DOW CONFIDENTIAL

R&S 004081

THE DOW CHEMICAL COMPANY

TEXAS DIVISION
FREEPORT, TEXAS 77541

cc — Nick M.
— Lew Nichols
— V. K. Rowe
— R J M

from Chet Otis
12/6/72

December 4, 1972

File - Vinyl Chloride

L. Adcock, OCD
R. L. Daniel, A-1201
D. E. Hamilton, Sarnia
W. Rittershausen, Stade
F. Vreugdenhil, Terneuzen
B. J. Williams, Ulsan
C. L. Melancon, Plaquemine
R. R. Oubre, A-2410

cc - Hoyle
a very interesting report - VK.

cc: Chet Otis, Midland
Irving Snyder, Midland
R. C. Walker, B-1903

CONTINUOUS AIR MONITORING FOR CHLORINATED HYDROCARBONS

Attached is a copy of equipment requirements for continuous air monitoring, source directory for equipment, and backup data. It is the recommendation of the Chlorinated Hydrocarbons Technology Center that each plant install one of these units so that we can have a permanent record of our chlorinated hydrocarbons levels throughout the plant. If you need further details please contact A. A. Allemang, 238-4640. We have enclosed background data so you can have some knowledge of the problems you will encounter.

C. A. Christian

C. A. Christian
Technical Manager
Chlorinated Hydrocarbons
Technology Center
A-1201

pm

encl

DOW CONFIDENTIAL

December 1, 1972

EQUIPMENT REQUIREMENTS FOR CONTINUOUS AIR MONITORING FOR CHLORINATED HYDROCARBONS

CHROMATOGRAPH

A single column, isothermal unit equipped with a flame ionization detector. Suitable chromatographs can be purchased from Varian Aerograph, Beckman Instruments, Hewlett-Packard, Perkin-Elmer, Amsco, and a number of other manufacturers.

RECORDER

One millivolt, with one second, full scale response time. Recommended are Bristol Dynamaster, Leeds and Northrup Speedomax XL-610, and Sargent SR-20.

PROGRAMMER

A process analyzer Sample Selecting System for use with a multi-stream analyzer (12 sample streams minimum). The programmer must be capable of operating solenoid and air operated valves. Suitable units are available from Beckman Instruments and Process Analyzers, Inc. A Dow designed unit is manufactured by Amsco.

AUTOMATIC ATTENUATOR

A solid state automatic attenuator is recommended. Acceptable units are manufactured by Esterlingangus, Arcas, and Process Analyzers, Inc. Non-solid state automatic attenuators are available from Hewlett-Packard and Perkin-Elmer.

SAMPLE VALVE

A rotary gas sample valve manufactured by Valco (available from Antek Instruments) is recommended. Slide valves, manufactured by Arcas or Beckman may also be used.

Air operated toggle valves (from In-Val-Co) should be used on the hydrogen supply to the detector as a safety feature.

COMPANY DIRECTORY

Amsco
P. O. Drawer HH
Angleton, Texas 77515

Antek Instruments, Inc.
6005 N. Freeway
Houston, Texas 77022

Arcas
2040 Kipling
Houston, Texas 77006

Beckman Instruments, Inc.
2500 Harbor Blvd.
Fullerton, Calif. 92634

Curtin Scientific Co.
P. O. Box 1546
Houston, Texas 77001

Esterlingangus
Div. of Esterling Corp.
Box 2400
Indianapolis, Indiana 46224

Fisher Scientific Co.
711 Forbes Ave.
Pittsburgh, Pa. 15219

Hewlett-Packard
1430 East Orangethrope Ave.
Fullerton, Calif. 92631

In-Val-Co
P. O. Box 556
Tulsa, Okla.

Leeds and Northrup
Summeytown Pike
North Wales, Pa. 19454

Perkin-Elmer Corp.
702-G Main Avenue
Norwalk, Conn. 06852

Precision Scientific Co.
3737 W. Cortland St.
Chicago, Ill. 60647

Process Analyzers, Inc.
6400 S.W. Freeway
Suite 400
Houston, Texas 77036

Sargent-Welch Scientific Co.
7300 N. Linder Ave.
Skokie, Ill. 60076

Varian Aerograph
2700 Mitchell Dr.
Walnut Creek, Calif. 94598

EXPOSURE TO CHLORINATED HYDROCARBONS

COMPOUND	OSHA STD.	V_1V_2 EXPOSURE	OCD EXPOSURE
Vinyl Chloride	500 ppm_m	7.0 ppm_m	0.35 ppm_m
Ethyl Chloride	1000	1.2	--
Vinylidene Chloride	25	0.34	--
Methylene Chloride	500	0.29	--
1,1-dichloroethane	100	0.32	--
Chloroform	50	<0.10	--
1,1,1-trichloroethane	350	0.86	--
Carbon Tetrachloride	10	<0.10	--
Ethylene Dichloride	50	0.64	4.8
Trichloroethylene	100	<0.10	--
Propylene Dichloride	75	<0.10	--
1,1,2-trichloroethane	10	0.18	0.10
Perchloroethylene	100	<0.10	--
1,1,1,2-tetrachloroethane	100	<0.10	--
1,1,2,2-tetrachloroethane	5	<0.10	--

NOTE

1. OSHA STD - Occupational Safety and Health Act maximum exposure level, 8-hour time weighted average

2. Dow standard for vinyl chloride is 50 ppm_m.

3. OCD found an area during their survey where personnel could be exposed to concentration of vinyl chloride as high as 1000 ppm_m.

R&S 004084

AAA:pm
12-4-72

AIR MONITORING FOR CHLORINATED HYDROCARBONS

SCOPE

This method is applicable to the determination of chlorinated hydrocarbons in ambient air at concentrations from 0.1 ppm.

EQUIPMENT

Chromatograph - Dow designed, Amsco built flame ionization detector

Conditions:
Column - 12' x 1/4"
14% Polyethylene grease SD446 on Chromosorb W-NAW, 60/80 mesh
Temperature 85°C
Carrier - Nitrogen, 50 mls/min.
Air - 250 mls/min.
Hydrogen - 25 mls/min.
Sample size - 2 ml.

Recorder - Bristol Dynamaster
Programmer - Dow designed, Amsco built
Automatic attenuator - Dow designed, Amsco built
Sample valve - air operated

MOBIL SAMPLING STATION

The base of the mobil sampling station is a trailer 36" x 72". A wooden cabinet (3/4" plywood) 60" x 30" x 30" is mounted on the trailer to house the chromatograph and associated equipment. Four gas cylinders, air, hydrogen and nitorgen are placed on the rear of the trailer and chained to the wooden cabinet. Racks are provided on the rear of the cabinet for the power cord, sampling lines, and air line.

To make the sampling station intrinsically safe all corners of the cabinet are sealed. All service lines enter through holes drilled in the rear of the cabinet and these are sealed with Silastic®. The doors of the cabinet are stripped with polyurethane. The cabinet is under a slight air pressure supplied by an air line connected to the plant air system. Automatic shut down switches are installed as follows: 1) loss of carrier gas pressure shuts down electrical power and hydrogen flow; 2) loss of cylinder air pressure shuts down hydrogen flow; and 3) loss of air purge to the cabinet shuts down electrical power and hydrogen flow. If a shut down occurs, manual reset is required before start up of the unit.

STANDARDIZATION

A standard mixture of the chlorinated hydrocarbons of interest is made. Ten microliters or a multiple thereof is placed in a calibrated one gallon bottle. The bottle is capped and stirred using a magnetic stirrer until all the liquid has evaporated. The cap is them removed

and a line from the chromatograph sample valve is dropped to the bottom of the bottle. Sample from the bottle is purged through the sample loop for one minute then the sample valve is manually operated. Mole parts per million of each chlorinated hydrocarbon is calculated from the number of moles added to the bottle in the 10 ul of standard mixture divided by the total moles of air in the bottle at ambient conditions. From the valves, peak height factors are developed for calculation of concentrations of chlorinated hydrocarbons in air.

FIELD SAMPLING

Samples are brought to the station through 1/4" Saran® tubing from remote locations 6', 15' and 30' above ground level. An air aspirator moves the air through the Saran® tubing into the chromatograph sample valve. A solenoid valve, downstream of the sample loop closes to allow the sample loop to come to atmospheric pressure. The programmer then activates the air operated sample valve. Sampling is at thirty minute intervals alternating between the three sample points.

A. A. Allemang
A-2422
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MONITORING PERSONNEL EXPOSURE TO CHLORINATED HYDROCARBONS

SCOPE

This procedure is a fast, effective and accurate method for determining personnel equivalent exposures to chlorinated hydrocarbons in an industrial work environment.

STANDARDIZATION

To prepare standard concentrations in air permeation tubes are used. Intramedic® polyethylene tubing from Curtin Scientific with an I.D. of 0.962", O.D. of 0.082", and 12 cm length was used to make the permeation tubes. The polyethylene was heated slightly in an open flame until soft and was then sealed by crimping with pliers. The tube was then filled to one-half volume with the chlorinated hydrocarbon to be tested, and the open end sealed, being careful to pinch the tubing to avoid contacting the liquid with the flame.

For lighter materials, i.e. vinyl chloride, one end of a piece of nylon tubing (Samuel Moore Co., 1/4" x 0.062" wall, 12 cm long) was capped with a brass Swagelok tubing fitting and the other end was fitted with a Microsep® (teflon backed chromatographic septum) in a Swagelok nut. Vinyl chloride was cooled in a dry ice-vinyl chloride bath and injected into the tube using a Hamilton syringe.

After preparation, the permeation tube was weighed and placed in an adsorption apparatus consisting of (Figure 1) two 1/2" x 2" steel swages coupled together and connected to a Moore air filter. (Fig. 2). Thirty (30) mls of activated carbon were charged to the air filter and supported by a double layer of screen. Glass wool was placed above the carbon. The screen is held in place by a plastic cap. Air is purged through the apparatus at 2.8 l/min. After 2-6 hours, the air flow is stopped and the permeation tube removed and re-weighed. The carbon was extracted with one mole of carbon disulfide which is analyzed by gas chromatography.

The grams of chlorinated hydrocarbon recovered are used with the weight loss of the permeation tube to calculate the efficiency of the adsorption-extraction procedure.

CHROMATOGRAPHIC

Instrument - Varian Aerograph Series 1400 temperature programmed, flame ionization detector.

Column - 12' x 1/4"
16% polyethylene grease SD 446 on 60/80 mesh Chromosorb W-NAW

Conditions - Temperature
Inlet - 110°C
Detector 200°C
Column - programmed from 60°C for 340 secs to 120°C at 20°C/min.

- Gases
Carrier - N_2, 30 ml/min.
Air - 250 mls/min
H_2 - 25 mls/min

- Sample Size - 10 ul

Elution Times - see attached

PERSONNEL MONITOR:

Unico C110 Air Sampler - See attached bulletin

To the side of this unit, a plexiglass holder, 1-3/8" square by 6½" long was attached. This held a glass adsorption column, 1" glass tubing, 5-3/4" long, closed at one end. A 1/4" glass tube extends down the center of this tube to within 1/2" of the bottom and protrudes 1/2" above the top of the 1" tube. Thirty grams of carbon is charged to the adsorption column. (Figure 3).

This unit is then strapped to the individual to be monitored. At the end of the sampling period (8 hours) the carbon is removed and extracted with CS_2 and analyzed by gas chromatography.

CALCULATIONS

Efficiency of the adsorption - Extraction

$$\text{Efficiency} = \frac{\text{grams recovered in } CS_2}{\text{weight loss of tube in grams}} \times 100$$

Exposure Concentration

$$\text{Sample concentration in air ppm mole} = \frac{(A)(B)}{(C)(D)}$$

Where: A = sample concentration in CS_2 from chromatogram, ppm.
B = moles CS_2
C = Adsorption-Extraction efficiency
D = Total moles of air sampled

Equivalent Exposure for a mixture of air contaminants

$$Em = \frac{C_1}{L_1} + \frac{C_2}{L_2} + \ldots\ldots \frac{Cn}{Ln}$$

Where: Em = equivalent exposure for the mixture
C = concentration of a specific contaminant
L = exposure limit for that contaminant (OSHA Standard) (attached)

A. A. Allemang
A-2422 11/22/72

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Figure 1

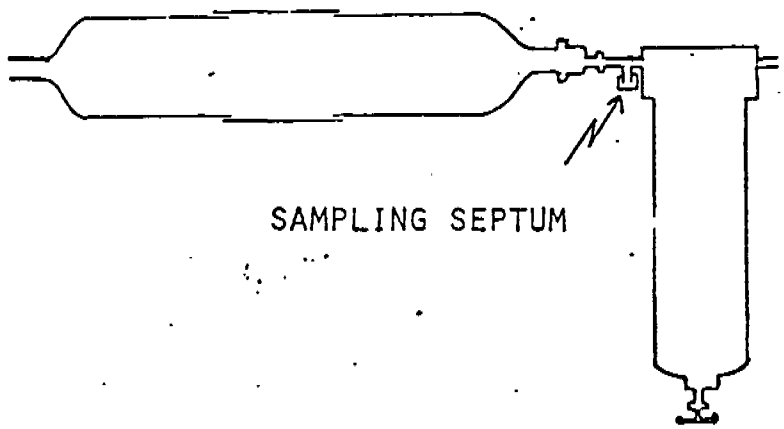


Figure 2

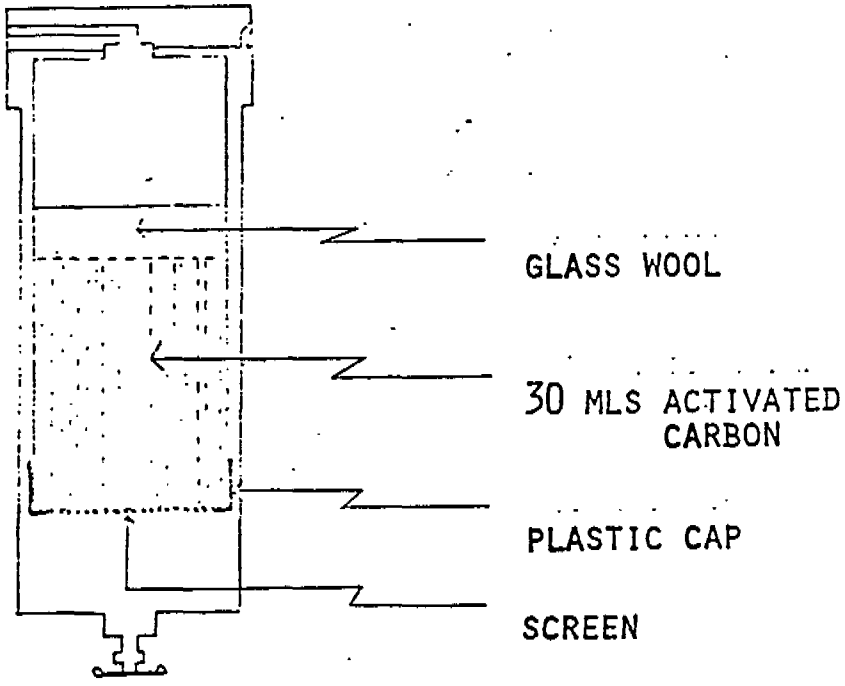
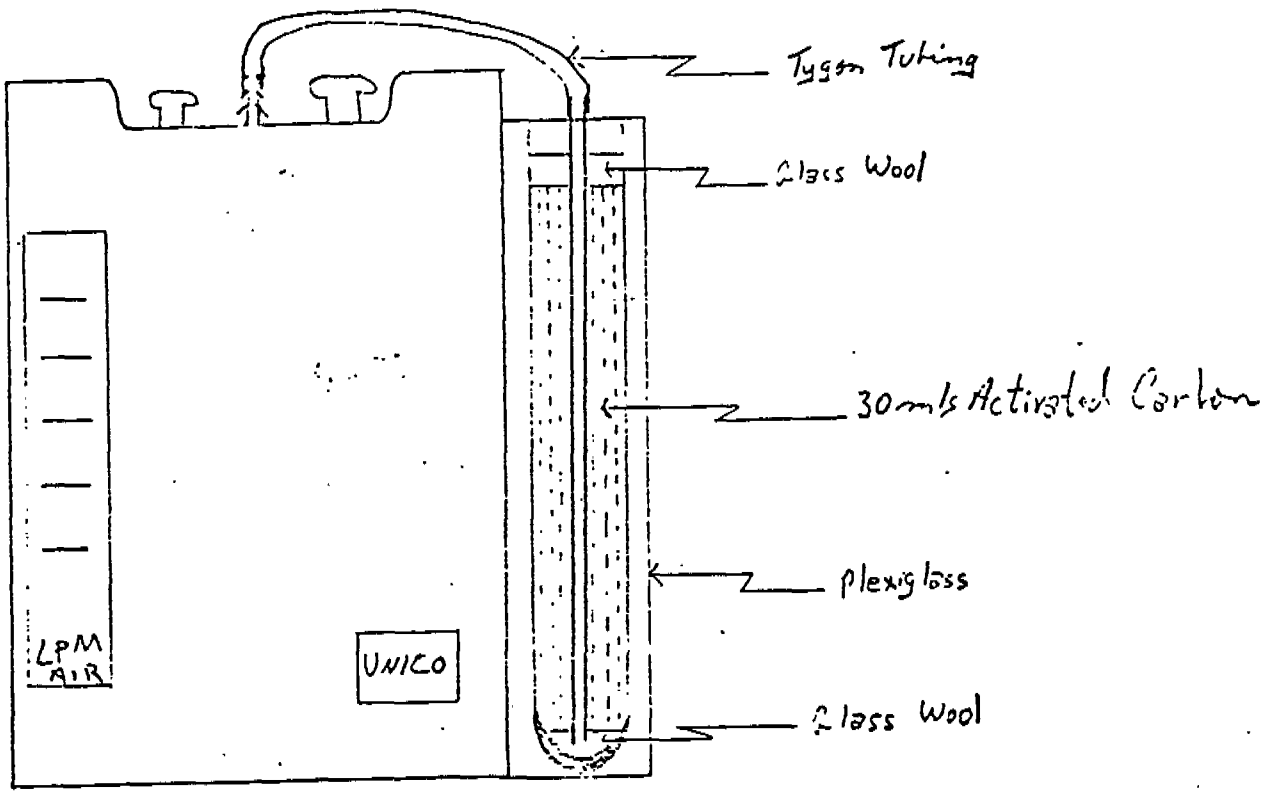


FIGURE 3


Tygon Tubing
Glass Wool
30 mls Activated Carbon
plexiglass
Glass Wool
LPM AIR
UNICO

ELUTION TIMES

(MINUTES FROM INJECTION)

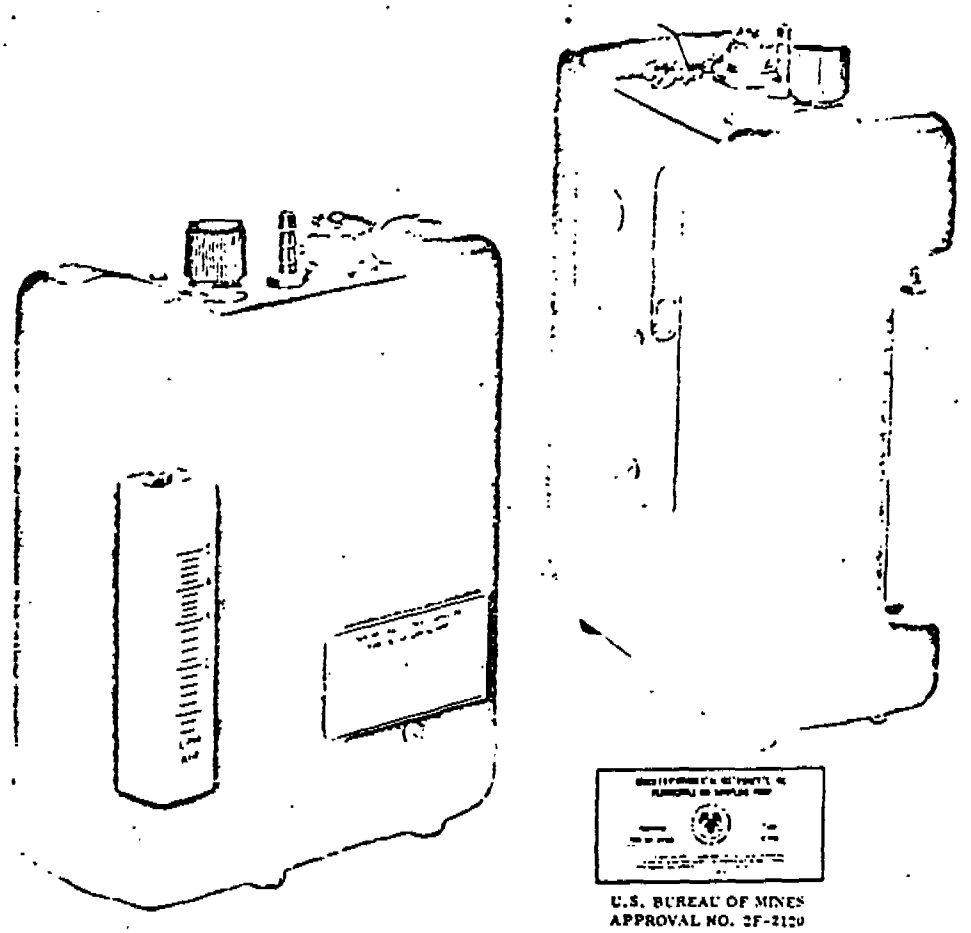
COMPOUND	TIME, MINUTES
VINYL CHLORIDE	2.1
ETHYL CHLORIDE	2.6
METHYLENE CHLORIDE	4.0
VINYLIDENE CHLORIDE	4.3
1,1-DICHLOROETHANE	5.5
CARBON DISULFIDE	6.5
CHLOROFORM	7.4
ETHYLENE DICHLORIDE	8.2
1,1,1-TRICHLOROETHANE	8.7
CARBON TETRACHLORIDE	9.6
PROPYLENE DICHLORIDE	10.1
TRICHLOROETHYLENE	10.9
1,1,2-TRICHLOROETHANE	12.7
PERCHLOROETHYLENE	16.8
1,1,1,2-TETRACHLOROETHANE	17.5
1,1,2,2-TETRACHLOROETHANE	22.1

R&S 004093

SLIDE 11

UNICO C110 AIR SAMPLER

APPROVED BY U.S. BUREAU OF MINES FOR INTRINSICALLY SAFE OPERATION IN EXPLOSIVE ATMOSPHERES



U.S. BUREAU OF MINES
APPROVAL NO. 2F-2120

R&S 004094

The only lightweight, compact personnel monitor powered by a rechargeable Nickel Cadmium battery designed to these exacting Bureau of Mines Specifications.

- Eight hours continuous Midget Impinger sampling at a calibrated flow of 2.8 liters per minute.
- Eight hours continuous sampling with a Two-Stage Respirable Mass Sampler.
- The Unico Model C110 is the only personnel air sampler capable of providing full-shift sampling at a calibrated air flow of 2.8 liters per minute.
- Eight hours continuous sampling through any filter media.

UNICO ENVIRONMENTAL INSTRUMENTS, INC.
FALL RIVER, MASSACHUSETTS 02720