

File: Vinyl Chloride / Ind. Hygiene.

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SHELL OIL COMPANY

ONE SHELL PLAZA
P.O. BOX 2463
HOUSTON, TEXAS 77001

March 28, 1974

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REGISTRATION

RAS 003863

Dr. T. R. Torkelson
The Dow Chemical Company
Ag - Organics Department
9008 Building
Midland, MI 48640

Dear Tork:

At the last meeting of the Technical Task Group on Vinyl Chloride Research, a number of the members asked for a copy of Shell's method of sampling and analysis for VCM.

Enclosed is a copy of the method which was developed at our Deer Park (Houston) Plant. If you have any questions regarding either the sampling or analytic method, please direct them to:

Mr. Richard E. Dilgren
Manager, Analytical
Shell Chemical Company
Deer Park, TX 77536
Phone: (713) 479-2331 Ext. 3134

Very truly yours,

Howard L. Kusnetz
Manager, Industrial Hygiene

Attachment



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

RAS 003864

SCOPE

1. This method is intended for the determination 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

- (i) Nylon Web Straps, 13-foot length. These straps are used to construct a harness to fit the worker and are used to support the air-sampling bag. See appendix for description.
- (j) Glass Syringe, 100-cc.
- (k) Hypodermic Needles, 1-1/2" length, 18-gauge.

PROCEDURE FOR 7- TO 8-HOUR AVERAGE SAMPLES

4. (a) Fasten the belt supporting the SKC Model 222-2 modified pump around the waist of the worker. The pump is worn on the worker's left side.
- (b) Fit a nylon webbing strap "jacket" equipped with a cloth sack to the operator. The cloth sack with inserted plastic bag is worn on the upper part of the worker's shoulders above chairback level. See Figures 1 and 2. Choose the proper 9" x 9" or 6" x 12" bag material according to the material expected to be sampled. See Tables I and II. In choosing the bag, consider bag loss and memory.
- (c) Attach the Teflon air intake line of the pump to the worker's collar by means of a spring-loaded clip, so that the open end of the line is 3 to 4 inches below the chin.
- (d) Route the Teflon tubing from the pump discharge over the worker's left shirt pocket, over the left shoulder, and across the back to the rubber serum stopper valve of the air bag. Secure the line in place by attaching it to the strap jacket supporting the cloth sack and bag by means of safety pins through tabs of glass tape wrapped around the line. Also pin the line to the cloth sack at the top edge of the sack between the shoulders. Inspect the line for best positioning so as not to interfere with worker's movement. Attach a 1-1/2-inch 18-gauge hypodermic needle, bent at a 90° angle, to the end of the pump discharge line and puncture the rubber serum stopper closure on the bag valve.
- (e) Turn the pump switch to the "ON" position. Note the time of day.
- (f) At the end of the 7- to 8-hour sample period, turn the pump switch to the "OFF" position, remove the sampling equipment from the worker. Note the time of day.
- (g) Before analysis, mix the contents of the plastic sampling bag by kneading. Withdraw air from the bag into a 100-cc glass syringe and return to the bag several times to make sure the air contained by the valve stem is the same as in the bag. Withdraw a measured volume of air for analysis by gas chromatography.
- (h) Recharge the pump battery for a 16-hour period before reuse.

NOTE: This pump has been found to have a constant pump rate over the 7- to 8-hour period. The pump rate should be verified once a week at the beginning and end of the shift. This can be done by attaching the pump discharge line to a soap film meter and timing the pump delivery with a stopwatch over a 5-minute period. The pump should be checked for proper working order each day before use by observing the volume of a single pulse (ca. 0.7-0.8 cc).

PROCEDURE FOR TAKING EXCURSION SAMPLES

NOTE: This procedure is used for taking samples for short periods of time from 10 minutes to 1 hour duration in areas of suspected higher-than-8-hour-average concentrations.

5. (a) Attach the Calibrated Instruments pump to a strap or web belt which can be worn loosely around the worker's neck with the pump resting against the worker's chest below the chin. See Figure 3. If the worker's duties involve bending over, attach a nylon strap around his body (under the arms) and through the strap supporting the pump. This prevents the pump from swinging away from the body when bending over.
- (b) Attach a cloth sack containing a plastic air bag to the strap or belt supporting the pump so the sack is positioned between the worker's shoulder blades. See Figure 4.
- (c) Route the 1/8" OD Teflon tube from the pump exhaust to the plastic air bag by going under the worker's left arm. Attach an 18-gauge needle, bent at right angles, to the end of the delivery tube and puncture the rubber serum stopper. Secure the delivery tube to the worker's clothing by means of safety pins pinned through tabs of glass tape wrapped around the delivery tube.
- (d) Turn the pump switch to the "ON" position and record the time of day.
- (e) When the sample has been collected, turn the pump switch to the "OFF" position and record the time of day.
- (f) Remove the sampling equipment from the worker.
- (g) Before analysis, mix the contents of the plastic bag by kneading the bag. Withdraw air from the bag with a 100-cc glass syringe and return the air to the bag several times to make sure the air contained in the valve stem is representative of the air in the bag. Withdraw a measured volume of air for analysis by gas chromatography.

BAG CLEANUP

6. Bags may be reused if they are cleaned after each use. The cleanup procedure is as follows:

Analytical Method HC-604-74

- (a) Puncture the serum stopper with an 18-gauge needle ^{and} evacuate the bag.
- (b) Fill the bag with clean water-pumped compressed air.
- (c) Evacuate the bag and fill with air.
- (d) Let the bag stand for 24 hours.
- (e) Repeat steps (a)-(d) as many times as necessary to reduce the bag memory to acceptable limits. Refer to Table II for bag memory data. Clean-up time is one day less than the cumulative time given in the table.

DOCUMENTATION

7. Record the following information in a bound permanent record book:

- (a) Name of the worker.
- (b) Job assignment or description.
- (c) Date of sample.
- (d) Time of day at start and end of sample period.
- (e) Bag material used to collect the sample.
- (f) Wind direction and speed.
- (g) Pertinent facts regarding conditions during period of taking the sample such as known high exposures and duration of high exposure, leaks, spills, etc.
- (h) Pump rate at beginning and end of sample period each time it is checked.
- (i) The analytical data for the sample.
- (j) The analyst should sign and date each page of the record book.

Houston Plant
March 5, 1974
WMA:oc

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APPENDIX

PUMP MODIFICATIONS

The SKC Model 222-2 pump can not be used as received to pump air into plastic bags. It was designed for drawing air through a trap. The major modifications consist of removing the supplied diaphragm pump and check valve and replacing them with a shortened 5-cc glass syringe to act as a pump and a different check valve. Figures 5 and 6 show the modifications from a side view and a top view.

The detailed procedure for modification of the pump is as follows:

1. Remove the three Phillips screws in the pump top. Lift the top and cut the rubber tubing inside. Raise the metal can surrounding the pump and drop the top cover through the can.
2. Loosen the three slotted screws in the bottom plate of the pump. This permits lifting the plate resting on top of the battery. Remove the screws holding the check valve and diaphragm pump. Discard the valve and diaphragm pump.
3. Enlarge one of the screw holes in the plate and insert an 8-32 x 2" flathead screw to serve as a pivot post for the syringe. Secure with a nut. See Figure 6 for proper location of pivot post.
4. Install a 6-32 x 2" flathead screw in one of the existing check valve screw holes. Secure with a nut. This screw will be used to secure the new check valve. See Figures 6 and 7.
5. Replace the slotted screws removed in Step 2 and position battery and clear plastic spacer in place between the bottom of the pump and the plate on top of the plastic spacer.
6. Cut a hole in the rubber sheet on the underside of the top cover plate of the pump. Refer to Figure 9 for the location. Use a 3/8" OD cork borer. Drill a 21/64" diameter hole in the metal cover. Install a 1/8" stainless steel 316 Swagelok Bulkhead Union (200-61-316) in the hole. Blow all metal fragments from pump.
7. Remove the screw holding the ball bearing race. Save parts.
8. Loosen the Allen head screws in side of the top 1-5/32" diameter aluminum drive disc. Lift off the disc.
9. Drill a hole through the disc, 6 mm off center, and tap with 5-40 threads.
10. Replace the drive disc and tighten the Allen head screws.
11. Cut a 9/16" length of 1/4" OD stainless steel tubing. Remove burrs from inside tubing. Secure a 20-gauge needle hub to the tubing by either cementing with epoxy cement or by silver soldering. The position of the needle relative to the tubing is 90°. When the epoxy cement has cured, make a bend in the 20-gauge needle close to the hub. The bend should be a 90° bend and downward. Refer to Figure 5 for correct position.

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Analytical Method HC-604-74 - Appendix

12. Using a glass saw, cut a 5-cc glass syringe with metal Luer-Lok tip at the 2.4-cc mark. Cut the plunger $1/16$ " longer than the syringe barrel.
13. Machine a brass plug to fit snugly inside the sawed-off glass plunger. Dimensions are $3/8$ " length, 0.33" diameter. Drill a hole (0.1015" diameter, #38 tap drill size) longitudinally in the center of the plug.
14. Cut a $7/8$ " length of $1/4$ " stainless steel tubing (remove burrs) and slip over the pivot post for the syringe.
15. Cut the connecting pin, which formerly connected the ball bearing race to the pump diaphragm, in half.
16. Screw one-half length of the connecting pin into the ball bearing.
17. Fasten the ball bearing to the aluminum drive disc with a 5-40 x $1/2$ " r und-head screw. Place enough flat washers under the bearing to raise it enough so the glass plunger will clear the top surface of the drive disc when the syringe is at the end of the intake stroke.
18. Carefully measure the distance from the base plate to the center of the piston rod. Add sufficient flat washer spacers to the pivot post to obtain the same measured distance between the base plate and the center of the syringe needle.
19. Apply epoxy cement to the inside of the glass plunger (the first $1/2$ " of the open end), the outside walls of the brass plug, and the hole in the plug. Remove the ball bearing from the disc. Assemble as a unit the ball bearing, piston rod, brass plug, glass plunger, syringe barrel, and needle hub. Lower the unit into place, slipping the needle hub over the pivot post and secure the bearing in place over the proper number of flat washers. Tighten the screw holding the bearing.
20. Start the motor and rotate the drive disc until the bearing is at the position of full compression. Stop the motor. Position the plunger in the syringe barrel to read zero volume. Position the brass plug in the open end of the syringe plunger. Let the epoxy cement cure with the parts remaining in this position.
21. Apply a "dot" of epoxy cement to the piston rod where it screws into the ball bearing race to prevent its unscrewing during later use. Also, apply epoxy cement to the juncture of the Luer-Lok tip portion of the syringe barrel and the needle hub to prevent loosening of the syringe barrel during later usage.
22. When the epoxy cement has cured, start the syringe motor and let it operate and inspect to see if properly aligned. A slight up-and-down motion of the needle hub on the pivot post is permissible. Slip one flat washer over the pivot post and then two nuts. Position the bottom nut so there is space the thickness of a washer remaining between the washer and the nut at all times during operation of the syringe. Do not tighten to bind the syringe. Tighten the second nut against the first nut to lock both nuts in place.

23. Fasten the new check valve [No. 3094(470V) valve from a Becton-Dickinson No. 3560 filling outfit, Curtin No. 221-523] to a 6-32 x 2" flathead screw installed in Step 4. Secure by wire or any other convenient means.
24. Attach an adapter (female Luer slip to 1/8" ID tubing, Becton-Dickinson Part No. L/606) to the discharge end of the check valve. Attach another adapter (Becton-Dickinson No. H/468L, male Luer-Lok slip to 1/8" ID tubing) to the syringe end of the check valve. See Figure 7.

NOTE: The adapters in Steps 24 and 25 are not shown in the photograph of an early model check valve. A later model uses the adapters.

25. Slip a 3" length of 1/16" OD Teflon tubing over the syringe needle and insert the other end inside the adapter on the syringe end of the check valve. Epoxy cement in place on the check valve adapter.
26. Cut a 5-1/2" length of 1/8" OD Teflon tubing. Attach one end to the adapter on the check valve discharge. Use a short sleeve of Tygon tubing to slip over the adapter and the Teflon tubing. Butt fit the Teflon tubing against the adapter so there will be minimum contact of sample with Tygon. The other end of the Teflon tube will be attached later to a 1/8" stainless steel 316 Swagelok bulkhead union, installed in the top cover of the pump.
27. Cut a 2-1/2-foot length of 1/16" OD Teflon tubing and attach to the check valve intake. Insert one end inside a one-inch length of 15-gauge SW Teflon spaghetti. This is a tight fit. Insert the end of the 15-gauge spaghetti into a 1/2" length of 1/8" OD Teflon tubing with an ID of 0.09". Butt fit the assembled pieces of Teflon tubing to the check valve intake with a short sleeve of Tygon tubing. If any part of the smallest Teflon tubing protrudes inside the check valve entrance, make sure it does not touch the small rubber poppet valve inside the check valve. Apply epoxy cement at the junctures of the various pieces of tubing. Let cure.
28. Remove the stainless belt loop on the side of the pump can and replace it with a loop that will accommodate a large belt. See Figure 8 for dimensions of the new loop.
29. Reassemble the pump inside its container. Pull the top cover through the can as the can is lowered over the pump. Slip the 2-1/2" x 1/16" Teflon air intake tube through the air intake hole in the top of the can. Attach the 5-1/2" length of 1/8" OD Teflon tubing from the discharge of the check valve to the bottom end of the bulkhead union. When everything is in place, fasten the top cover in place with the three Phillips screws.
30. Attach a spring-loaded clip to the end of the air intake tube as the tube may be attached to the worker's collar. A glass tape tab may be formed around the Teflon tubing and the clip can be fastened to the tab.
31. Cut a 2-1/2-foot length of 1/8" OD Teflon tubing. Attach one end to the Swagelok bulkhead union on top of the pump cover. This tube is the pump discharge line. To the other end attach an adapter (Becton-Dickinson male Luer-Lok slip to 1/8" ID tubing, Part No. H/468L). Using a sleeve of Tygon tubing, butt fit the Teflon against the adapter.

32. Attach fiberglass tape tabs at various locations along the length of the pump discharge line so the line can be pinned to the strap harness used to support the plastic bag. Loops in the line that interfere with the worker's movements must be avoided.
33. Bend a 1-1/2-inch length 18-gauge needle at right angles midway on the length of the needle. This needle will be attached to the Luer-Lok adapter on the end of the pump discharge line and penetrate the rubber serum stopper closure of the plastic bag.

GAS SAMPLE BAGS

Before using the plastic sample bags, open the Halkey-Roberts valve wide open. Seal around the base of the valve stem with epoxy cement to prevent the valve from leaking in the open position. The valve openings are closed with rubber serum stoppers.

Stick two 2-inch lengths of plastic electrical tape, criss-cross fashion, to the bag on the side opposite the valve. This protects the bag from punctures caused by pressing the metal valve against a hard surface during cleaning the bag or changing septums.

New aluminum foil-polyester bags should be leak tested before use. This can be done by inflating with clean air and immersing under water. Leaks are sometimes found at the sealed edges of new bags.

STRAP HARNESS FOR 7- TO 8-HOUR SAMPLES

A nylon strap harness was constructed to support a cloth sack containing the plastic air bag. It is not desirable to pin the cloth sack directly to the worker's clothing. In cold weather, the worker often needs to wear a coat. It is undesirable to wear the coat over the bag. If all of the air lines and air bag are attached to the strap harness, he may remove the harness with sampling equipment intact while putting his coat on or taking it off and then return the strap harness to its normal wearing position.

The harness may be constructed from nylon strap tie-downs for automobile car top carriers. These are available at auto accessory stores. Approximately 13 feet of material is needed.

The harness consists of a waistband with a buckle on one end, a shoulder strap over each shoulder, a horizontal strap across the shoulders, and buckle straps in an area below the chin. The waistband is cut to 50 inches length. The two shoulder straps (42" each) are sewed to the waist band at a point 20 inches from the buckle. The other end of one of the shoulder straps is sewed to the waistband at a point 5 inches from the buckle. A loop is sewn in the other end of the second shoulder strap so the waist band can slip through the loop. A strap 11 inches long is attached to each shoulder strap 20 inches from where the shoulder straps attach to the waistband in the back. This forms a horizontal strap across the shoulders for attaching a cloth sack. Short 6-inch straps, one with a buckle, are sewn to each shoulder strap at a point 15 inches above where the shoulder straps attach to the waistband in front of the worker.

BAG LOSS

Bag loss data for Teflon bags and the aluminized-polyester bags were determined by preparing a mixture of the organic chlorides at the 5- and 40-ppm level in 1000 cc of air in each bag. Each mixture was analyzed in duplicate immediately after make-up and again after standing 8 hours and 24 hours. The loss of peak area (FID detector) for each component was calculated as the percent loss of component. The experimental data are summarized in Table I.

BAG MEMORY

Teflon and aluminized-polyester bags were filled with 1000 cc of an air mixture of the organic chlorides at the few multiples of 10 ppm level and stored for 24 hours. The bags were then evacuated and filled with air several times to get rid of the concentrated air mixture. One thousand cc of clean air was measured into each bag, and the bag was allowed to stand for 24 hours at room temperature before analysis. After analysis, the bags were emptied and flushed as above and again filled with 1000 cc of air and allowed to stand for 24 hours before analysis. This process was repeated after each 24-hour period.

The bag memory samples were analyzed by gas chromatography with an FID detector. Preconcentration of the sample was achieved by trapping sample sizes ranging from 100 cc to 600 cc in a liquid-nitrogen-cooled trap before charging to the gas chromatograph. The experimental data are given in Table II.

In determining the time of cleanup required for reuse of the bag, it must be remembered that the cleanup time is one day less than the cumulative number of days in the table. For example, if the bag was cleaned for one day followed by air removal and the bag was used on the second day, the value in the table for the second day is the contribution from the bag to 1000 cc of sample for a 24-hour period. If an eight-hour sample were taken and analyzed immediately, the bag memory effect would be less than shown in the table.

TABLE I
RAG LOSS DATA

	<u>Teflon (6" x 12")</u>			<u>Aluminum-Polyester (9" x 9")</u>		
	<u>Initial ppm (v)</u>	<u>Storage Time</u>		<u>Initial ppm (v)</u>	<u>Storage Time</u>	
		<u>8-Hr, % Loss</u>	<u>24-Hr, % Loss</u>		<u>8-Hr, % Loss</u>	<u>24-Hr, % Loss</u>
Vinyl Chloride	5	-1	-6	4	-1	-2
	43	-2	-7	44	0	-2
Ethyl Chloride	5	0	-5	4	0	-1
	46	-4	-7	44	0	-1
Isopropyl Chloride	6	0	-4	5	0	-1
	49	-2	-5	47	0	-1
Allyl Chloride	8	-2	-9	5	-1	-4
	54	-4	-9	52	-1	-3
Ethylene Dichloride	4	-8	-19	4	-7	-18
	41	-7	-19	33	-1	-6
1,2-Dichloro- propane	5	-4	-15	3	-4	-10
	33	-7	-17	25	-3	-4
cis 1,3- Dichloropropene	-	-	-	3	-8	-24
	35	-12	-29	24	-9	-13
Epichlorohydrin	5	0	-26	2	-7	-40
	27	-2	-28	20	-6	-19
trans 1,3- Dichloropropene	5	-18	-42	2	-11	-35
	33	-11	-35	19	-8	-17
1,2,3-Trichloro- propane	2	-13	-45	1	-12	-25
	11	-22	-47	4	-21	-20

TABLE II
BAG MEMORY DATA

TEFLON (6" x 12")

	Initial Exposure ppm (v)	ppm (v)				
		Day 1	Day 2	Day 3	Day 4	Day 5
Vinyl Chloride	40	0.5	0.09	0.05	0.02	0.06
Ethyl Chloride	42	0.5	0.01	0.01	N.D.	0.01
Isopropyl Chloride	57	0.7	0.06	0.03	0.03	0.02
Allyl Chloride	67	1.9	0.08	0.02	0.02	0.02
Ethylene Dichloride	35	2.1	0.13	0.04	0.02	0.02
1,2-Dichloropropane	41	2.2	0.22	0.09	0.06	0.06
cis 1,3-Dichloropropene	31	2.7	0.29	0.06	0.03	0.01
Epichlorohydrin	44	3.4	0.27	0.07	0.05	0.01
trans 1,3-Dichloropropene	45	4.2	0.41	0.10	0.06	0.03
1,2,3-Trichloropropane	16	1.3	0.22	0.22	0.10	0.09

ALUMINIZED-POLYESTER (9" x 9")

	Initial Exposure ppm (v)	ppm (v)				
		Day 1	Day 2	Day 3	Day 4	Day 5
Vinyl Chloride	40	0.4	0.09	0.08	0.06	0.05
Ethyl Chloride	42	0.4	0.04	0.03	0.02	0.01
Isopropyl Chloride	57	0.9	0.03	0.01	<0.01	<0.01
Allyl Chloride	67	1.6	0.16	0.09	0.07	0.05
Ethylene Dichloride	35	2.1	0.29	0.13	0.10	0.08
1,2-Dichloropropane	41	3.5	0.51	0.13	0.06	0.05
cis 1,3-Dichloropropene	31	2.5	0.43	0.18	0.11	0.09
Epichlorohydrin	44	4.5	0.87	0.49	0.31	0.25
trans 1,3-Dichloropropene	45	4.0	0.86	0.46	0.32	0.24
1,2,3-Trichloropropane	16	1.7	0.72	0.65	0.33	0.24

R&S 003876



Figure 1. FRONT VIEW OF WORKER AND EIGHT HOUR SAMPLING EQUIPMENT

R&S 003677



Figure 2. REAR VIEW OF WORKER AND EIGHT HOUR SAMPLING EQUIPMENT

R&S 003878



Figure 3. FRONT VIEW OF WORKER AND EXCURSION SAMPLING EQUIPMENT



R&S 003880

Figure 4. REAR VIEW OF WORKER AND EXCURSION SAMPLING EQUIPMENT

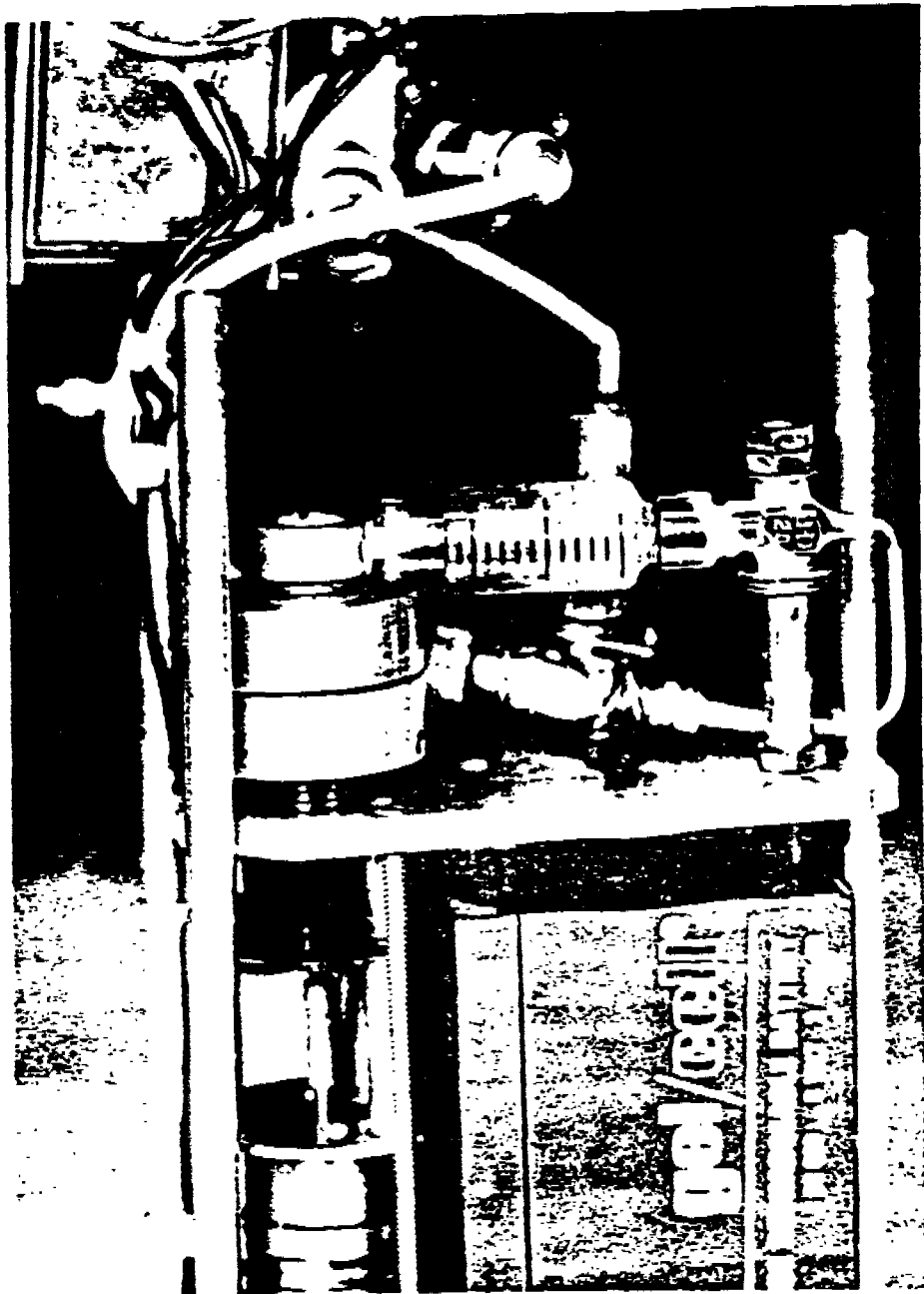


Figure 5. SIDE VIEW OF MODIFIED PUMP, CASE REMOVED

R&S 003681

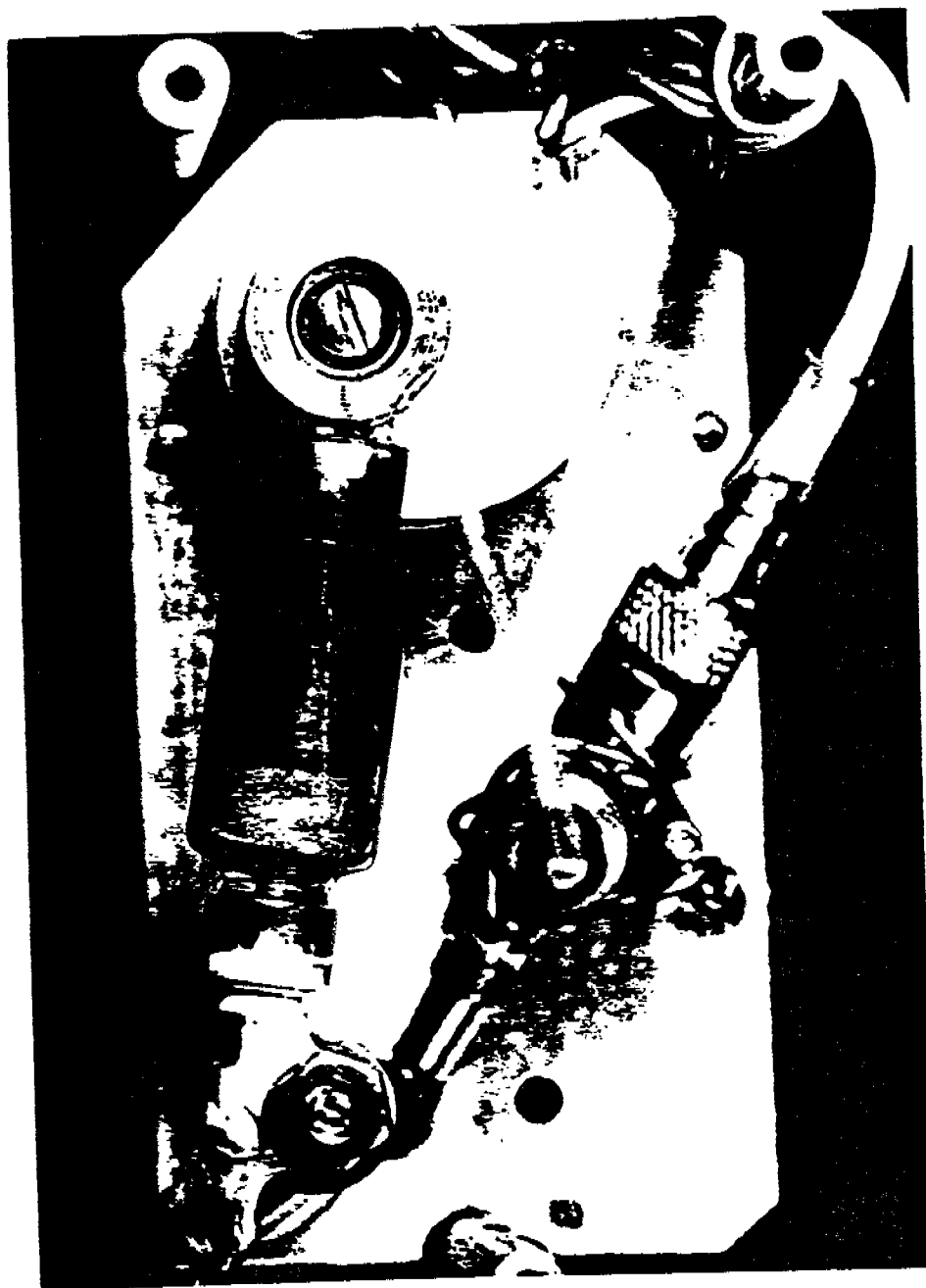


Figure 6. TOP VIEW OF PUMP MODIFICATIONS

R&S 003883

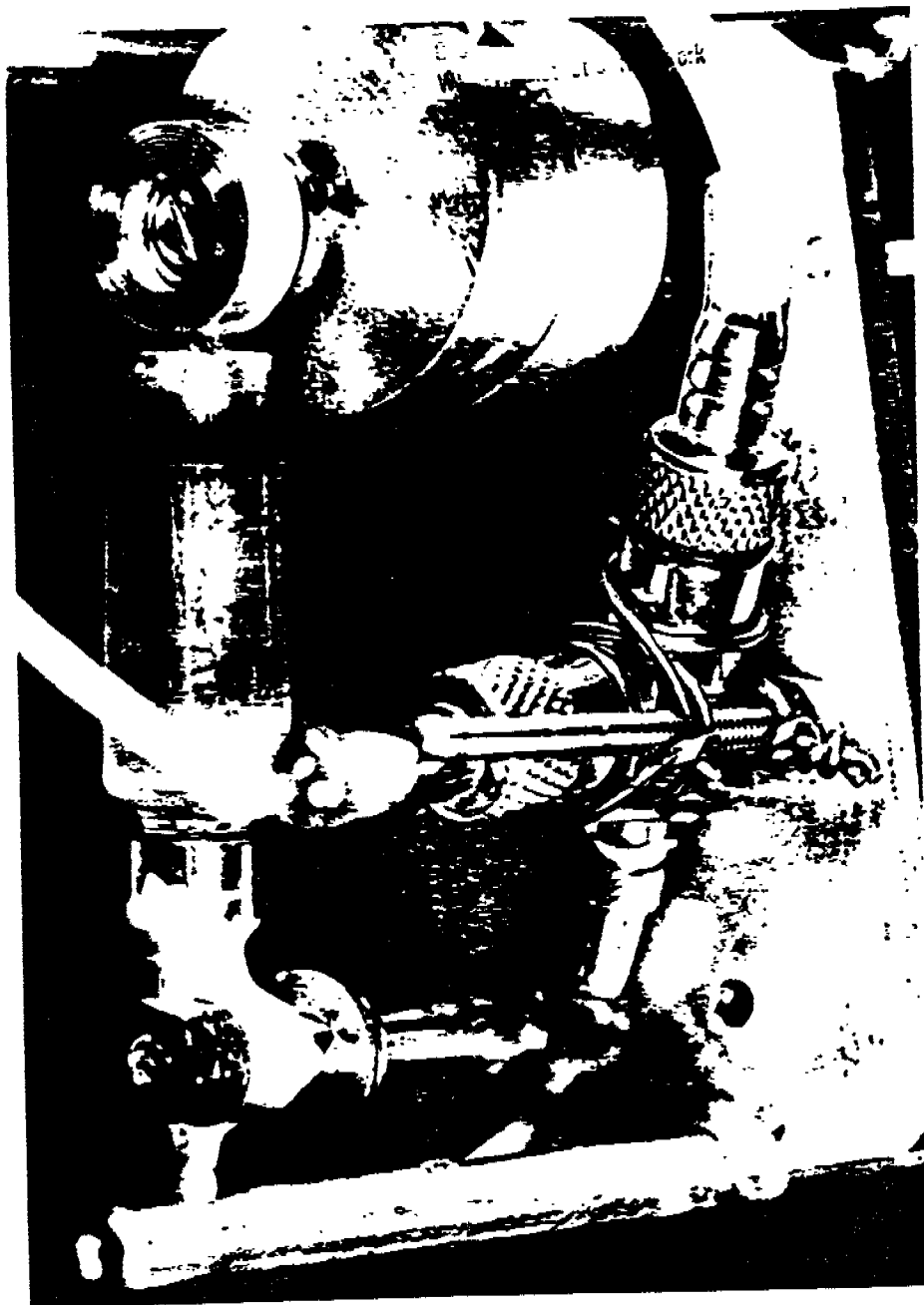


Figure 7. SIDE VIEW OF CHECK VALVE INSTALLATION

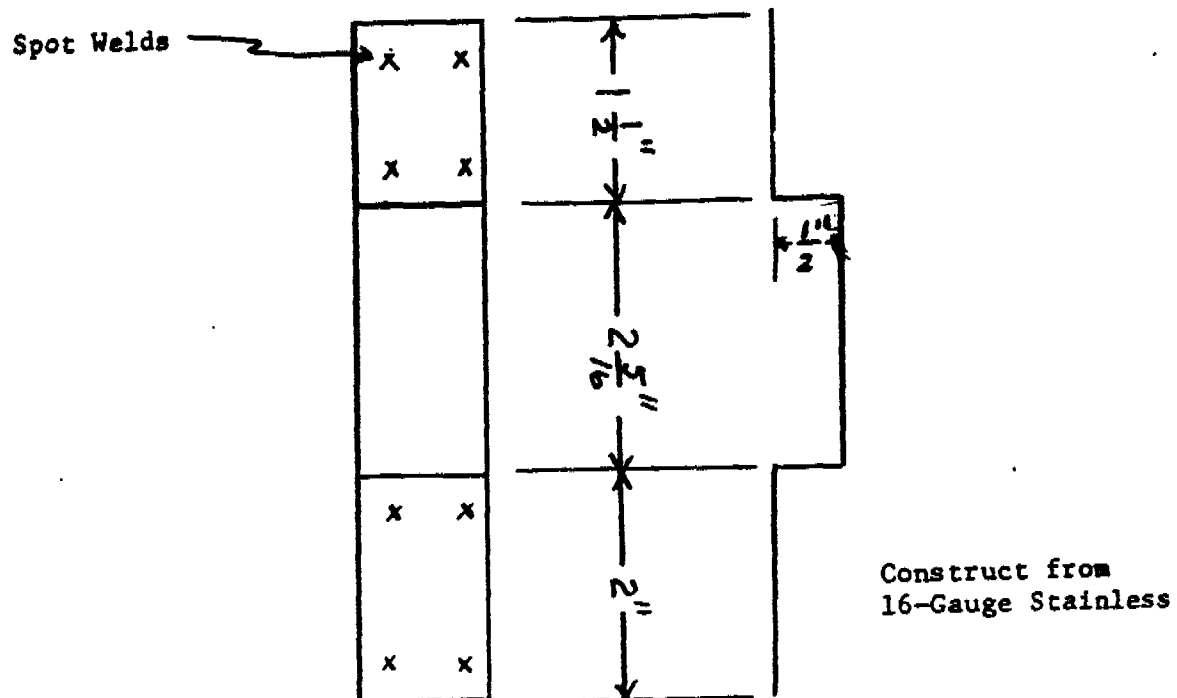


FIGURE 8. BELT LOOP STRAP FOR PUMP

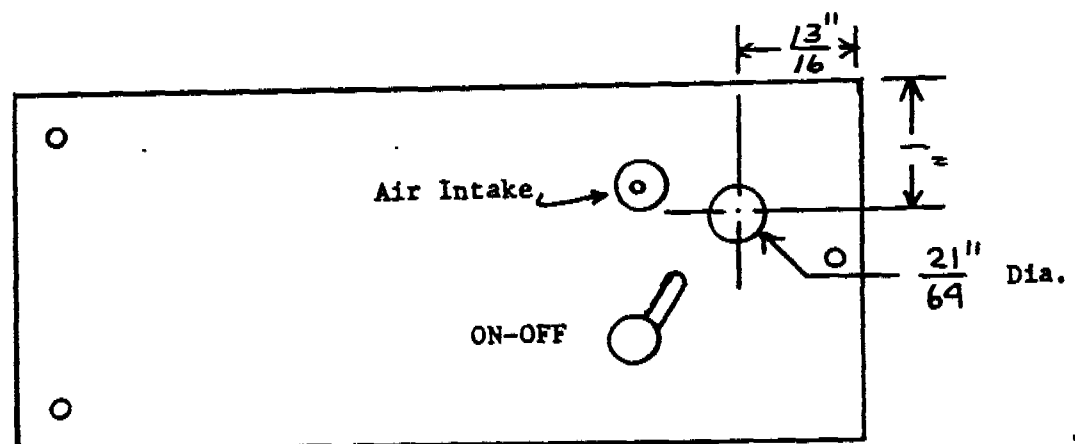


FIGURE 9. TOP VIEW OF TOP PUMP COVER

R&S 003884

SHELL CHEMICAL COMPANY
HOUSTON PLANT

ANALYTICAL METHOD HC-604-74-

PROCEDURES FOR SAMPLING AMBIENT AIR IN WORKER ENVIRONMENT

SCOPE

1. This method describes procedures for taking 7- to 8-hour average samples of ambient air from the workers' environment. Procedures are also described for taking excursion samples of short duration.

METHOD SUMMARY

2. The worker wears a pump which pumps air from his breathing zone into a plastic bag worn on his back. At the end of the sample period, the air in the bag is mixed by kneading the bag to give an average sample for the sample period. The sample is analyzed by gas chromatography.

APPARATUS

3. (a) Personal Pump, Model 222-2 available from SKC, Inc., P. O. Box 8538, Pittsburgh, Pa. 15220. The pump must be modified as described in the appendix. This pump is used for collecting 7- to 8-hour average samples.
- (b) Battery Charger for above pump, available from SKC, Inc.
- (c) Personal Pump, nominal pump rate 0.0772 liter/minute, available from Calibrated Instruments Co., 731 Saw Mill River Road, Ardsley, N. Y. 10502. This pump is used for excursion-type samples.
- (d) Gas Sample Bags, aluminum foil-polyester laminate, Halkey-Roberts No. 30 AC valve, assorted sizes: 9" x 9", 1.5-liter capacity; 12" x 18", 7-liter capacity. Available from Calibrated Instruments Company.
- (e) Gas Sampling Bags, Teflon, FEP, Type A, 5-mil thickness, Halkey-Roberts No. 30 AC valve, assorted sizes: 9" x 9", 1.5-liter capacity; 12" x 12", 4-liter capacity; 15" x 15", 9-liter capacity. Bags are available from Fluorodynamics, Inc., Diamond Stat Industrial Park, Newark, Delaware 19711. The following sizes are also available from Alltech Associates, 202 Campus Drive, Arlington Heights, Illinois 60004: 6" x 12", 1.8-liter capacity, Cat. No. 4120X4100; 8" x 12", 2.6-liter capacity, Cat. No. 4122X4100; 10" x 12", 3.5-liter capacity, Cat. No. 4124X4100.
- (f) Belt, Motorola Part No. NLN-6352-A.
- (g) Rubber Serum Stoppers, sleeve type, plug OD 11 mm, sleeve OD 17 mm.
- (h) Safety Pins.

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INVESTIGATION OF THE DISEASES PRODUCED BY VINYL CHLORIDE

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The rapid development of the polyvinyl chloride industry in our country has raised for us a problem in industrial hygiene, toxicology and occupational pathology.

In the aim of investigating this problem, a group of hygienists and clinicians have examined the conditions of work and the diseases affecting the workers of two plants manufacturing polyvinyl chloride.

The clinical manifestations encountered raise the problem of interpretation of the etiopathogenesis, of theoretical as well as practical importance, and of defining the clinical picture as well as of the necessary preventive and therapeutic measures.

Our study was necessary in view of the fact that the existing scientific facts at our disposal were few and lacking in detail, especially as regards the observed clinical manifestations.

Danishevskii (1) had demonstrated that the monomers, the starting products, exert an aggressive action from the biologic point of view. They have the property of producing destruction of the skin and of the mucosa. Some of them are allergens. They act on the parenchymatous organs by producing degenerative changes and on the hematopoietic system, leading to an anemia of hemolytic type.

Hervieux and Tessier (11) found, among 145 workers of a polyvinyl plastics factory, 17 cases of chemical dermatitis.** Pletsitzer, Bondar and Smirnova (cited by Danishevskii), in studying the chronic effects of the vapors of vinyl chloride, observed in man the development of toxic angioneurosis.

* Dr. Lefevre gives the reference as Medicina interna 6, No. 8:963-77, 1962; in Index Medicus (5:K-1277, 1964) the above reference is given. The original is being ordered.

** In fact, in their account, the authors speak of 17 cases of "intolerance" or only 10 cases of pruritus, without eruption, of the forearms and of the face appearing in the summer, as seeming to be due possibly to vinyl chloride.

Th so few clinical studi s have not permitted, at th pr s nt tin , the characterization of a clinical picture.

Concerning experimental work, Mastromatteo, Fischer, Christie and Danziger (7) in studying the toxic action of vinyl chloride on a group of 5 rats, 5 mice and 5 guinea pigs, demonstrated the appearance of congestion of the liver and lungs after repeated exposure to narcotic doses of 10, 20 to 30%. In the animals that were sacrificed or that died during exposur , a congestion of the liver and kidney, and in some cases, even a fatty degeneration of the liver were observed.

Among the toxic substances, Lazareev includes vinyl chloride among the mild narcotics.

In pursuing the study of the clinical symptomatology of workers exposed to the monomer vinyl chloride, and by means of laboratory tests, we concluded that our findings permit the definition of a clinical picture which may aid the practicing physician in the recognition of the first symptoms of acute or chronic intoxication by vinyl chloride and of recommending measures f r prevention and treatment.

Laboratory studies have added some data concerning the mechanism of the pathogenesis of these intoxications.

These circumstances have convinced us to publish our findings.

Material and Method of Investigation

In the course of 4 years, we have had under observation 168 workers engaged in the manufacture of polyvinyl chloride (PVC) in two factories: 54 workers in plant "A" and 114 in plant "B".

For the most part, the subjects were young, below 30 years of age and have never worked in any other industry.

Pre-employment medical and detailed laboratory examinations were carried out in order to prevent the hiring of those who would present some contraindications. Records were maintained in the personnel file for each employee of the results obtained in the course of routine medical examinations and on the occasion of the thorough examination, clinical as well as laboratory, done annually.

In addition to the medical examination, the following laboratory analyses were done: -

Dysproteinemia test

Electrophoresis of serum proteins

BSP hepatic "clearance"

Cold pressor tests

... Digital plethysmography in certain cases.

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The cases that exhibited clinical nervous, digestive, cutaneous and angioneurotic manifestations, were routinely hospitalized in the clinic for occupational diseases in order to carry out the complex laboratory tests and to establish therefrom, if possible, the cause of the intoxication.

Thereafter, it was necessary to examine the clinical manifestations and the results of the tests in order to characterize the clinical picture and to formulate preventive measures.

Results and Discussion

We have observed that at first contact with the poison, most frequently at the time of changing the charges, during emptying or leakages due to various causes, particularly the nervous manifestations appeared. After 3 months to 1 year of employment, digestive disturbances were added to the nervous disorders. In certain cases, the nervous manifestations changed into angioneurotic manifestations (Raynaud syndrome); finally, in other cases there was scleroderma or chemical dermatitis. At times, all these disturbances appeared at the same time (see clinical observations).

In order to characterize this clinical picture more clearly, we are presenting the objective symptomatology observed in its increasing order of disturbances, so that the physician may recognize this intoxication from its first symptoms. We are describing them with the frequency found for the various clinical manifestations so that their significance may be appreciated.

In the order of appearance of the symptomatology produced by vinyl chloride, we shall arrange them into the following groups of manifestations: nervous, digestive, angioneurotic, and cutaneous.

Nervous Disorders

Certain workers stated that at the first exposure to the monomer, or vinyl chloride, the first inspirations have an agreeable taste which they could not define exactly. This is compatible with the opinion of Sebit (cited by Danishevskii) who stated that the monomer, or vinyl chloride, has a pleasant ethereal taste, and with the opinion of Lazareev (4) who holds that this substance cannot be tasted except at narcotic doses of 7 to 10%.

After several inspirations, a euphoric state sets in; 11% of the subjects sing, whistle or laugh. (The euphoric state and the pleasant taste persist for only a short time). Most often, during exposure to the poison, the subjects experience a heavy feeling in the legs, are no longer able to coordinate movements and become dizzy (47%). According to them, this state is similar to alcohol intoxication.

These disturbances occurred most frequently in the course of the manufacturing process, at the end of the charge, during the discharge of latex, as at other times when the monomer is released in concentrations as high as, according to Petro (9), 5.5 mg./m^3 which is greatly in excess of the maximum permissible limit of 0.03 mg./m^3 .

*1.2 about
2.5 ppm*

Translator's note: (applicable to Romania). In the USA, the TL is 0.03 mg./m^3 or 500 ppm.

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Subsequently, in 45% of the cases, a somnolence sets in, which diminishes alertness and can occasion work accidents.

After a stay in the open air, the symptoms diminish progressively, then disappear.

In the case of 6 workers who were engaged in the repair of certain defective parts, complete narcosis appeared, which disappeared after they were removed into the open air.

After a period of several months of working in this environment, a state of somnolence persists after working hours. At home, the subjects exhibit a hypersomnia, sleeping between 9 and 14 hours a day. One person slept, with a brief interval, continually for two days. The sleep is deep, without dreams.

From this point of view, particular attention must be paid to night work, because the workers could easily fall asleep at the work site.

When there is an abundance of vinyl chloride vapors, there are complaints of formication of the lower extremities followed by a sensation of heat over the entire body.

Since the monomer vinyl chloride is lighter than air, it could be that it acts directly on the integument; this would agree with the opinion of Danizewski (1).

Anorexia, attributed to the toxin in 23% of the cases, sets in rapidly.

In 12% of the cases loss in weight of 4 to 17 kg. occurred.

After repeated exposure, headaches are reported (36% of the cases), nervousness (9%), faulty memory (3%), insomnia (3%) and a general asthenia (7%).

These symptoms indicate the establishment of a neurologic asthenia subsequent to more prolonged exposure to the poison.

We wish to point out that in most of the cases, we have observed these clinical symptoms without considering the significance of the resistance of the organism.

In general, after the first symptoms, protective measures for the workers were instituted so as to prevent the appearance of acute intoxication.

According to existing knowledge, it seems that the poison has a momentary narcotic action, even after repeated exposure.

In certain cases, a neurologic asthenia sets in.

Digestive Manifestations

After a variable period of time, in the course of which the neurologic manifestations predominate, digestive symptoms appear.

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The first symptom which presents itself is anorexia (23% of the cases). This indicates a general intoxication. Subsequently, vertigo appears (in 18% of the cases) and, more rarely, edema.

Later, pains in the epigastric region follow (16% of the cases), a feeling of discomfort, of heaviness, of pressure in the right hypochondrium (7% of the cases) or of the left hypochondrium (5% of the cases).

The patients present pains, of the boring type, which however do not assume the nature of pancreatic attacks. All express a distaste for fats.

Upon objective examination, in 30.2% of the cases, a hepatomegaly without icterus has been established. The liver exceeds by the costal border 2 to 3-finger widths without a lowering of the upper limit of the liver. Upon repeated examinations we have found that the border of the liver has an elastic consistency, then becomes harder and acquires the consistency of epidemic hepatitis.

We have found that 6% of the hepatomegalies became later complicated by splenomegaly. After removal from exposure, without other treatment, the hepatomegaly regressed and in the majority of the cases, the overall condition became normal.

Our observations show that in many cases hepatomegaly develops without any association with the digestive symptoms.

We have observed the fact that in 6.8% of the cases who had formerly experienced epidemic hepatitis, the hepatomegaly had appeared more rapidly, although at the time of their employment in the factory, the liver was within normal limits.

The enlargement of the liver pointed out to us the difficulty of an etiopathogenic interpretation.

The question arose of the diagnosis of toxic hepatomegaly or of that due to anicteric virus infection. This is why most of the patients afflicted with hepatomegaly were hospitalized in the department of occupational diseases.

Granted that:

the hepatomegaly appears after repeated exposure to the poison;

the border of the liver is of soft and uneven consistency;

the hepatomegaly disappeared after change in work without other treatment;

it appeared in a group of people who were subjected to treatment by injection among whom there were cases of epidemic hepatitis;

in spite of the absence of these manifestations in the other sections of the industry, it had not been supposed, at first, that the enlargement was of toxic nature.

The hypothesis of an occupational origin is favored also by the fact that in patients subjected to chronic intoxication by lead or mercury, before the

establishment of attacks of developing illness (leucocytosis) we can observe a similar hepatomegaly which disappears after treatment with EDTA (10).

Laboratory tests carried out by us were:

electrophoresis of serum proteins

thymol reaction

zinc sulfate test

bromsulphalein (BSP) test, and

liver biopsy.

Electrophoresis of serum proteins (see Table I in Appendix) shows among the 36 cases with hepatomegaly:

a diminution of albumin, below 53%: 11 times;

an increase of more than

5% of α_1 -globulins: 10 times

9% of α_2 -globulins: 20 times

13% of β -globulins: 9 times

21% of γ -globulins: 10 times.

This shows that the electrophoretic pattern is identical with that of viral hepatitis - in which principally the α_2 -globulin is increased.

We noted that the thymol reaction, the zinc sulfate, and the Greenstedt tests were positive only in 6 cases which shows us that in the determination of the disturbances, the electrophoresis of serum proteins is of particular value.

Two cases of 11 showed a pathologic change in response to the BSP test, indicating that the liver lesions are not localized in the parenchyma.

Since we have found hepatomegaly without protein changes and with a normal BSP, one might be led to believe that the poison produces a transient congestion of the liver, identical with that demonstrated experimentally; this in turn shows that the hepatomegalies which we have observed are of toxic nature.

As a result of repeated intoxication, the congestion can change into a toxic acute hepatitis, accompanied by electrophoretic changes similar to those of viral hepatitis, and finally, these lesions can become chronic. In 2 cases in which hepatomegaly persisted for more than a year and in which the border of the liver was of firm consistency, a liver biopsy revealed the picture of chronic hepatitis.

Among 20 patients with hepatomegaly, the serum aldolase was found to be increased between 0.75 mg. P and 1.200 mg. P in 17 cases (Manta, Muresan and Sirbu) (6), which demonstrates that the aldolase level is the most sensitive test.

A fact to be kept in mind is that we have also found a modification of the protein metabolism among workers exposed to the toxin who were not afflicted with hepatomegaly (see Table II).

Of the 26 cases examined, we found:

an albumin level lower than 53%: 14 times,

an increase of more than 5% of α_1 -globulins: 6 times

9% of α_2 -globulins: 16 times

13% of β -globulins: 8 times

25% of γ -globulins: 3 times.

This shows us that disturbances of the protein metabolism can precede hepatomegaly in certain cases, and that the poison sufficiently influences this metabolism.

Therefore, the hepatomegalies that we have found are principally of toxic nature. At first, they are in effect congestive, and later they assume the forms of acute hepatitis, identical with anicteric viral hepatitis; certain ones of them can become of chronic nature.

We wish to emphasize the fact that the disturbances of the protein metabolism can appear in certain cases before the onset of hepatomegaly.

Our investigations show that electrophoresis of serum proteins and determination of aldolase activity are of greatest importance in the biochemical diagnosis.

At the last examination, in 9% of the cases, a dyspeptic syndrome of ulcerating type was demonstrated, although we were unable to discover any radiologic changes to this effect.

In the knowledge of the predominantly narcotic action of the poison, it is more probable that the derangement of the cortical dynamics after repeated exposure leads to a disturbance of the diencephalic centers which comes into play in the pathology of these manifestations.

We continue our observations.

Angioneurotic Manifestations

These were demonstrable in 6% of the cases in the form of the Raynaud syndrome. (Distribution as to sex: 3/4 of the cases were men.)

We might mention the fact that in 3.6% of the cases with Raynaud's syndrome, there was also scleroderma and hepatomegaly.

In order to illustrate the clinical picture more clearly, we wish to cite the following observations:

Case 1: VV., male, aged 26 years, has been engaged for 2 years in the process of polymerization. Family and personal history, normal. Smokes 10 to 20 cigarettes daily.

At the beginning, the patient observed that during the release of toxic vapors, there was first a euphoric state and then a state similar to inebriation. At home, he slept between 9 and 14 hours daily.

At work, his hands immersed in the latex, he felt formication, numbness, and then a sensation of heat. When the solution was white, he observed a coloration of the skin. In contact with cold water, it was observed that the fingers became pale, then red and cyanotic. Concomitantly, the same phenomenon appeared on the great toes. This occurred also upon exposure to cold air.

At the same time, he was affected by persistent edema of eyelids, of the face, the neck and chest; the skin became glossy, the nails "uneven" and the face assumed the appearance of a full moon.

From the clinical point of view, a Raynaud's syndrome was evidenced, hepatomegaly with scleroderma of the face, neck and thorax, even of the lower and upper extremities, but particularly of the fingers (dermatologic examination made by Dr. Capusan). Musculocutaneous biopsy showed typical changes of dermatomyositis (Dr. V. V. Papilian).

The plethysmogram showed significant inhibition of the vasomotor centers.

In addition, the urinary 17-ketosteroids were increased to 8.5 mg. in 24 hours.

The lunar facies made us think of a thyroid insufficiency. The iodine uptake confirmed this belief.

The dysproteinemia tests, electrophoresis of serum proteins and the BSP test gave normal results.

By its narcotic action, the poison produces first cortical inhibition; then appear the disturbances of the diencephalic centers, principally the vasomotor and metabolic disorders. The symmetrical nature of the vascular disturbances, the plethysmographic changes and even the tissular disturbances and the scleroderma vouch in favor of this fact.

The thyroid insufficiency, evidenced by the iodine uptake, shows that the poison has either a direct influence on the thyroid or an indirect one via the "hypothalamus-hypophysis," which produces inhibition of thyroid function.

After removal from exposure, the scleroderma and the vasomotor disturbances greatly diminished.

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In half of the cases, plethysmography showed an inhibition of the vasomotor centers. As to the remaining cases, the relationships were normal. Especially in the cases where the plethysmogram was normal, the disturbances disappeared completely after removal from the toxic exposure, but in the rest of the cases, they greatly diminished, which would indicate their connection with the toxic environment.

By means of the cold pressor test and by tension oscillography, Raucher, Suciu and Pislaru have found paradoxical reactions and an absence of reactivity in 66% of the cases in plant "A" and in 55% of the cases in plant "B," which pointed out to us that vinyl chloride determines the vasomotor disturbances in a great number of the cases. Only 6% of the cases had clinical manifestations (Raynaud's syndrome).

As concerns the changes in arterial tension, we found that the maxima as well as the minima were more than 10 to 15 mm below normal values.

Cutaneous Manifestations

Pruritus, which was found in 4.8% of the cases, without being accompanied by skin changes, was the earliest symptom.

Later, two different categories of cutaneous manifestations could appear. The first noted was contact dermatitis, then scleroderma could be observed.

1. Contact Dermatitis (4.4%).

On the face and hands (uncovered parts), pruritus followed by urticaria were noted. Papules, microvesicles and large vesicles appeared on the face and hands. There were cases where the microvesicles and the scabs disappeared spontaneously, but in others they were torpid and, after return to work, they reappeared with intensity.

Case 2: K.I., chemical technician, 28 years old. According to his personal history, he had suffered epidemic hepatitis in 1942. Since then, he has had frequent anginal attacks. He has been working for a year and 8 months in the division where sodium mersolate is mixed with different substances. In December 1960, micropapules in plaque-form appeared on the forearms and face, then microvesicles, scabs of which remained. These eruptions were pruriginous. Upon hospitalization in the department of occupational diseases, zones of microvesicles and areas of scabs were noted on the face and forearms, as well as large vesicles at other sites, which after opening, left the skin covered with large scabs.

The vesicles contained a serohemorrhagic secretion.

Sedimentation rate, 2.4 mm/hour.

Leucocytes 6,000 per mm³ of which 76% were polynuclear, 10% lymphocytes, 8% monocytes, 6% eosinophils.

R d cells: 4,600,000 per mm³

Hemoglobin level: 92%.

Plethysmography revealed an inertia of the vasomotor centers.

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The lesions disappeared after treatment with an ointment of d lta-cortis n and aureomycin. They reappeared immediately upon his return to work, even upon touching certain objects with his hands. This shows that not only the mersolato but vinyl chloride as well are responsible.

Change in work brought complete disappearance of the dermatitis.

2. Scleroderma (3.6% of the cases).

In the course of work, certain workers note a pleasant odor, followed at times by emotional and motor disturbances, dizziness and somnolence which, in the case of some, persists after the end of the working day. Others report formication and numbness of the extremities.

Case 3: T.R., age 20 years, has worked for a year and 6 months at the autoclaves. He has worked at no other site. Family and personal history revealed nothing remarkable.

After a year and a half of exposure, diffuse pains developed in the lower and upper extremities, with edema. They were interpreted to be rheumatic pains and treatment brought no relief. An anygdalectomy was performed.

After return to work, a generalized pruritus developed on the face, neck, chest, the abdomen and the extremities.

Dermatologic examination (Dr. Capusan) revealed edema of the eyelids, face, with disappearance of ridges. The skin over the abdomen and the chest could no longer fold.

On the face and chest, grayish spots were seen, that merged together as in the case of chloasma in pregnancy. This clinical picture was interpreted as scleroderma.

The liver was enlarged by 2 finger-widths. The Takata-Ara reaction was faintly positive. The thymol test yielded 14 units.

The proteinogram showed:

total proteins: 8.6 g%

albumin: 48.70%

α_1 -globulins: 4.85%

α_2 -globulins: 10.50%

β -globulins: 14.70%

γ -globulins: 21.20%

Consequently, clinical and laboratory examinations demonstrated the presence of toxic hepatitis.

* The latter statement appears to be insufficiently supported.. (Translator's note)

The ASLO titer showed normal results (250 U of antistreptolysin O). Plethysmography evidenced a marked depression of the vasomotor centers that did not respond to stimulation. Thurn's test showed an inhibition. Dilution and concentration tests gave normal results. The specific dynamic activity of proteins was normal.

The iodine uptake test indicated hypofunctioning of the thyroid.

Arterial tension was 14/7 cm Hg.

Urine was normal.

In this case, as a result of exposure to the poison, disturbances of the vasomotor centers and of the protein metabolism (changes in the proteinogram in the dysproteinemia test) developed. Thyroid insufficiency and chronic hepatitis were found concomitantly.

Mastromatteo states that in polyvinyl chloride intoxication, a thyroid insufficiency exists.

It is interesting to note that in this case, in the period of one year from the time of removal from the toxic environment, the scleroderma, the Raynaud syndrome and hepatomegaly have disappeared. This proves that a toxic source was connected with these phenomena.

In the cases of scleroderma, the majority of the subjects presented a thyroid insufficiency and an inhibition of the vasomotor centers.

In 3 cases a dermomuscular biopsy was performed, which revealed chronic dermatomyositis. In one case only did the manifestations of scleroderma fail to regress after removal from the working environment. In the other cases, these symptoms disappeared, which substantiates for us the idea that these changes are operative in a reversible period.

The manifestations of the scleroderma, accompanied by disturbances of the vasomotor centers appear as a result of exposure to vinyl chloride and disappear after cessation of work in this environment, proving that this is the poison that in this case has produced the vasomotor disturbances and the metabolic of the hypothalamus. The participation of the thyroid in their production reduces the problem of this thyroid insufficiency to 2 eventualities: direct action of the poison on the gland, or consequence of thyroid inhibition of central origin.

The manifestations of collagenosis, verified histologically, which occur in cases of intoxication by narcotic substances, reveal to us that in the pathogenesis of collagenosis there occurs at first, in these cases, a disturbance of protein metabolism due to the activity of the central nervous system and followed by the appearance of an endocrine disorder (thyroid insufficiency).

The reversibility of the disturbances indicates in our opinion that there is a possibility of recovery if intervention takes place in the initial phase.

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Cases of collagenosis after administration of hydrazin phthalazine or other substances whose action is predominantly on the central nervous system are described in the literature. This would confirm our observations.

As a result of investigations into the environmental conditions performed by hygienists and physicians, recommendations were formulated for the protection of the workers and for leakproofing the equipment. In spite of these measures, some cases of the disease have occurred during the past year.

Thanks to treatment instituted according to the indications of repeated clinical examinations, and removal from the working environment, we have succeeded in controlling the oldest cases, given that they were undertaken during a period of reversible disorders.

The recognition by certain physicians of the manifestations that we have just described has permitted the detection of intoxications from the start, and the institution of adequate measures of prevention and treatment.

CONCLUSIONS

1. Vinyl chloride and the vinyl monomers possess a narcotic action and produce, depending upon concentration, in addition to characteristic neurologic manifestations, a state of euphoria (12%), followed by a state of inebriation similar to that of alcohol intoxication. In certain cases narcosis can appear.

After leaving the working environment, a state of somnolence (45%) persists, with hypersomnia.

Vinyl chloride acts on the skin and produces a sensation of formication and of heat.

2. After repeated exposure, a neurologic asthenia sets in in which somnolence predominates.

3. After a variable period of time, dyspeptic disturbances are added to the neurologic manifestations; these are at first not characteristic; they are in the form of epigastric pains (16%), swelling, discomfort, feeling of heaviness in the right hypochondrium (7%) or the left (5%) with anorexia, particularly for fats.

In 30.2% of the cases, congestive hepatomegaly appears, which may mimic toxic hepatitis without jaundice; some cases may become chronic.

In 6% of the cases, the hepatomegaly is accompanied by splenomegaly. The proteinogram and the aldolases are the most sensitive tests and show changes similar to those of acute hepatitis: increase in α -globulins and of the β - and

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γ-globulins; the thymol test, Greco's test and the zinc sulfate test are positive only in a few of the cases.

4. After 3 years of exposure in 9% of the cases a syndrome typical of ulcer without radiologic changes becomes manifest.

5. In 6% of the cases the Raynaud syndrome has appeared, particularly among the young men. Plethysmography shows in half of the cases an inhibition of the vasomotor centers.

6. In addition, allergic dermatitis in 4.4% of the cases, and scleroderma in 3.6%, has been observed.

7. The clinical and laboratory findings are of great importance in occupational pathology because in numerous cases diseases appear in man that cannot be reproduced in the animal (Raynaud's syndrome and scleroderma).

The sudden and frequent appearance of these manifestations in the PVC division of several plants, and in certain divisions in normal individuals who are still relatively young, and their disappearance in the majority of the cases after the institution of protective measures and change of work, have shown us decisively that vinyl chloride and the vinyl monomers have played a part in the production of these manifestations.

Translated by Irene R. Campbell
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