



INDUSTRIAL CHEMICALS DIVISION

SHELL CHEMICAL COMPANY

A DIVISION OF SHELL OIL COMPANY

ONE SHELL PLAZA

HOUSTON, TEXAS 77002

August 15, 1973

Gentlemen:

The necessity for limiting and controlling human exposure to high concentrations of vinyl chloride has been long recognized by industry. A 500 ppm ceiling value is specified by the Department of Labor, under the Occupational Safety and Health Act, as the permitted employee exposure level to vinyl chloride. The most recent Manufacturing Chemists Association safety data sheet for vinyl chloride reports this value. A copy of this data sheet is enclosed for your information.

In June of 1972, the American Conference of Governmental Industrial Hygienists (ACGIH) adopted an eight hour time weighted average Threshold Limit Value (TLV) of 200 ppm (vol/vol) for vinyl chloride. Documentation covering the considerations leading to the adoption of this value may be obtained by request to the Chairman, TLV Committee, American Conference of Governmental Industrial Hygienists, P. O. Box 1937, Cincinnati, Ohio 45201.

While the ACGIH adopted a 200 ppm level for vinyl chloride, the TLV Documentation cites studies which recommend levels from 50 ppm to 500 ppm. As you may be aware, the Manufacturing Chemists Association has contracted with independent consultants, on behalf of a group of vinyl chloride producers and consumers to conduct animal exposure studies and a comprehensive epidemiology study of vinyl chloride workers. It is hoped that results from these studies will aid in clarifying what exposure limitation would be most appropriate. However, until these results are available and in view of the range in recommendations, we considered it prudent in our operations to establish a vinyl chloride TLV of 50 ppm; further, measurements indicate that this is a feasible level for us. We urge you to give consideration to the vinyl chloride exposure levels which may be appropriate for your operations. —

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We would be pleased to make available our techniques for measuring low concentrations of vinyl chloride if you would consider them helpful.

Very truly yours,
SHELL CHEMICAL COMPANY

R. J. Reynolds
Manager, Vinyl Chloride
Business Center

Attachment: MCA Safety Data Sheet SD-56 (1972 Version)



DETERMINATION OF
VINYL CHLORIDE MONOMER IN AIR
Gas Chromatographic-Flame Detector Method

SCOPE

1. This method is intended for the determination of traces of vinyl chloride monomer (VCM) in air in the range from 5 to 1000 ppm v/v.

METHOD SUMMARY

2. A one-ml sample of air is analyzed by gas chromatography on either of two columns, having quite different selectivity, using a flame ionization detector. If a significant concentration is observed the identification of VCM is confirmed on another type of column. Results are calculated by comparison with a known standard.

Note 1. CAUTION. VCM is toxic and flammable and should be handled in a hood away from sources of ignition. The liquid should be kept cool to avoid polymerization. No copper or copper alloy should be used in contact with VCM.

APPARATUS

- 3.(a) *Chromatographs* with flame detector, sensitive enough to detect 10 ppm of VCM in one ml of air with at least 10% scale deflection on the recorder, under the conditions of the method.

(b) *Columns*, five feet long by 1/8-inch O.D., 0.012" wall, stainless steel tubing, one packed with 80-100 mesh Durapak Carbowax 400/Porasil C and the other with Durapak n-octane/Porasil C.¹

(c) *Accessories*, one-ml gas-tight syringe, 50-microliter gas-tight syringe, 100-ml glass sample cylinders, vacuum pump for evacuating these; or a bottle can be used which can be flushed with the air to be analyzed and then serum capped. If glass sample cylinders with stopcocks are used, the syringe needle must reach through the stopcock into the storage chamber.

Note 2. A coulometric detector in the chloride mode would provide specific response for organic chlorides, eliminating the risk of interference from non-chloride atmospheric contaminants. An electron capture detector would probably also be satisfactory but has not been tested for this

¹ Available from Waters Associates, Framingham, Mass.

application. Since the non-specific flame detector is used in this method two different types of column are employed to reduce materially the probability of an erroneous finding of VCM.

REAGENT

4. VCM, Matheson Company² or equivalent. A lecture bottle is convenient.

PROCEDURE

5. Set up the chromatograph as described in Table 1. Prepare a 100 ppm v/v VCM in air sample by adding 10 microliters of VCM vapor per 100 ml of air to a glass sampling vessel or to a serum capped bottle of known volume. The vapor can be obtained from the gas cap over the VCM liquid in the supply cylinder by venting the material at a moderate rate through a short length of tubing and sampling the exit end of the tubing with the 50 microliter syringe. Mix the blend by rotating the vessel in a random manner or by shaking with previously enclosed glass beads. Analyze one ml of this blend using either column and note the retention time and the peak height. Repetitive analyses should agree within about ± 5 ppm. Obtain samples of the air to be analyzed and analyze them in the same way. If VCM is found in significant concentrations repeat the calibration and analyses on the other column to confirm or refute the identification of VCM.

Table 1. Conditions for Gas Chromatography

Helium Carrier Gas: flowing 30-40 ml/minute.
Hydrogen: 30 ml/minute, adjusted for optimum response.
Air: 350 ml/minute.
Injector and detector temperatures: 50-150°C.
Column temperature: Isothermal in the range 20-25°C.

CALCULATION

6. Calculate the VCM content of the unknown air sample, using peak heights corrected for the attenuation, as follows:

$$\text{VCM, ppm v/v} = 100 \times \frac{\text{Peak height of unknown}}{\text{Peak height of standard}}$$

PRECISION

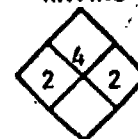
7. Limited data indicate that the precision is about ± 5 ppm at 100 ppm and about ± 2 ppm at the 10 ppm level.

² Matheson Company, LaPorte, Texas 77571



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HAZARD
RATING



MATERIAL SAFETY DATA SHEET

Information on this form is furnished solely for the purpose of compliance with the Occupational Safety and Health Act of 1970 and shall not be used for any other purpose. Use or dissemination of all or any part of this information for any other purpose may result in a violation of law or constitute grounds for legal action.

SECTION I	
MANUFACTURER'S NAME Shell Chemical Company	EMERGENCY TELEPHONE NO. (713) 473-9461
ADDRESS (Number, Street, City, State, and ZIP Code) P.O. Box 2463, Houston, Texas 77001	
CHEMICAL NAME AND SYNONYMS Vinyl Chloride, Chloroethylene, Chloroethane	TRADE NAME Vinyl Chloride Monomer (VCM)
CHEMICAL FAMILY Vinyl Halide	FORMULA

SECTION II HAZARDOUS INGREDIENTS*						
COMPOSITION	%	SPECIES	LD ₅₀		LC ₅₀	
			ORAL	DERMAL	CONCENTRATION	HOURS
Vinyl Chloride	100					
Vinyl chloride has anaesthetic properties at high concentrations (80,000-120,000 ppm). Cardiac arrhythmias have been found in dogs at these levels. Liver changes have been reported in rabbits at 200 ppm, but not in rats, guinea pigs or dogs. Studies on exposed workers over a 17 year period at a mean air concentration of 160 ppm failed to reveal any overt condition attributable to VCM. One Italian report in 1970 indicated tumor development in rats at 30,000 ppm.						

SECTION III PHYSICAL DATA			
BOILING POINT (°F)	7	SPECIFIC GRAVITY (H ₂ O=1) 20°	0.91
VAPOR PRESSURE (mmHg) @ 68° F.	2580	PERCENT VOLATILE BY VOLUME (%)	100
VAPOR DENSITY (AIR=1)	2.15	EVAPORATION RATE (_____=1)	
SOLUBILITY IN WATER	Slight		
APPEARANCE AND ODOR	Colorless, sweet smelling gas		

SECTION IV FIRE AND EXPLOSION HAZARD DATA			
FLASH POINT (Method used)	-108° F., T.O.C.	FLAMMABLE LIMITS	
		at ordinary temperature	3.6 33.0
EXTINGUISHING MEDIA	CO ₂ , dry chemicals		
SPECIAL FIRE FIGHTING PROCEDURES	Do not use water except as a spray or fog.		
	Wear self contained breathing apparatus.		
UNUSUAL FIRE AND EXPLOSION HAZARDS	Handle as an extremely flammable liquid and gas. Material		

SECTION V HEALTH HAZARD DATA	
THRESHOLD LIMIT VALUE	OSHA - 500 ppm (ceiling); ACGIH - 200 ppm (TWA); Shell - 50 ppm (TWA)
EFFECTS OF OVEREXPOSURE	See over. Also prolonged contact with skin results in freezing.
EMERGENCY AND FIRST AID PROCEDURES	
Remove victim to area free of vinyl chloride vapors. Give artificial respiration if necessary. Remove contaminated clothing to prevent freezing. Remove from eyes with large amounts of water.	

SECTION VI REACTIVITY DATA			
STABILITY	UNSTABLE	X	CONDITIONS TO AVOID Avoid sunlight and/or heat and exclude all oxygen
	STABLE		
INCOMPATIBILITY (Materials to avoid)		air, oxygen	
HAZARDOUS DECOMPOSITION PRODUCTS		H Cl, CO and phosgene on combustion	
HAZARDOUS POLYMERIZATION	MAY OCCUR	X	CONDITIONS TO AVOID air, sunlight and/or heat
	WILL NOT OCCUR		

SECTION VII SPILL OR LEAK PROCEDURES	
STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED	Remove all sources of ignition. Remove all personnel not wearing protection equipment shown in Sect. VIII. Use forced ventilation from explosion-proof equipment. Allow to evaporate.
WASTE DISPOSAL METHOD	Do not permit material to enter sewers. Use controlled evaporation. Guard against fire and explosion hazards.

SECTION VIII SPECIAL PROTECTION INFORMATION			
RESPIRATORY PROTECTION (Specify type)		Air pack or organic canister mask as required.	
VENTILATION	LOCAL EXHAUST	highly recommended	SPECIAL
	MECHANICAL (General)	Highly recommended - use explosion-proof equipment	OTHER
PROTECTIVE GLOVES	Rubber	EYE PROTECTION Chemical goggles and/or face shields	
OTHER PROTECTIVE EQUIPMENT		To prevent all contact with body as required.	

SECTION IX SPECIAL PRECAUTIONS	
PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING	Prevent any leakage. Provide sufficient ventilation to prevent high concentrations. Keep away from all sources of ignition. Handle as an extremely flammable material which is stored under pressure.

D. M. Sheets, Supervisor
Regulatory Affairs - Chemical Products
Shell Chemical Company
D.M. Sheets

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