ug) in sample.
V_m = total sample volume (L) under ambient conditions.
V_c = total sample volume (L) at 25°C and 760 mm Hg.

$\frac{99}{212}$ = the molecular weights (g/mole) of phosgene and carbanilide are 99 and 212 g/mole, respectively.

13.4 The phosgene concentrations can be converted to ppbv using the following equation:

$$C_A \; (ppbv) = C_A \; (ng/L) \times \frac{24.4}{99}$$

where

C_A (ng/L) is calculated using V_s.

14. Performance Criteria and Quality Assurance

This section summarizes required quality assurance (QA) measures and provides guidance concerning performance criteria that should be achieved within each laboratory.

14.1 Standard Operating Procedures (SOPs).

14.1.1 Users should generate SOPs describing the following activities in their laboratory: 1) assembly, calibration, and operation of the sampling system with make and model of equipment used; 2) preparation, purification, storage, and handling of sampling reagent and samples; 3) assembly, calibration, and operation of the HPLC system with make and model of equipment used; and 4) all aspects of data recording and processing, including lists of computer hardware and software used.

14.1.2 SOPs should provide specific stepwise instructions and should be readily available to and understood by the laboratory personnel conducting the work.

14.2 HPLC System Performance

14.2.1 The general appearance of the HPLC chromatogram should be similar to that illustrated in Figure 4.

14.2.2 The HPLC system efficiency and peak asymmetry factor should be determined in the following manner: A solution of carbanilide corresponding to at least 20 times the detection limit should be injected with the recorder chart sensitivity and speed set to yield a peak approximately 75% of full scale and 1 cm wide at half height. The peak asymmetry factor is determined as shown in Figure 7, and should be between 0.8 and 1.8.

14.2.3 HPLC system efficiency is calculated according to the following equation:

$$N = 5.54 \frac{t_r}{W_{1/2}}$$

where

N = column efficiency (theoretical plates).

t_r = retention time (seconds) of carbanilide.

$W_{1/2}$ = width of component peak at half height (seconds).

A column efficiency of >5,000 theoretical plates should be obtained.

14.2.4 Precision of response for replicate HPLC injections should be ±10% or less, day to day, for calibration standards. Precision of retention times should be ±2%, on a given day.

14.3 Process Blanks

14.3.1 Before use, a 10-mL aliquot of each batch of sampling reagent should be analyzed as described in Section 11. The blank should contain less than 50 ng of carbanilide per 10-mL aliquot.

14.3.2 At least one field blank or 10% of the field samples, whichever is larger, should be shipped and analyzed with each group of samples. The field blank is treated identically to the samples except that no air is drawn through the reagent. The same performance criteria described in Section 14.3.1 should be met for process blanks.

14.4 Method Precision and Recovery

14.4.1 Analysis of replicate samples indicates that a precision of ±15-20% relative standard deviation can be readily achieved (see Table 1). Each laboratory should collect parallel samples periodically (at least one for each batch of samples) to document its precision in conducting the method.

14.4.2 Precision for replicate HPLC injections should be ±10% or better, day to day, for calibration standards.

14.4.3 Before using the method in the field, each laboratory must confirm the performance of the method under its particular conditions. Since static, dilute, gas phase standards of phosgene are unstable, a dynamic flow/permeation tub system should be assembled as described in the literature (1). ASTM Method D 3609(3) should be used as the protocol for operating such a system.

14.4.4 Once a suitable dynamic flow/permeation tube system has been constructed, a series of three samples from the outlet gas stream (60 L) should be sampled at three different spike levels (achieved by adjusting the air

flow through the permeation chamber). Precision and recovery data comparable to those shown in Table 1 should be achieved.

REFERENCES

1. Spicer, C. W., R. M. Riggin, M. W. Holdren, F. L. DeRoos, and R. N. Lee, Atmospheric Reaction Products from Hazardous Air Pollutants, Final Report on Contract 68-02-3169 (WA-33/40), U.S. Environmental Protection Agency, Research Triangle Park, N.C., July, 1984.

2. Method 219, "Phosgene in Air," Manual of Analytical Methods, National Institute for Occupational Safety and Health.

3. Annual Book of ASTM Standards, Part 11.03, "Atmospheric Analysis," American Society for Testing and Materials, Philadelphia, Pennsylvania, 1983.

4. Riggin, R. M., "Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air," EPA-600/4-83-027. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1983.

5. "Method 6 Determination of SO_2 Emissions from Stationary Sources," Federal Register, Vol. 42., No. 160, August, 1977.

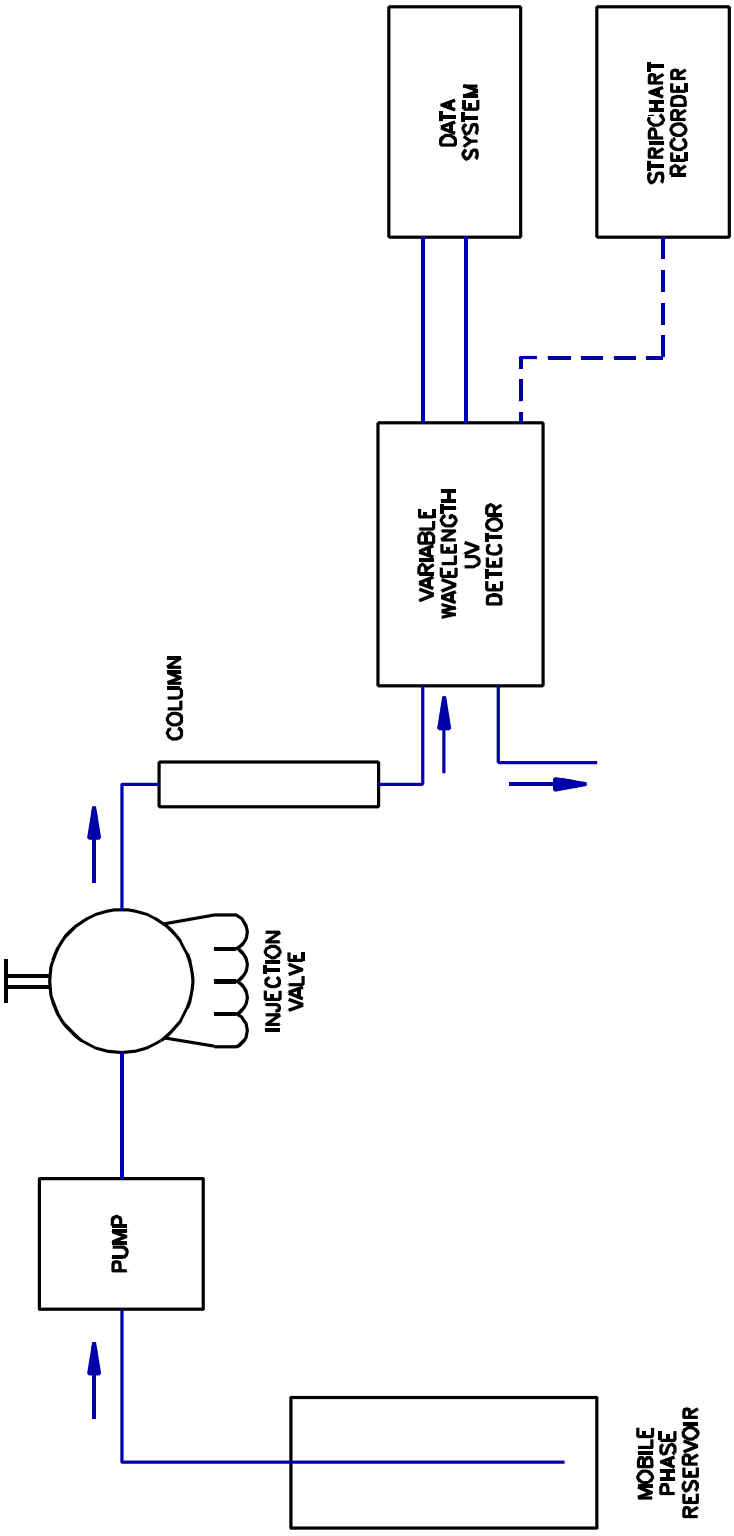


FIGURE 1. TYPICAL HPLC SYSTEM

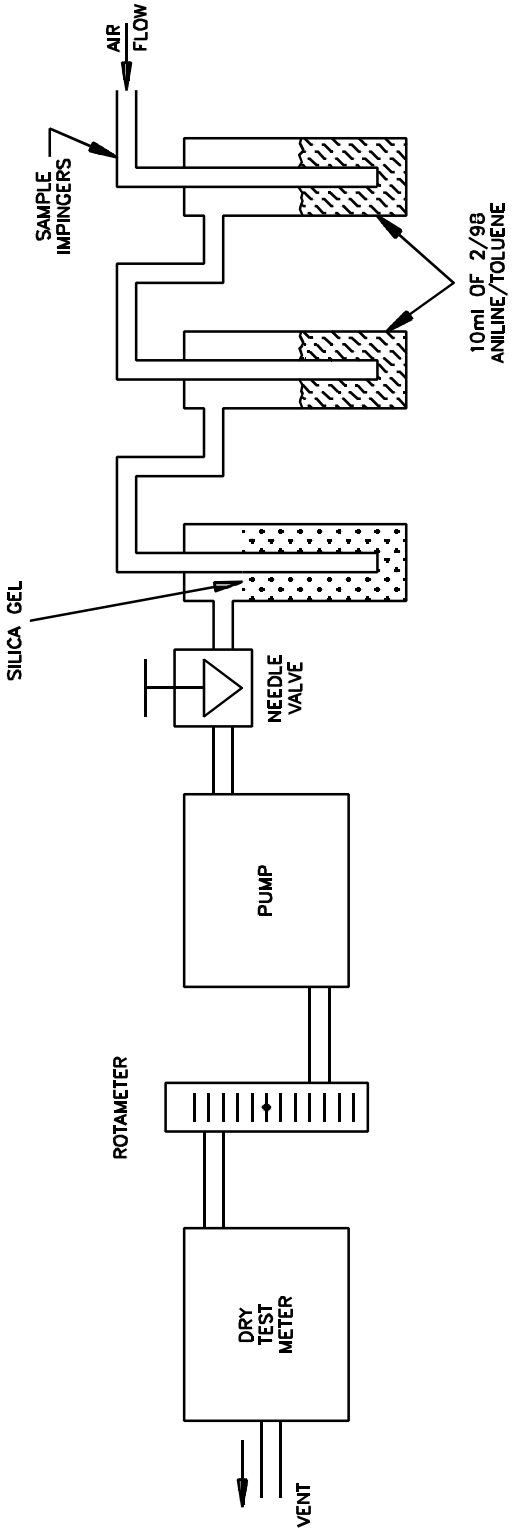


FIGURE 2. TYPICAL SAMPLING SYSTEM FOR MONITORING PHOSGENE IN AMBIENT AIR

SAMPLING DATA SHEET
(One Sample per Data Sheet)

PROJECT: _____ DATES(S) SAMPLED: _____

SITE: _____ TIME PERIOD SAMPLED: _____

LOCATION: _____ OPERATOR: _____

INSTRUMENT MODEL NO: _____ CALIBRATED BY: _____

PUMP SERIAL NO: _____

SAMPLING DATA

Sample Number: _____

Start Time: _____ Stop Time: _____

Time	Dry Gas Meter Reading	Rotameter Reading	Flow Rate, *Q mL/min	Ambient Temperature °C	Barometric Pressure, mm Hg	Relative Humidity, %	Comments
1.							
2.							
3.							
4.							
N.							

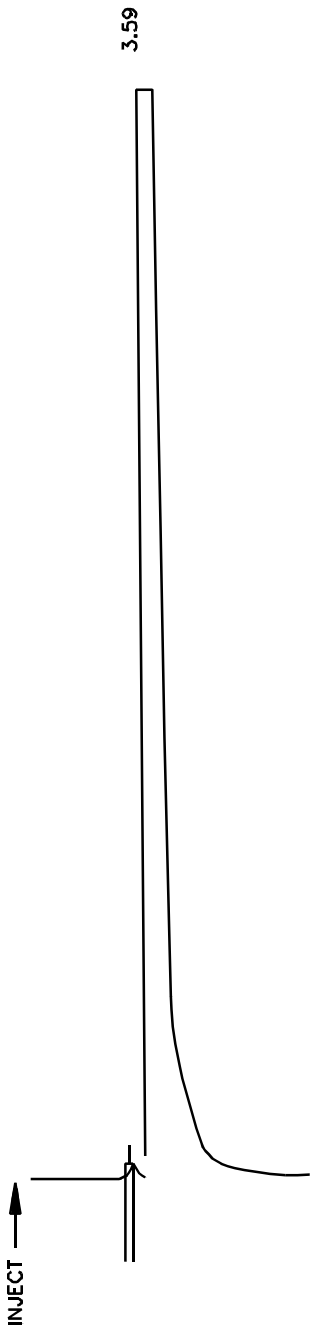
Total Volume Data**

V_m = (Final - Initial) Dry Gas Meter Reading, or = _____ L

$$\frac{Q_2 + Q_3 \ldots Q_N}{N} \times \frac{1}{1000 \times (\textit{Sampling Time in Mi}} = \_\_\_\_\_ \text{ L}$$

* Flow rate from rotameter or soap bubble calibrator (specify which).
** Use data from dry gas meter if available.

FIGURE 3. TYPICAL SAMPLING DATA FORM



OPERATING PARAMETERS
HPLC

Column: C-18 RP
Mobile Phase: 30% Acetonitrile/70% Distilled Water
Detector: Ultra violet operating at 254 nm
Flow Rate: 1 ml/min
Retention Time: 3.59 minutes

AUG. 22, 1986 15.25:17 CHART 0.50 CM/MIN
RUN #50 CALC #0
COLUMN SOLVENT OPR ID: 3

EXTERNAL STANDARD QUANTITATION

PEAK#	AMOUNT	RT	EXP RT	AREA	RF
	2.75300	2.74		2753 L	0.000000E0
	10020.20000	3.59		10020345 L	0.000000E0
TOTAL	10023.00000				

FIGURE 4. CHROMATOGRAM FOR 3 ppbv OF PHOSGENE SPIKED INTO CLEAN AIR

OPERATING PARAMETERS
HPLC

Column: C-18 RP
Mobile Phase: 30% Acetonitrile/70% Distilled Water
Detector: Ultra violet operating at 254 nm
Flow Rate: 1 ml/min
Retention Time: 3.59 minutes

CONC	AREA COUNTS
1µg	2126577
2µg	4243289
3µg	6312128
4µg	8373790
5µg	10020345

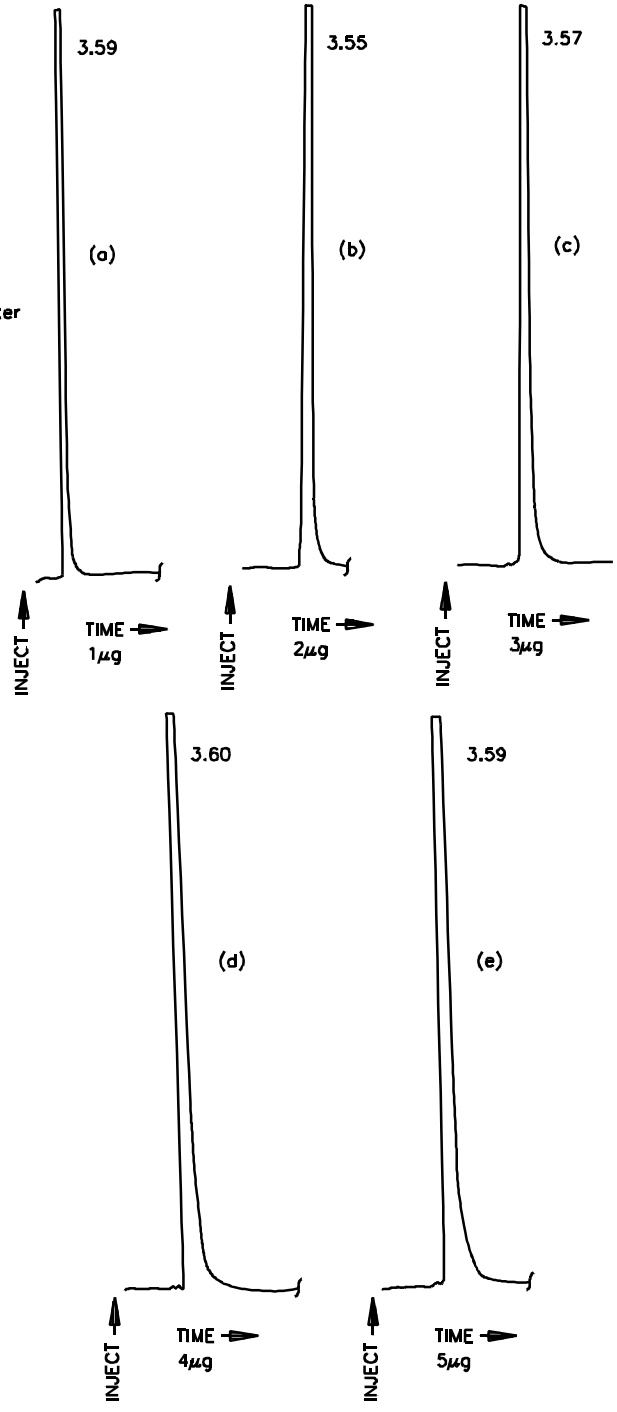


FIGURE 5a-5e. HPLC CHROMATOGRAM OF VARYING CARBANILIDE CONCENTRATIONS

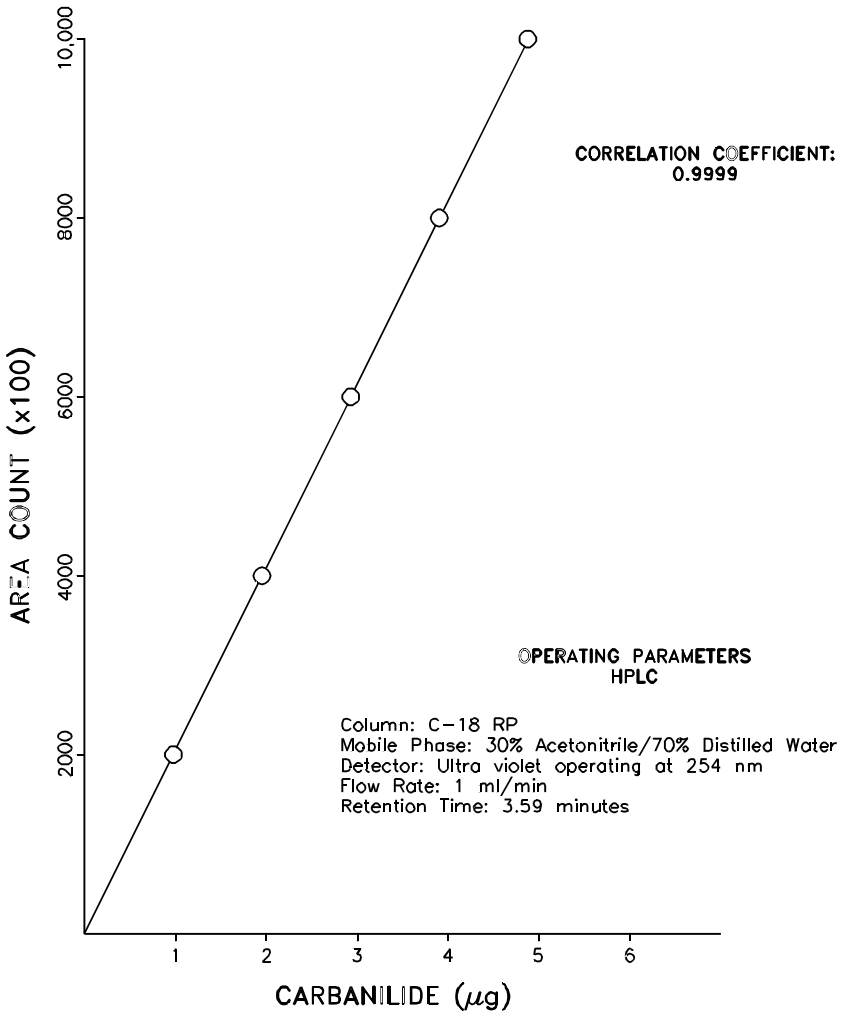
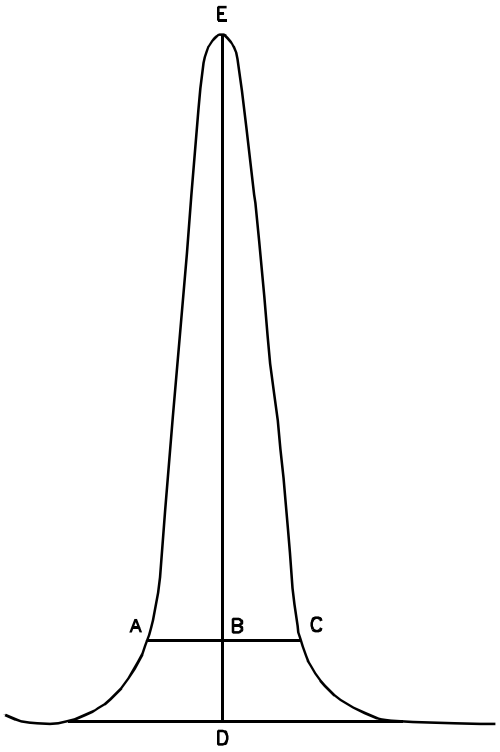


FIGURE 6. CALIBRATION CURVE FOR CARBANILINE



Asymmetry Factor = $\frac{BC}{AB}$

Example Calculation:

Peak Height = DE = 100mm
10% Peak Height = BD = 10mm
Peak Width at 10% Peak Height = AC = 23mm
AB = 11mm
BC = 12mm

Therefore: Asymmetry Factor = $\frac{12}{11}$ = 1.1

FIGURE 7. PEAK ASYMMETRY CALCULATION

TABLE 1: PRECISION AND RECOVERY DATA
FOR PHOSGENE IN CLEAN AIR

Phosgene Concentration, ppbv	Recovery, %	Standard Deviation
0.034	63	13
0.22	87	14
3.0	99	3
4.3	109	12
20	99	14
200	96	7