# OFFICE OF ENFORCEMENT

EPA-330/2-77-017a

Survey of Vinyl Chloride Levels
in the Vicinity of
Keysor-Century, Saugus, California

NATIONAL ENFORCEMES

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# Environmental Protection Agency Office of Enforcement EPA-330/2-77-017a

SURVEY OF VINYL CHLORIDE LEVELS
IN THE VICINITY OF
KEYSOR-CENTURY, SAUGUS, CALIFORNIA

March 1978

National Enforcement Investigations Center - Denver Region IX - San Francisco

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#### I. INTRODUCTION

The Keysor-Century Corporation operates a polyvinyl chloride (PVC) and phonograph record manufacturing facility north of Los Angeles at Saugus, California. This plant is one of four PVC manufacturers in the Los Angeles area. It operates 24 hrs/day, 7 days/week producing PVC from vinyl chloride monomer (VCM) and vinyl acetate (VA) by suspension polymerization. A brief process description is included in Appendix A. Because it produces polymers containing vinyl chloride, a carcinogen, the facility is subject to requirements of the National Emission Standards for Hazardous Air Pollutants (NESHAP) under 40 CFR, Chapter I, Part 61, Subpart F. This limits VCM in exhaust gas emissions to 10 ppm. In addition, the plant is subject to the Occupational Safety and Health Administration (OSHA) employee exposure standard (29 CFR 1910.93) of 1 ppm averaged over an 8-hour period, and a maximum of 5 ppm averaged over any period not exceeding 15 minutes. The action level (level below which no control action is necessary) under this regulation is 0.5 ppm averaged over an 8-hour work day.

Engineering-Science, Inc. (ES), under contract to Environmental Protection Agency (EPA) Region IX, visited the Keysor-Century facility seven times beginning in late 1976 to conduct a NESHAP inspection. This included a preliminary visit, two compliance inspection visits, a plant boundary survey, and three visits to determine the sources of excess emissions and to recommend accelerated temporary and permanent control measures. Recommendations included installation of a fume incinerator to dispose of VCM from major in-plant emission points. As part of their task, ES reviewed data from the Company's 10-station plant monitoring system which indicated VCM concentations at times were 1,000 to 5,000 ppm, with frequent concentrations of 100 to 500 ppm at all monitoring stations.

Engineering-Science calculated VCM concentrations 500 ft downwind from the plant. With a moderate wind (2.5 m/sec or 5 mph) and a 100 ppm VCM concentration above the plant, a 0.2 ppm concentration was estimated at steady state conditions. However, at lower wind speeds or higher plant emissions it was estimated that the downwind concentrations would be greater with a potential for exceeding OSHA standards.

For the plant boundary survey on March 17, 1977, ES used a portable VCM gas monitor with a minimum sensitivity of 2 ppm. VCM concentrations were below instrument detection limits, however wind conditions that day only permitted sampling upwind of the plant. The hills east of the plant [Fig. 1, Section III] restrict access to much of the plant boundary. During the survey the in-plant monitoring system showed levels between 0.3 and 16.5 ppm.

ES evaluated the Company's Leak Detection and Elimination Program (Region IX later rejected the program as inadequate) and questioned whether the locations of the monitoring sites used in the program were adequate. In addition, the routine occurrence of high VCM concentrations indicated the program for controlling leaks was ineffective.

As a result of the earlier ES evaluations and the consideration that an elementary school is across the road (350 m) from the plant, and other businesses and residences are also in the immediate vicinity, EPA Region IX requested that the National Enforcement Investigations Center (NEIC) immediately conduct a survey of the plant and its environs to (a) determine ambient levels of vinyl chloride in the area surrounding the Keysor-Century plant and (b) to assess the adequacy of the monitoring system as a means of measuring plant vinyl chloride levels and detecting and eliminating leaks. This first study was conducted April 25-30, 1977.

During May 1977, Keysor-Century submitted a revised Leak Detection and Elimination Program, along with data indicating reductions in inplant VCM concentrations. (This program was approved by EPA Region IX on September 27, 1977.)

A second field study was requested by EPA Region IX in early August to determine whether the VCM levels had varied from the time of the original survey. This study was conducted August 3-6, 1977.

EPA Region IX requested that the Company install a fume incinerator because of the continuing high VCM concentrations documented during the second NEIC field study. This incinerator was installed and operational about November 24, 1977. Prior to this, on October 1, 1977, the Company began a round-the-clock composite sampling program which continues to date. This is discussed later (Section IV).

Following installation of the fume incinerator, the California Air Resources Board (CARB) collected a series of composite air samples (October 30-November 8, 1977), in the plant vicinity. EPA Region IX requested a third study to determine whether this unit had reduced ambient VCM levels in the vicinity of the plant. This NEIC study was conducted November 27-30, 1977, and included concurrent sampling by CARB.

During the three NEIC studies the plant was operating between 90- 95% capacity.

#### II. SUMMARY AND CONCLUSIONS

Field surveys in the vicinity of the Keysor-Century plant detected vinyl chloride by three procedures: grab sampling, composite sampling and continuous monitoring.

#### First NEIC Study .

During the April 1977 survey, the highest VCM level measured was 2.7 ppm during a period of approximately 10 minutes (0103-0113) on the continuously recording Wilks MIRAN\* located at the Saugus Elementary School. Thirty-seven of 240 grab samples (10 minutes) also showed the presence of VCM, as did two additional grab samples collected when field crews smelled the characteristic vinyl acetate odor. The maximum concentration measured by grab sampling was 0.59 ppm at a service station (Station 559) directly west of the plant. At Station 553, southeast of the facility, one-third of the samples (8 of 24) showed the presence of VCM with the maximum value 0.40 ppm.

The composite samples (8 to 18 hrs.) showed VCM present on 8 occasions. The highest level found was 0.75 ppm (9.6 hr. average), again at the service station (Station 559). In conjunction with grab samples collected during the composite period, this level would indicate that peak values at the station may have occasionally exceeded 10 ppm. Although the laboratory procedures used will also detect EDC and TCE, these compounds were not found in any samples.

A comparison of the Keysor-Century tank car unloading schedule with all sampling results indicated that VCM was detected by grab

<sup>\*</sup> Brand name.

and/or composite samples when tank cars were unloaded during nighttime hours. Thus, atmospheric stability, usually associated with nighttime hours, and the hills located east of the plant, acted to minimize dispersion of leaks from the tank cars and other VCM sources at the plant.

Evaluation of the in-plant monitoring system showed that while the system was operating satisfactorily, it was only adequate for monitoring general VCM concentrations in eight plant areas. The system was not adequate, nor was it installed, to detect leaks from specific pieces of equipment. In addition, areas such as the collection pond and the VCM and VA recovery vents nearby are not monitored. Measurements taken during the evaluation in these and other areas of the plant exceeded the 10 ppm NESHAP emission limitations.

The high "incipient leak" (background) levels as defined by Keysor-Century and the periodic VCM emissions >10 ppm could cause minor leaks to go unnoticed if, in fact, these were important compared to the higher emissions measured. Also, wind direction and turbulence were shown to transport emissions to monitoring stations in other locations of the plant away from points of origin. Thus, the Leak Detection and Elimination Program and the in-plant monitoring system were ineffective in meeting the purpose for which required, i.e., detecting and eliminating leaks from equipment in vinyl chloride service. When overall plant levels are reduced to more acceptable levels, the monitoring system may be more useful.

#### Second NEIC Study

An August 1977 study was conducted during nighttime hours. Results showed that VCM concentrations from composite samples were generally higher than during the first survey. The geometric mean value of grab sample concentrations were about 60% higher than during the first study (5.2 vs 3.2 ppb). In addition, one 10-min grab sample (Station 553, Sequence 2) showed a 6.2 ppm VCM concentration, the highest level recorded by this procedure. This tends to verify data observed by the MIRAN and the earlier assumptions made regarding composite sample concentrations.

## Keysor-Century and CARB Results

Evaluation of 8-hr composite samples collected by Keysor-Century at three stations around the plant (Stations 501, 503, and 504) indicated a median value of about 20 ppb prior to installation of a fume incinerator, and below detectable levels afterwards. Data collected by CARB at the same stations after controls were installed showed a median value of 45 ppb. Also, two consecutive 2-hr samples CARB collected at the Saugus School showed levels of 6.2 and 1.8 ppm VCM.

## Third NEIC Study

The November 1977 NEIC study included concurrent sampling by CARB. Grab sampling data again showed a median value of about 5 ppb. Composite samples collected were below NEIC detection limits (0.08 ppm); however, the more sensitive CARB procedure also showed a median value of 5 ppb for their 4-hr composites.

Fume incinerator installation may impact some of the high VCM concentrations observed earlier, however the median value (5 ppb) for grab samples has not been reduced nor has the occurrence of occasional high concentrations in composite samples. This indicates either the necessity for correcting operation and maintenance procedures and/or the need for additional control measures.

In the absence of ambient air standards, two possible approaches are presented for selecting rational ambient VCM levels to protect the general population in the plant vicinity. One would apply a safety factor to OSHA levels, the second would adopt a continuous exposure level consistent with some lifetime carcinogen risk. For VCM a lifetime risk of 3 x  $10^{-5}$ , consistent with other government standards, has been estimated at 1 ppb $^3$ . The following Table provides a comparison of various control options with results obtained during the November survey. The Table indicates that even with a minimal safety factor, the Company will still exceed allowable ambient concentrations in the plant vicinity.

PERCENT OF TIME CONCENTRATIONS EXCEEDED

SELECTED LEVELS

	Saf	Coi	Control Level			
1	1/10	1/30	1/100	1 ppb		
<0.02 <0.03 <0.1	2 1 6	10 4 21	33 · 13 52	88 20 -		

<sup>\*</sup>Estimated from 4-hr CARB data

<sup>\*\*</sup>Estimated from 15-min NEIC data

#### III. FIELD STUDIES

## A. FIRST NEIC STUDY - APRIL 25-30, 1977

Three different procedures were employed during the first survey to determine the impact of plant emissions on air quality in the Saugus vicinity. Large charcoal tubes were placed at fixed locations and composited ambient air continuously for approximately 12-hour periods. Field teams collected grab samples on small charcoal tubes for 10- to 20-minute periods six times daily. A MIRAN\* continuous recording infrared analyzer was installed and recorded vinyl chloride levels at the Saugus Elementary School during the study period. A review of chain of custody procedures verified that these were followed on all charcoal tube samples.

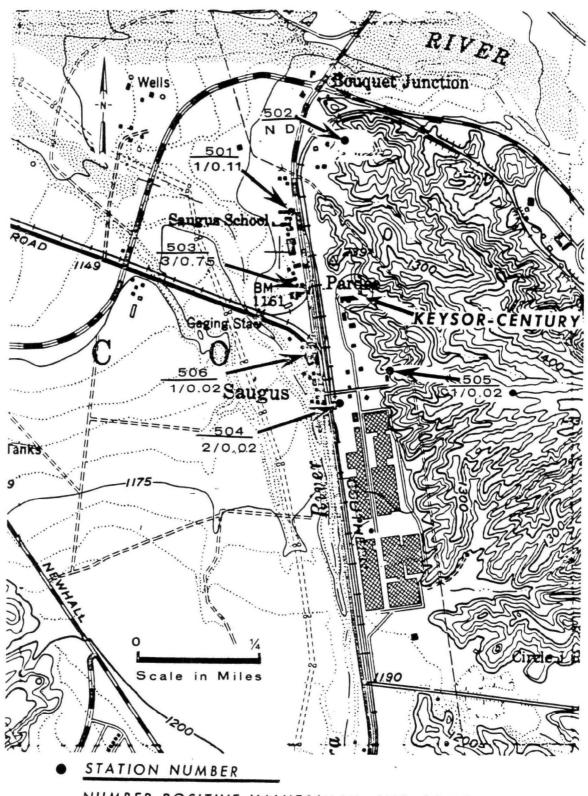
#### Composite Sampling

Six stations [Table 1 and Figure 1] were established around the plant to concurrently collect air samples in large charcoal-filled glass tubes which were fabricated\_at the NEIC chemistry laboratories. These tubes were comprised of three sections, each containing 1.5 g of 14 x 35 NuChar\* separated by glass wool and were fused shut before leaving the laboratory. In the field the fused ends were opened, attached to a critical orifice and vacuum pump, and an air sample composited for approximately 12 hours before the tube was replaced. Seven sequential samples were collected at each station during the study period. An additional sample was composited over the preceding 18-hr period at the Saugus Elementary School. At the completion of the sampling period, the tubes were sealed with fiber tape and cooled with dry ice until analyzed for VCM, ethylene dichloride, and trichloroethylene at NEIC using specified laboratory procedures [Appendix B]. Volumetric flow in the system was checked daily with a 100-ml bubble meter. Flow through the system was controlled at approximately 0.1 liter/min.

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Table 1
LOCATION OF COMPOSITE SAMPLING STATIONS

Station No.	Location
501	East end of north side of Saugus Elementary School, northwest of Keysor-Century plant and west of San Fernando Rd.
502	Southwest of sewage treatment plant (STP) 26 at grit chamber building, north of Keysor-Century.
503	Southeast corner of Mohawk Service Station due west of Keysor-Century and west of San Fernando Rd.
504	North end of east side of Railroad Station on south- east corner of Dayton and San Fernando Road, south of Keysor-Century plant.
505	North side of Wendell's Machine Products Company at east end of Drayton Street, south of Keysor-Century Plant.
506	East side of Paint'n Place on southwest side of intersection of Magic Mountain Parkway (State 126) and San Fernando Rd, southwest of Keysor-Century Plant.



NUMBER POSITIVE VALUES/MAX. AVG CONC.-ppm

Figure 1. Composite Sampling Station Locations and First Study Results

#### Grab Sampling

Ten grab sampling stations [Table 2 and Figure 2] were established around the facility and sampled at 4-hour intervals, six times daily over a 4-day period. Each day sampling was started one hour earlier. Thus, at the end of the 4-day period, samples were collected each hour of the day; i.e., 24 samples collected at each station. Samples were collected in small commercially available charcoal-filled glass tubes specifically designed for organic vapors. The sealed tubes were opened before use by breaking the end tips, then sealed with plastic caps and cooled with dry ice when sampling was completed. The samples were analyzed for vinyl chloride, TCE and EDC at the NEIC laboratories.

Portable, battery-operated pumps were used to draw ambient air through the tubes. The small pumps collected about 0.2 liters/min and the large about 0.8 liters/min. The battery operated pumps provided greater flexibility in establishing sampling locations since power was not a requirement.

At the start of every sampling period each pump was calibrated using a 100-ml bubble meter. Pumps not operated from car (12-volt) battery power were frequently recharged to maintain the maximum pumping capacity.

Table 2

LOCATION OF GRAB SAMPLING STATIONS

Station No.	Location
550	West side of bridge on Magic Mountain Parkway 0.2 mi west of San Fernando Rd. intersection
551	West side of San Fernando Rd 0.4 mi south of Drayton Rd
552	North side of Railroad Station on southeast corner of Drayton and San Fernando Rd intersection
553	0.05 mi north of Drayton Rd termination
554	On Springbrook Rd at Keysor-Century Plant gate
555	At entrance to STP No. 26 north of Keysor-Century Plant
556	Dirt road on hill due east of Keysor-Century waste- water pond
557	East side of San Fernando Rd 0.65 mi north of Drayton Rd
558	East side of Saugus Elementary School
559	East side of Mohawk Service Station west of Keysor- Century Plant

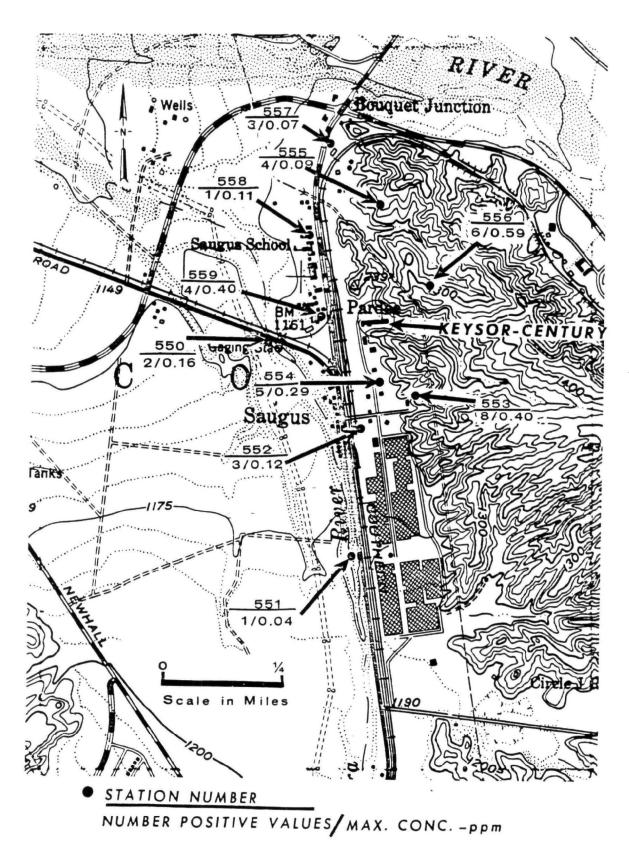


Figure 2. Grab Sampling Station Locations and First Study Results

#### Continuous Monitoring

A Wilks Scientific MIRAN Portable Gas Analyzer was installed to sample the air outside the north side of the Saugus Elementary School. The instrument is a single-beam, infrared spectrometer with a folded path gas cell extending to 20 m and a wavelength range selectable from 2.5 to 14.5  $\mu m$ . Vinyl chloride has absorption peaks at 6.15, 9.8, 10.9 and 13.9  $\mu m$  with varying sensitivities. Interferences from water vapor and other organics used at the PVC plant (EDC, TCE, and VA) are present to varying degrees at these wavelengths. The MIRAN was coupled to a strip chart recorder which permitted continuous monitoring of vinyl chloride levels at the school throughout the study. The 10.9  $\mu m$  wavelength was used since EDC has no response in this region, while the interference from vinyl acetate is weak and TCE is medium compared to vinyl chloride signal levels. The minimum detectable VCM concentration is slightly less than I ppm at this wavelength. Following the field work, the MIRAN analyzer was returned to NEIC and recalibrated at the instrument settings used. This instrument was not used on the later studies.

## B. SECOND NEIC STUDY - AUGUST 3-6, 1977

The analytical results from the first study were used to plan the second study. Sampling results showed that only 10 of the 37 positive determinations occurred during sampling runs starting on the 12-hourly periods 0700-1800. Of these, five occurred on a single run. This indicated that meteorological conditions (nighttime inversions) probably had a significant effect on the VCM levels measured. As a result, subsequent surveys were limited to nighttime hours.

## Composite Sampling

This sampling was conducted using the same collection systems described earlier. Only five of the original stations were available

since the individual at Station 506 was no longer in business. The sampling time was divided into two 6-hour periods (beginning at approximately 1800, 1700, and 1600 on succeeding days) at the remaining stations. In addition, 12-hour samples were collected during daytime hours at two stations (Station 503 and 504).

#### **Grab Sampling**

All sampling stations and apparatus remained the same as during the first study. The time between runs was reduced from four to three hours permitting 13 samples to be collected at each station. Unlike the initial study where samples were shipped to the laboratory during the survey, these samples were kept preserved on dry ice during the entire study period and returned to the NEIC Denver laboratory with the sampling team.

### C. <u>KEYSOR-CENTURY MONITORING - BEGINNING OCTOBER 1, 1977</u>

Keysor-Century established monitoring sites at NEIC Stations 501, 503 and 504 on October 1, 1977. They concurrently collect 8-hr composite samples in Tedlar\* bags at these stations during each of the three daily shifts. The Tedlar bags are returned to the Company laboratory for direct analysis by gas chromatography.

#### D. CARB STUDY - OCTOBER 30-NOVEMBER 8, 1977

The California Air Resources Board (CARB) study, after installation of the fume incinerator, entailed collection of a series of 2- and 8-hr composite samples at the NEIC composite sample Stations 501, 503 and 504. The samplers were designed to collect a composite sample during a

<sup>\*</sup> Trademark

preset interval by pumping air into a Tedlar bag. At the end of the compositing interval the sampler automatically begins filling another bag. When sampling was completed, the Tedlar bags were analyzed at the CARB laboratory in El Monte, California, by a procedure requiring sample concentration followed by gas chromatography.

# E. THIRD NEIC STUDY - NOVEMBER 27-30, 1977

The third and final study was conducted in cooperation with the CARB. CARB personnel collected three 4-hr composite samples in Tedlar bags at three of the same NEIC sample stations used earlier. At the end of the 12-hour period, the three bags from each station were transported to the CARB laboratory for immediate analysis. These results were made available to EPA. Keysor-Century was also routinely collecting 8-hr samples at these same stations during this period.

#### Composite Sampling

NEIC samples were collected using the same equipment described above. The five sampling stations were the same as used for the second survey. In hopes of increasing sensitivity to intermittent emissions (by decreasing dilution volume), the sampling intervals were reduced to three 4-hour periods during nighttime hours. At Stations 501 and 505 sampling intervals were further reduced to two hours on several occasions.

## **Grab Sampling**

Sampling stations and apparatus remained the same as during the first two studies. To collect a larger sample volume, collection time was increased from the 10 minutes used on the earlier studies to 15 minutes.

#### IV. FIELD SAMPLING RESULTS AND DISCUSSION

#### A. FIRST NEIC STUDY - RESULTS

Vinyl chloride was measured in the study area by all three methods -employed. In most cases when VCM was found, it occurred at a number of stations during a particular sampling sequence rather than at single stations.

#### Composite Samples

Forty-three composite samples were collected at the six stations established around the plant. Eight samples showed the presence of vinyl chloride concentrations ranging from 0.01 to 0.75 ppm [Table 3]. The detection limits for the charcoal tubes under the sampling conditions were about 0.01 ppm for vinyl chloride and 0.1 ppm for TCE and EDC. These varied with sampling time (volume). The number of samples that showed vinyl chloride and the maximum value at each station are shown in Figure 1. Vinyl chloride was not detected in composite samples collected at Sewage Treatment Plant No. 26 (Station 502).

Table 3

RESULTS OF COMPOSITE SAMPLING FOR VINYL CHLORIDE

Station/ Sequence	Date	Starting Time	Sampling Time (min)	Concentration (ppm)		
501/0	4/25	1453	1115	0.11		
503/1	4/26	0839	683	0.03		
504/1	4/26	0902	628	0.02		
505/1	4/26	1202	458	0.02		
506/1	4/26	1302	448	0.02		
503/4	4/27	1919	862	0.05		
504/4*	4/27	1836		0.01		
503/6	4/28	1837	936	0.75		

<sup>\*</sup> Pump failed during sequence. Concentration computed on basis of full 839 min sampling period.

The maximum value found (0.75 ppm at Station 503) was higher than the OSHA Action Level for occupational exposure. During most of that sampling period, field teams indicated winds were calm to easterly before turning southwesterly late in the sampling period. Table 3 shows that vinyl chloride was observed at four stations on the first sequence and at two stations on the fourth sequence. However, when the maximum value was detected only Station 503 showed the presence of vinyl chloride. EDC and TCE were not detected in any of the composite samples.

#### <u>Grab Samples</u>

The grab sampling program entailed collection of 240 samples (24 samples at 10 stations) during a 4-day period. Of these, 37 showed vinyl chloride in concentrations ranging from 0.02 ppm to 0.59 ppm [Table 4]. The detection limit for this procedure using the small sampling pump was about 0.02 ppm for vinyl chloride and 0.2 ppm for EDC and TCE.

Vinyl chloride was measured at least once at each station. It was measured 8 times (33% of samples) at Station 553 where the maximum value was 0.40 ppm. That level was exceeded at Station 556 on the east overlooking plant property where the maximum of 6 measured values (25% of samples) was 0.59 ppm. Figure 2 indicates the number of samples showing VCM and the maximum value at each station.

It should be noted here that the grab sampling procedure is more sensitive than composite sampling for several reasons. The small tubes require less solvent in the desorption process resulting in a more concentrated sample. Also, while the large charcoal tubes may collect a larger mass than the smaller tube during the sampling period,

Table 4

RESULTS OF GRAB SAMPLING - VINYL CHLORIDE
FIRST STUDY

			Wind	Nomi	nal								
Sequence	550	551	552	553	,554 (ppm)	555	556	557	558	559	Direction	Startin	
1	-	_	-	-	-	_	_	_	_	_	Calm	4/26	0700
2	_	_	-	_	_	_	_	_	_	_	NW	4/20	1100
3	_	_	_	_	_	_	_	_	_	_	SW		
4	_	0.04	0.02	0.02	_	_	_	_	_	7			1500
5	_	_	-	0.40	0.20	_	_	0.07	-	0 40	Variable		1900
6	0.02	-	0.02	-	0.04	_	0.02	0.07	- 0 17	0.40	Ca 1m	4.407	2300
7	-	_	0.02	_	U.U4 _	_	0.02	0.02	0.11	0.06	SE	4/27	0300
8	_	_	_			-	-	-	-	_	Variable		0600
9	_	_	_	_	-	-	-	_	-	-	S		1000
10	_	_	-	_	-	-	-	-	-	-	S		1400
11	_	-	-	-	-	-	0.59	-	-	-	SW		1800
12	-	-	-	-	-	-	-	-	-	-	NW		2200
	-	-	_	-	-		-	-	-	-	Calm	4/28	0200
13	-	-	-	0.23	-	-	0.27	-	-	-	Ca 1 m		0500
14	-	-	-	-	-	-	-	-	-	-	NW		0900
15	-	-	-	-	-	-	-		_	_	S		1300
16	-	-	-	0.04	-	0.09	-	_	_	-	S		1700
17	-	-	-	-	-	_	-	_	_	_	Calm		2100
18	-	-	_	0.14	0.17	_	_	_	_	0.02	Calm	4/29	0100
19	-	_	_	0.38	0.29	0.06	_	_	_	-	Calm	7/ 23	0400
20	0.16	-	0.12	0.04	_	_	0.17	_	_	0.13	SW		0800
21	-	-	-	_	_	0.04	-	_	_	0.13	SW		1200
22	_	-	-	_	_	0.04	_	_	_	-	SE SE		
23	_	_	_	_	_	-	0 00	-	-	-	SE ''		1600
23 24	_	_	_	0.11	0.08		0.08	0 07	-	-	W		2000
<b>∟</b> ▼	_	_	_	0.11	0.00	-	0.04	0.07	-	-	Calm		2400

this will be averaged over a much larger sampling volume (60 vs 2 liters). Thus, it is possible that when vinyl chloride concentrations are measured by both samplers at the same location it will only be detected by the small charcoal tube and not the larger one.

On two occasions 10-minute samples were collected at locations where a vinyl acetate odor was detected. The first occurred during sequence 16 when the field team was between Station 555 and 556. This sample showed a 0.3 ppm vinyl chloride concentration which was later confirmed by gas chromatography/mass spectrometry (GC/MS) analysis (Appendix B). A lower value was observed at Station 555 (0.09 ppm) and none was observed at Station 556 during-that sequence.

On the second occasion, the odor was detected at the railroad crossing on San Fernando Road (midway between Stations 558 and 559) leading to STP 26 during sampling sequence 24. The sample yielded a VCM concentration of 0.06 ppm. Four of the grab sampling stations also showed measurable concentrations during that sequence [Table 4].

## Continuous Monitoring

The continuous monitor was installed at the Saugus Elementary School on Monday, April 25, and operated through Friday, April 29, 1977. During that period an infrared signal was detected once, on April 29, beginning shortly after midnight and extending until about 0130 hr when the recorder returned to background. The recorder output during this time period [Figure 3] shows that the maximum level observed was about 2.7 ppm as vinyl chloride.

This concentration, while just within the detection limit of the large charcoal tubes, was not measured at Station 501 adjacent to the monitor.

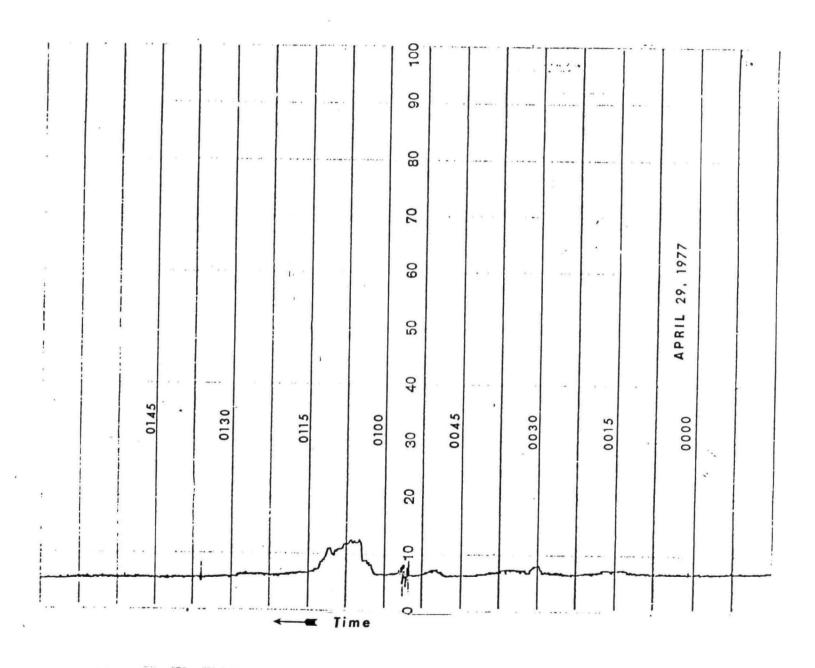


Figure 3. Miran Recording Showing Infrared Sianal at 10.9 um

The recording [Figure 3] shows a zero offset of about 5% of full scale. This was manually set to provide a continuous record of the MIRAN output even when the instrument showed a measurable amount of drift throughout the day. This would not affect the results observed.

Other organic interferences released with the vinyl chloride could have contributed to the signal. Thus, the same signal could have been recorded by 9.1 ppm VA or 3.5 ppm TCE or combinations thereof. However, TCE was never detected on any of the charcoal tubes during the survey period and the sampling team in the area gave no indication of the characteristic VA odor. (Water vapor and EDC are transparent at this wavelength). Any contribution to the signal by these other organics would have reduced VCM concentrations below detectable on the large charcoal tubes. The grab samples collected during the sampling sequence (18 which began at 0119 hr on April 29 and extended through 0310 hr) were positive at three locations [Table 4], Station 553 (collected at 0144), Station 554 (0147) and Station 559 (0212). The sample collected at the school (0310) was negative for VCM.

## B. <u>SECOND STUDY - RESULTS</u>

Only the composite and grab samplers were used for VCM detection on the second study. Vinyl chloride was detected with both methods.

## Composite Samples

Thirty-three composite samples were collected at the five stations monitored during this study. Of these, 5 were collected during the 12-hr daytime hours, and the remaining 28 collected during 6-hr nighttime periods. The results are shown in Table 5. Only one of the daytime samples was positive. The positive values only appeared at two stations (503 and 505).

Comparison with values obtained during the first study (range 0.01 to 0.75 ppm) indicated that these latter data are substantially higher. A decrease in instrument sensitivity (2.5 vs 5.0  $\mu g$ ) would account for loss of the lower more probable values, while shorter sampling intervals reduced the volume diluting any VCM collected.

Table 5
RESULTS OF COMPOSITE SAMPLING FOR VINYL CHLORIDE

Station/ Sequence	Date	Starting Time	Sampling Time (min)	Concentration (ppm)		
503/2	8/4	0132	318	0.23		
503/3	8/4	0652	716	0.24		
505/7	8/5	1633	345	0.32		
505/8	8/5	2200	367	0.35		

## **Grab Samples**

During 13 sampling periods, primarily during nighttime hours, 16 of the 125 samples collected were positive [Table 6]. An examination of these data indicates one extremely high value (6.2 ppm) at Station 553, and the general indication of higher values than measured during the first study. Data comparisons show about the same percentage of positive values during both studies. However, an instrument sensitivity decrease during the second study (0.1 vs 0.2  $\mu g$  VCM) would have eliminated some of the more probable lower values seen during the earlier study.

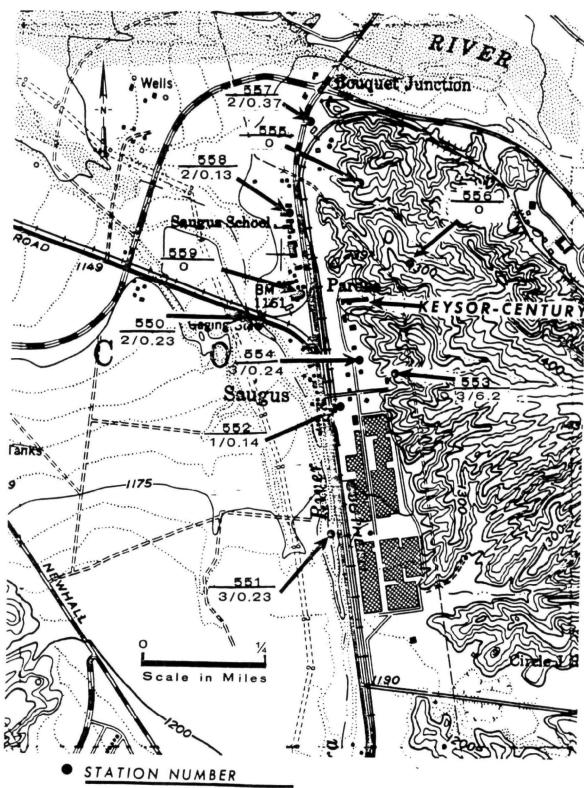
As before, when VCM was detected, it was measured at several stations during a particular sampling sequence. Figure 4 shows the number of positive samples and the maximum value at each station. Urlike the earlier study, VCM was not detected at Stations 555, 556 or 559.

Table 6

RESULTS OF GRAB SAMPLING - VINYL CHLORIDE SECOND STUDY

C		·····			ation Nu	mber					Wind	Nominal	
Sequence	550	551	552 ———	553	554 (ppm)	555	556	557	558	559	Direction		Starting Time
1	-	-	-	-	-	-	*	-		_	Vaniable	0/2	1000
2	-	0.21	-	6.18	0.18	_	*	_	_	'	Variable Calm	8/3	
3	-	_	-	-	0.24	_	*	_	_	_		0.44	2200
4	0.23	-	_	_	-	_	*	0.37	0.07		Calm	8/4	
5	-	_	0.14	_		_	*		0.07	-	Calm		0330
6	0.12	_	-	_	_		•	-	-	-	Calm		9600
7	0.12	_	_	-	-	-	-	-	-	-	SW		1700
Ó	_	_	-	-	-	-	-	-	~	-	Ca1m		2000
0	-	-	-	-	- ,	-	-	-	-	-	Calm		2300
9	-	-	-	-	- '	-	-	-	-	-		8/5	0200
10	-	-	-	-	-	-	-	_	_	-	Calm	<b>U, U</b>	0500
11	-	-	-	-	0.10	-	_	0.33	_	_	\$		1600
12	-	0.23	-	0.84	~	-	-	-	• _	_	Calm		
13	-	0.21	-	0.51	-	-	-	_	0.13	-	Calm		2100 0100

<sup>\*</sup> Site not accessible



NUMBER POSITIVE VALUES MAX. CONC. - PPM

Figure 4. Grab Sampling Results - Second Study

#### C. KEYSOR-CENTURY RESULTS

The Company monitoring program on occasion measured VCM at each sampling station during every shift. The maximum 8-hr value, 0.4 ppm, was reported on two occasions. The highest 24-hr average value, 0.16 ppm, determined by averaging three consecutive 8-hr values at a single station occurred on two occasions, at the same time and location as the maximum 8-hr values.

#### D. CARB RESULTS

The first CARB sampling program yielded a series of 2- and 8-hr composites at the three sampling sites described earlier. During this survey two consecutive 2-hr composites collected at the Saugus School showed 6.2 and 1.8 ppm VCM respectively. The maximum 8-hr average, 2.0 ppm, (calculated from four 2-hr values) occurred during that period, as did the maximum 24-hr average (calculated from 2-hr or 8-hr composites) of 0.70 ppm. The second highest 8-hr and 24-hr averages were 0.15 ppm and 0.11 respectively.

#### E. THIRD NEIC STUDY - RESULTS

As in the second study, only composite and grab samples were collected. Samples were collected concurrently by CARB for analyses by their more sensitive procedure. This methodology was not readily adaptable to NEIC field studies.

#### Composite Samples

None of the 46 composite samples showed detectable VCM levels. With a 5  $\mu g$  VCM detection limit, the 4-hr samples would only have detected average concentrations of 0.08 ppm and the 2-hr composites 0.16 ppm.

While CARB composites (discussed below) showed measurable VCM concentrations, the levels found were below NEIC detection limits.

#### **Grab Samples**

As indicated earlier, grab sampling provides a much more sensitive VCM measurement technique. Thus, while NEIC composite samples did not detect VCM, 15 grab.samples collected during 15 sampling cycles (150 samples) were positive [Table 7 and Figure 5]. Increasing sampling time from 10 to 15 minutes increased the analytical sensitivity, allowing measurement of lower concentrations than found during the second study. Weather conditions were markedly different from those experienced during the earlier two studies. Where calm conditions were generally experienced earlier, northwesterly winds were usual during this sampling period. This would mean that the VCM transport mechanism to the various sampling stations probably varied from those considered earlier. This difference could also account in part for the reduced concentrations at the composite sampling stations.

Three samples contained a sufficient VCM level (>1.2  $\mu$ g/ml in carbon disulfide) to permit analysis by GC/MS [Appendix B]. A positive identification of vinyl chloride was made in samples 553/06, 553/09 (0.41 and 0.29 ppm), and 554/06 (0.69 ppm).

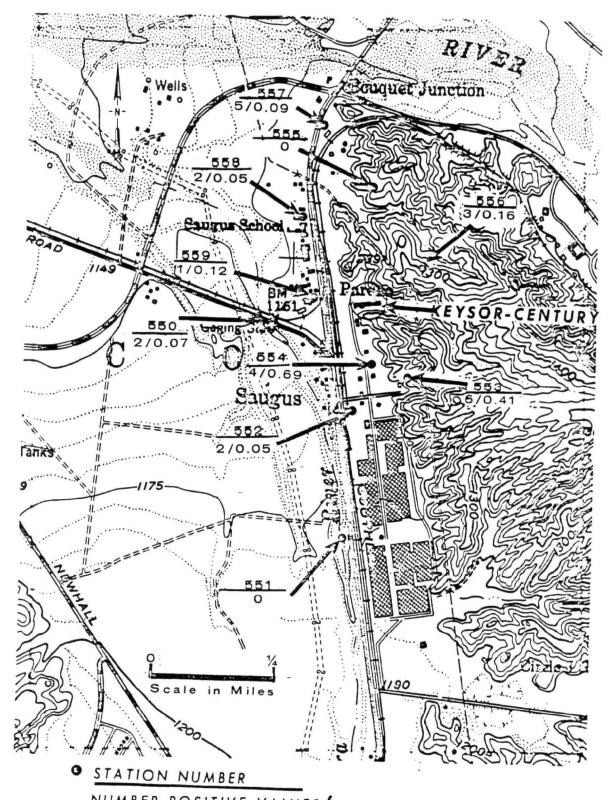
#### F. DISCUSSION

The discussion following not only includes reference to NEIC data but also that collected by CARB and Keysor-Century since their results represent a significant contribution to the data base.

Table 7

RESULTS OF GRAB SAMPLING - VINYL CHLORIDE
THIRD STUDY

_		Station Number											Nominal	
Sequence	550	551	552	553	554 (ppm)	555	556	557	558	559	Wind Direction		Starting Time	
1	_	_	_	_	_	_	_			•	Art I	11.407	1000	
2	_	_	0.05	_	0.02	_	_	_	-	-	NW	11/27	1800	
3	-	-	0.03	-	0.02	-	-	-	_	-	МИ		2100	
J	_	-	-	-	, –	-	-	-	-	-	MM	11/28	2400	
4	-	-	-	-	-	~	-	-	-	-	Calm	-	0300	
5	-	-	-	0.18	-	-	-	0.06	0.04	-	Calm		0600	
6	-	_	-	0.41	0.69	~	_	0.04	_	_	NW		1730	
7	-	-	-	0.16	0.09	-	0.10	-	-	_	Nr1		2000	
8		_	_	-	-	_	0.16	_		_				
9	_	_	_	0.29	-	_	0.10				NW		2300	
10	_		_	0.23		-		0.09	-	-	NW	11/29	0200	
iĭ	0.04	-	-		-	-	0.09	، 0.07	-	-	MM		0500	
	0.04	-	-	-	-	-	-	-	-	0.12	NW		1600	
12		-	-	-	-	-	_	0.07	0.05	-	NN		1930	
13	0.07	-	0.04	-	_	-	-	-	-	-	NW		2200	
14	-	-	_	0.07	_	_	-	_	_	_	NW	11/30	0100	
15	-	-	-	0.26	0.14	-	_	_	_	_	NW	11/30	0400	



NUMBER POSITIVE VALUES MAX. CONC. - ppm

Figure 5. Grab Sampling Results - Third Study

Both the composite and grab sample results from the first NEIC study indicated that VCM was measurable in the Saugus vicinity a significant portion of the time. The grab samples showed that, for short periods, levels of 0.40 ppm (a maximum of 0.59 ppm was detected) may be observed close to the plant. In fact, values greater than 0.1 ppm might be expected 5% of the time. Additionally, low levels (<0.1) could be detected at 0.8 km (0.5 mi) from the plant (Stations 551 and 557).

The composite samples were generally lower than the grab samples, except for two results (501/0 and 503/6) of 0.11 and 0.75 ppm for samples collected over time periods greater than 15 hours. It is unlikely that the VCM levels maintained these averages over the sampling period, but more probable that the levels fluctuated and reached much higher values for short time periods. In the case of sample 503/6, this would indicate that levels may easily have reached 10 ppm for short periods when compared to the four results from the companion grab sample station (559) during the same period (N.D., 0.02, N.D., 0.13).

When the VCM tank car unloading schedule (liquid only) was compared to periods when charcoal tubes showed positive results, an interesting correlation was observed [Figure 6]. During all nighttime periods that a tank car was unloading either the grab, composite, or both, sampling systems showed detectable levels of VCM. However, the fact that several samples were positive when unloading was not occurring shows that other sources at the plant also contribute. Figure 6 also gives an indication that the impact of the unloading is greater during nighttime hours when atmospheric stability is enhanced either by calm winds and/or ground level inversions. Thus, grab samples showed VCM present between 0700 and 1700 hr on only one of the four days (April 29) when southerly winds may have been strong enough to limit vertical mixing.

Because nighttime VCM levels appeared more significant than daytime levels, the second NEIC study concentrated on that time period. Composite

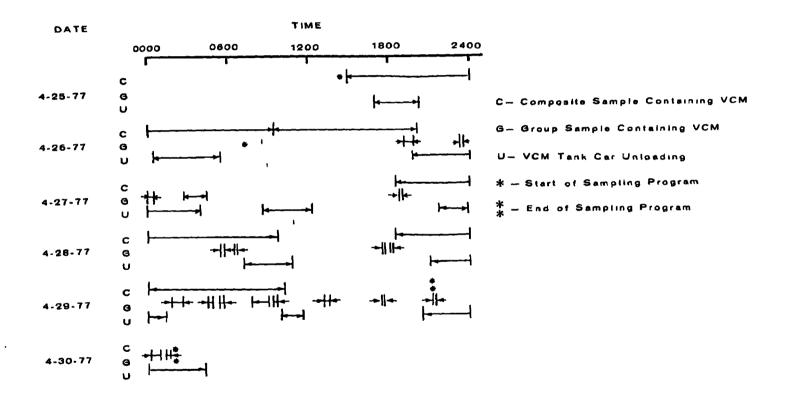


Figure 6. Comparison of VCM Unloading and VCM Detection
by Composite and Grab Sampling

samples were in general higher than those measured earlier. The grab samples also showed higher values. The single highest value (6.2 ppm at Station 553) verified that these levels were possible in the Saugus vicinity, could be observed at isolated stations, and may not be measured by the composite samplers.

A comparison of statistical (log-normal) distributions\* of nighttime grab sample data from the first two surveys (sampling runs started between 1800 and 0500) indicated that the geometric mean for the second survey was almost twice that of the first (5.2 vs 3.2 ppb). Clearly there was no indication of emission reduction between surveys.

Examination of the Keysor-Century data collected before installation of the new fume incincerator indicated the 8-hr data had a geometric mean of about 20 ppb VCM. The 24-hr mean (average of three consecutive 8-hr samples) was similar. The data distribution showed a slight drop-off from the usual log-normal distribution at low concentrations. Following installation of the fume incinerator, the Keysor-Century data were reported as below the instrument detection limits. However, analysis of CARB data indicated the 8-hr median and 24-hr geometric mean to be about 45 ppb for the combined data from all stations.

The third NEIC survey, also after installation of the fume incinerator, indicated that while extreme values were reduced, the geometric mean value for the 15-min grab samples were still about 5 ppb VCM. The 4-hr CARB composites collected during the sample study period showed the same mean value. As indicated earlier, the NEIC composite samples were all below detectable limits.

<sup>\*</sup> NOTE: Generally, ambient air quality data has been found to have a log-normal probability distribution where the median and geometric mean value are equal. However, in locations such as this, where only a single source is present, the distribution may fall off significantly at lower concentrations. To differentiate these two cases, geometric means are only used in the former case, while median values are given in the latter.

The data indicate that installation of the fume incinerator has generally (but not in all cases) reduced the high VCM levels observed in earlier studies. The excursions measured by CARB data show that even with controls, significant levels are possible. The source of these levels whether a result of poor operations, maintenance problems, or usual procedures, has not been reported. The data also show that 5 ppb VCM may be the average level expected in the vicinity from the Company's routine level of operation since this was not reduced by the controls already installed.

Ambient standards do not presently exist for exposure of the general population to VCM and it is not likely that any will be promulgated in the near future. It has also been observed that disagreement exists among the medical profession as to levels of concern, as well as factors of safety that might be applied to existing standards to protect the health of the general population (see Appendix D).

Two possible approaches were examined as a means of addressing the safety of those living in the Saugus area. Here consideration must be given to the fact that this group includes the young, old and infirm whose health status can be significantly different from that of the employed and whose exposure may be 24-hr/day for long periods of time.

One approach having precedent  $^{1,2}$  is to apply a safety factor to existing OSHA standards. A factor of 1/10 could be applicable to those levels in the vicinity (outside the plant) for persons who might be exposed for an eight-hour period and a factor of 1/30 applicable for those of the general population in residence in the area (three 8-hour periods). This technique has been used to regulate radiation levels for substances which are also considered to be carcinogenic and without a lower threshold limit. This safety factor would lower the 8-hr average to 33 ppb (1 ppm = 1,000 ppb  $\div$  30 = 33), the 15-min maximum to 167 ppb, and the action level to 17 ppb average over an 8-hr period for the general population exposure. Other factors of safety are also feasible.

A second approach would be to select a control level from data used to establish the NESHAP standard. These data indicated that a continuous exposure to 1 ppb VCM causes a lifetime carcinogenic risk to the individual of about 3 x  $10^{-5}$ . This level is in the range of other government standards for carcinogen risks. It has been suggested that action be taken whenever the long-term average concentration exceeds 1 ppb.  $^3$ 

Using data collected during the third survey, it is possible to show the time that established levels would be exceeded for the various control strategies discussed above (Table 8).

Table 8

PERCENT OF TIME CONCENTRATIONS EXCEEDED

SELECTED LEVELS

		Saf	Control Level		
	<u>1</u>	1/10	1/30	1/100	1 ppb
8-hr avg* 15-min max** Action Level*	<0.02 <0.03 <0.1	2 1 6	10 4 21	33 13 52	88 20 -

<sup>\*</sup>Estimated from 4-hr CARB data

The Table shows that even if a minimal safety factor (1/10) is considered acceptable, plant emissions presently exceed these limitations; e.g., the 8-hr average is exceeded 2% of the time. If the 1 ppb control level is considered, the Company may be required to reduce emissions below the 10 ppm NESHAP emission limitation to meet this control level in the plant vicinity.

<sup>\*\*</sup>Estimated from 15-min NEIC data

# V. IN-PLANT MONITORING SYSTEM EVALUATION

Concurrent with the first air monitoring survey, an inspection was conducted on April 28, 1977, to assess the adequacy of the gas chromatograph (GC) monitoring system installed by Keysor-Century to measure plant VC levels and to detect and eliminate VC leaks. To accomplish this objective, the GC monitoring system and the in-plant monitoring stations were examined relative to major emission sources. In addition, VC concentrations were monitored using an IST\*\* portable VC monitor (range 2 to 20 ppm) to compare results with the GC monitoring system and to determine if station relocation is necessary.

Plant operating logs were also obtained to correlate in-plant VC concentrations with specific process operations.

## SEQUENTIAL VC MONITORING SYSTEM

The GC monitoring system collects air samples in nine plant areas:

- 1. Environmental laboratory
- 2. Dryer area\*
- 3. Slurry tank area
- 4. VCM and VA charge pump area (west transfer area)
- 5. VCM unloading compressor area (tank farm)
- 6. VCM recovery system area (east transfer area)
- 7. Monomer work area\*
- 8. West reactor deck\*
- 9. East reactor deck\*

<sup>\*</sup> Located on second level about 6 m (20 ft) elevation, others are located at about 1 m (4 ft) elevation.

<sup>\*\*</sup> Trademark

Figure 7 shows the sampling port locations relative to the major areas of the plant. The sample ports for the monitoring stations (MS) are glass cylinders, 5 cm (2 in) in diameter by 10 cm (4 in) high, containing a bronze bead filter and are connected to the environmental laboratory by 1 cm (0.375 in) stainless steel lines. Once inside the laboratory high-density polyethylene lines connect the sample lines to the analysis system. A 1/8-hp vacuum pump draws the samples through a 16-port selector valve for GC analyses. The monitoring stations are identified by their location(s) on the selector. The samples are analyzed with a Hewlett-Packard Model 5834A gas chromatograph with a reported detectable VCM limit of 50 ppb. Some of the monitoring sites are sampled twice during a sampling sequence. Typically, each analysis, including purge time, takes about 3 minutes. Some stations (e.g., MS 5 and MS 6) are sampled every 48 minutes and other stations (e.g., MS 2/10 and MS 3/11) monitored twice in a sampling sequence, are sampled every 24 minutes. After each analysis the selector valve and sample line leading to the GC are purged for about 25 seconds with the gas from the next sample. The air samples from the monitoring stations are exhausted by the common vacuum pump to a charcoal filter. The GC results are reported on a continuous monitoring log maintained by Company personnel.

## IN-PLANT MEASUREMENTS

The in-plant measurements for vinyl chloride were made with an IST AG5000 vinyl chloride gas monitor that has a range of 2 to 20 ppm. The range of this instrument severely limited its usefulness in this case. Specifications and interference data for the IST monitor are given in Appendix C. Because of possible interference from other hydrocarbons used in PVC production, the in-plant measurements were compared to the GC measurements when possible, to confirm the measured in-plant vinyl chloride concentrations. Additionally, the location of possible sources

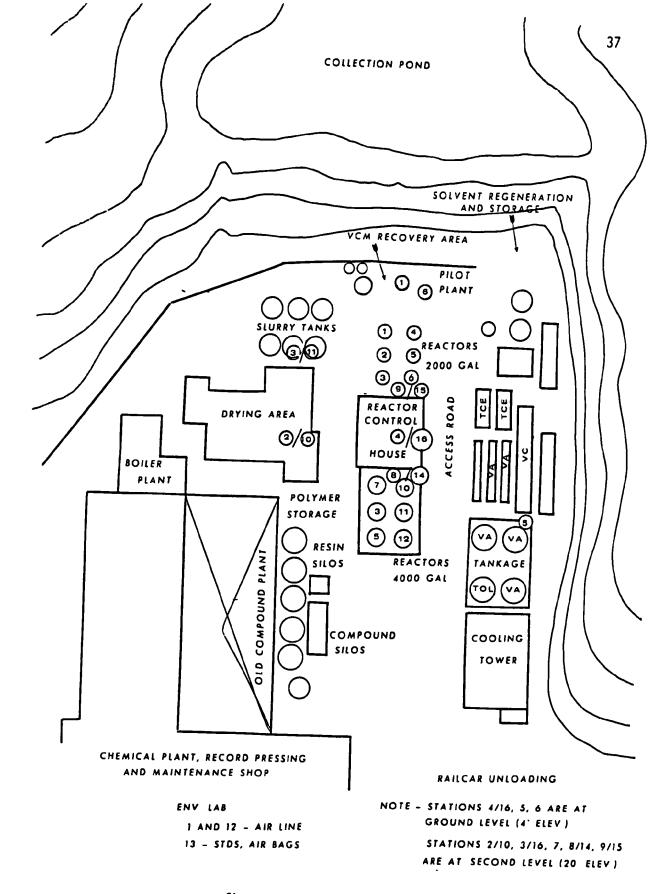


Figure 7. Location of Manitoring Sites

of interference and wind direction were noted when the in-plant measurements were taken to help account for discrepancies. Table 9 compares in-plant measurements with the GC analyses taken from the continuous monitoring log of April 28, 1977. Figure 8 shows the location of the in-plant measurements relative to the GC monitoring stations and major equipment.

Measurements 1, 3, 9, 19 and 21 were in plant areas where high emissions (>10 ppm) are routinely generated and were indicative of unit operations that routinely occur in the process. Measurement 1 (>20 ppm) was taken about 1.5 m (5 ft) east of the VCM unloading compressor and next to MS 5. The compressor was pumping VCM vapor from the railcar to a storage tank at the time of the reading. This compressor has a pressure relief valve that routinely exhausts VCM vapors while in service. High readings (>10 ppm) were recorded by the GC system and entered in the continuous monitoring log during the period that VCM vapors were being transferred. Measurements 3 and 9 did not correlate with GC readings, however, there were possible interferences from VA sources noted at the time of these measurements. Measurement 3 (>20 ppm) was taken at the VCM charge pump and measurement 9 (>20 ppm) at the opening of a slurry tank. Normally there would be no direct emission from the VCM charge pump; however, any VCM remaining in the resin slurry would be emitted from the open vent of the slurry tank. The exact magnitude of the VCM emissions could not be determined due to the limited range of the portable monitor and possible interference from VA. Measurement 19 (>20 ppm) was taken at the wastewater pond area located about 30 m (100 ft) above the plant. This area is not monitored by the plant monitoring system. In addition to the pond being a possible source of VCM, VA, and EDC, the VCM recovery system vent [2.5 cm (1 in) pipe] and the VA recovery system vent [10 cm (4 in) pipe] terminate at the edge of the pond.

Table 9

VC MEASUREMENTS AT THE KEYSOR-CENTURY PVC PLANT

April 28, 1977

			VC Concentration (ppm)			
Reference Number on Plot Plan	Location	Time	IST Portable Gas Monitor	Keysor-Century Monitor System (VC Specific)	Comments	
1	1.5 m (5 ft) east of VC compressor next to MS 5	0915	>20	5.3 at MS 5 at 0916	Pumping VC vapor from railcar to VC storage tank	
2	4.6 m (15 ft) south of VC charge pump in aisle	0925	0-5	1.1 at MS 4 at 0916	Possible VA interference	
3	l m (3 ft) above VC charge pump	0935	>20	1.1 at MS 4 at 0916	Possible VA interference from VA charge pump	
4	Next to MS 6	0940	<1	1.8 at MS 6 at 1003	VC recovery system pump about 1 m (3 ft) away	
5	O.6 m (2 ft) above VC recovery system pump 1 m (3 ft) east of MS 6	0942	<2	1.8 at MS 6 at 1003		
6	4.6 m (15 ft) below experimental 200 gal reactor 6 m (20 ft) east of MS 6	0945	<1	1.8 at MS 6 at 1003		
7	Next to MS2/10 dryer second level	0950	<1	0.4 at MS 2 at 1003	Slurry tanks have opening to atmosphere $^{\omega}$	

Table 9 (Continued)

			V( <u>Concentra</u>	; ition (ppm)		
Reference Number on Plot Plan	Location	Time	IST Portable Gas Monitor	Keysor-Century Monitor System (VC Specific)	Comments	
8	Next to MS 3/11 slurry tanks second level	0955	<2	0.8 at MS 3 at 1003		
9	At opening of slurry tank #4 10' west of MS 3/11	1000	>20	0.8 at MS 3	Possible VA interference	
10	Next to MS 7 VCM recovery area second level	1010	<1	0.3 at MS 7 at 1003		
11	Next to 200 gal experimental 3m (10 ft) north of MS 7	1013	<1	0.3 at MS 7 at 1003	Monomer was being added to reactor	
12	Next to MS 9/15 reactor area second level	1016	<1	1.2 at MS 9 at 1003		
13	Along walkway next to #5 reactor about 8m (25 ft) from MS 9/15	1022	3	1.2 at MS 9 at 1003	IST readings ranged from 0-15 ppm	
14	Along walkway next to #2 and #3 reactors about 8m (25 ft) from MS 9/15	1032	<10	0.7 at MS 9 at 1052	Variable wind during readings	

			VC Concentration (ppm)			
Reference Number on Plot Plan	Location	Time	IST Portable Gas Monitor	Keysor-Century Monitor System (VC Specific)	Comments	
15	Between reactor #10 and #7 at MS 8/14	1036	5-10	at MS 8 10.5 ppm at 1003, 0.8 ppm at 1052		
16	Along walkway next to reactor #12 12m (40 ft) east of MS 8/14	1043	3-7	at MS 8 10.5 ppm at 1003, 0.8 ppm at 1052		
17	Next to reactor #8	1049	0-10	0.8 at MS 8 at 1052	Variable wind during readings 5-10 mph	
18	<pre>lm (3 ft) above VC charge pump, next to MS 4/16</pre>	1057	3-7	0.5 at MS 4 at 1052		
19	Earth berm above plant to the east about 3m (10 ft) from VC recovery exhaust	1110	>20	-	VA and other HC interference from pond	
20	At MS 9/15 next to reactor #7	1332	7	8.3 at MS 9 at 1327, 2.6 at MS 6 1.5 at MS 7 at 1327	Before opening reactor #4	
21	At #4 reactor opening	1345	>20	n. -	Reactor opened steam/water vapor interference	
22	At MS 9/15 after #4 reactor opened	1350	7	8.7 at MS 15 at 1348, 26.7 at MS 6, 14.2 at MS 7 a+ 1248	Wind blowing away from MS 9/ toward MS 7 and MS 6	
2.	ica loa ar		< 1	-	Ma ·	

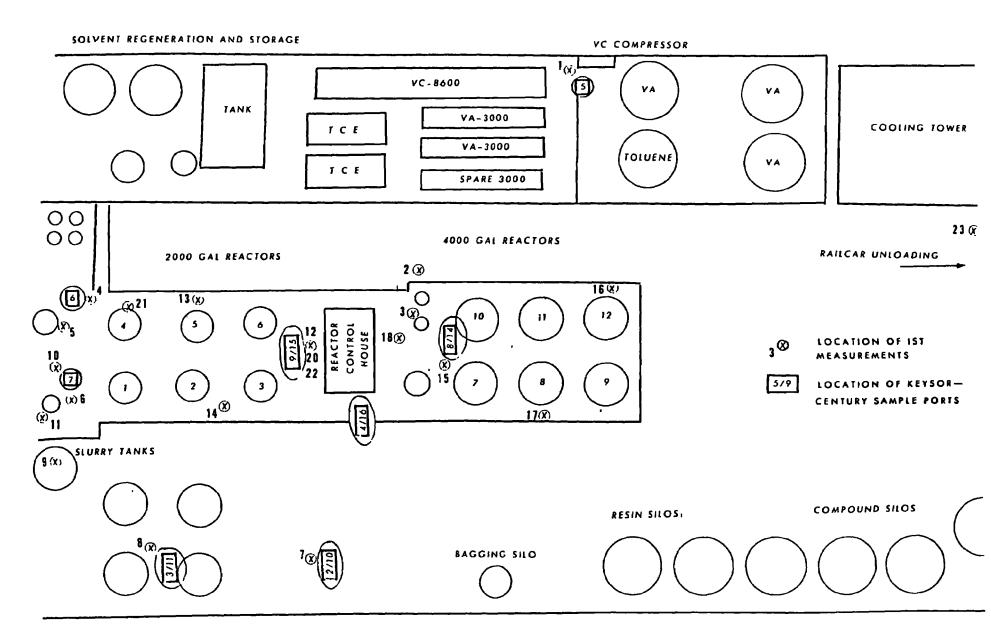


Figure 8 Location of Measurements taken with Portable IST Monitor

Measurement 21 (>20 ppm) was taken immediately after the #4 reactor was opened and before it was filled with water. Any residual VCM and VA remaining in the reactor could have been vented to the atmosphere when it was opened. Measurements 20, 21 and 22 were taken to determine if the GC monitors at the reactor level (MS 9/15) would be affected by the opening of the reactor. As indicated in both the IST and GC readings, MS 9/15 was not affected because of the wind direction as noted at the time of the reading. MS 6 and MS 7 which were downwind at the time monitored an increase in VCM concentrations. MS 6 is at ground level in the monomer recovery area and MS 7 is on the second level, indicating that the wind velocity and direction in the plant directly affects where and at what concentration VC emissions will be detected. A review of the continuous monitoring log for the week of April 24, 1977, indicated that higher concentrations were monitored during the evening and early morning hours when the air is expected to be more stable.

One objective that could not be accomplished during this survey was to relate high VC concentrations to specific pieces of equipment. VC levels often exceeded the limited range of the portable monitor. Other problems were the slow response time (sometimes as long as 5 minutes) of the instrument to changing concentrations and, as discussed above, interference from other hydrocarbons and water vapor.

# EVALUATION OF THE LEAK DETECTION AND ELIMINATION PROGRAM

The Leak Detection and Elimination Program as submitted to EPA Region IX on December 3, 1976, by Keysor-Century Corporation consisted of three main points:

- 1. VCM monitoring system
- 2. Leak definition
- 3. Plan of action when a leak is detected

### VCM Monitoring System

The VCM monitoring system, which is dynamically calibrated twice daily, appeared to be operating properly at the time of the evaluation. The readings taken by the portable monitor were comparable with readings taken by the GC system in cases where no interferences were noted. Additionally, many instances of high VC concentrations (10 to 214 ppm) were recorded by the GC monitoring system on the day of the inspection. Although the monitoring system appeared to be operating satisfactorily, it did not appear adequate for detecting leaks from specific pieces of equipment. The sampling ports are at least 3 m (10 ft) away from the equipment in VCM service. Because the plant is in the open, wind currents alter the areas actually being monitored by a specific sampling port. As shown by measurements 20 through 22 [Table 9], a reactor opening was monitored by ports located in the monomer recovery area and no effect was recorded on ports in the reactor area mainly due to the wind direction at the time of the opening. Generally speaking, the sampling ports are located to monitor general VCM levels in nine plant areas rather than monitoring specific equipment in VCM service.

### Leak Definition

Another indication that the monitoring system was only monitoring general VCM levels was the plant's definition of a leak. As part of the leak detection program, Keysor-Century defined incipient leak (background) levels for the nine plant areas based on previously monitored sample port concentrations. These leak levels range from 45 to 250 ppm and were to be updated as new equipment was installed and more stringent controls implemented. These leak levels had to be exceeded before further action was taken to eliminate the "leak". Based on these levels

and process operations that emit high concentrations (>10 ppm) of VCM on a routine basis, it was apparent that minor leaks, e.g., agitator seals, piping connections, etc., could go undetected due to the high VCM background levels in the plant area. It appeared that the background levels of VCM in the plant should be reduced before changes (such as adding more stations) are made to the monitoring system. Once the incipient leak level can be reduced to <10 ppm, a more effective leak detection system can be instituted.

### Plan of Action When a Leak is Detected

The third major part of the program is the action taken to correct a reported leak. Once a leak is detected, the shift supervisor is notified and he is responsible for finding and correcting the "leak" as defined by Keysor-Century. No specific written procedure could be provided by the plant manager, although the intended procedure called for a person to use a portable detector to find small leaks and pinpoint the major ones after notification.

The effectiveness of this procedure could not be properly evaluated since the Company could not provide leak detection or maintenance logs on how many leaks have been detected and what was done to correct them. No checklists or written procedures could be provided to indicate that success of the Leak Detection and Elimination Program is dependent on how the plant personnel find the leaks and eliminate them. Unless written procedures are adopted and abatement actions are documented, the success of the program cannot be evaluated. Because of regular recording of high VC concentrations by the GC monitoring system, it can only be presumed that the Leak Detection and Elimination Program as initiated by Keysor-Century was ineffective at the time of the inspection.

### REFERENCES

- Maximum Permissible Body Burdens and Maximum Permissible Concentrations of Radionuclides in Air and in Water for Occupational Exposure, U. S. Department of Commerce, National Bureau of Standards, Handbook 69, August 1963.
- Permissible Dose from External Sources of Ionizing Radiation, U. S. Department of Commerce, National Bureau of Standards, Handbook 59, 1954.
- 3. Personal Communication, Roy E. Albert, Chairman CAG, to R. L. O'Connell, Enforcement Director, EPA Region IX, August 8, 1977.

Appendix A

Process Description

#### PROCESS DESCRIPTION

The following description and flow diagram [Figure A-1] was obtained from an ES report to Region IX and from an earlier NEIC visit (May 30, 1974) to the facility.

Briefly described, PVC copolymer is produced from vinly chloride and vinyl acetate by suspension polymerization in twelve batch reactors: six 7,500-liter (2,000-gal), and six 15,000-liter (4,000-gal). Two pilot reactors [750-liter (200-gal) and 47-liter (12.5-gal)] are used to evaluate new materials. The plant capacity is approximately 55 m. ton (61 ton)/day.

Additives include a gelatin suspension agent, deconal peroxide catalyst, sodium bicarbonate buffer, and trichloroethylene (TCE) with some resins as chain transfer agent. TCE has been found to be carcinogenic. Reaction times for the small and large batches average 4 to 4.5 hr and 6 to 8 hr, respectively. Reactors are usually charged twice each day and no more than three reactors are brought to a critical state at one time. Stripping of reactants takes place when the process is about 90% complete. The excess VCM and VA in the reactors are recovered under pressure and vacuum respectively, condensed in chilled water cold traps, and recycled.

The reactor batches are directed to any of six open slurry tanks (approximately 30,000 liters) where the resin is held in suspension until centrifuged. After 20 to 25 batches, the reactors are cleaned with ethylene dichloride (EDC) which is recovered and processed for reuse. EDC is presently being tested for carcinogenicity.

There are two parallel drying systems to accommodate the resinwater slurry produced, each complete with a centrifuge, flash dryer, cyclone, screening equipment and baghouses for particulate emission

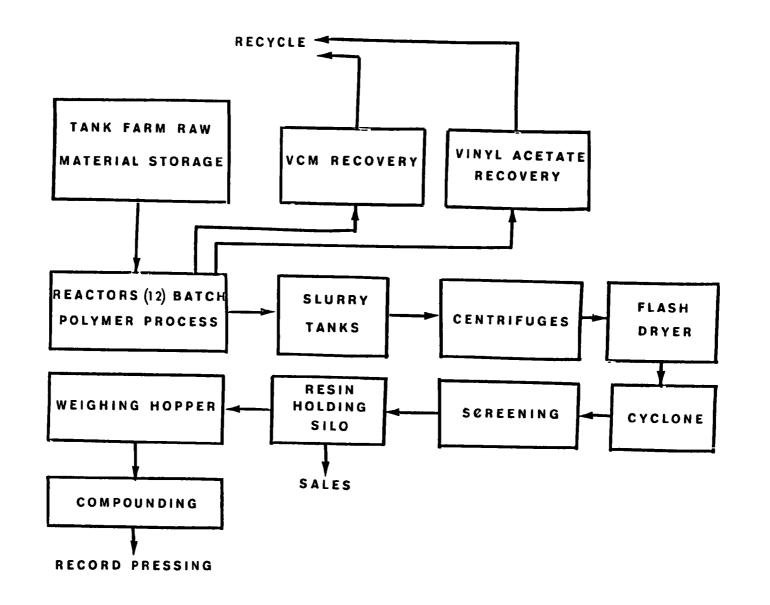


Figure A-1. Keysor - Century Corporation Process Flow

control. Dried resin for in-plant use is transferred to holding silos for temporary storage. From here it is conveyed to the weighing hopper where it is weighed for compounding and use in record manufacture. Resin for sale is held in storage silos to await shipment.

## Appendix B

Methodology and Gas Chromatograph/Mass Spectrometry Confirmation

### METHODOLOGY

A. Large charcoal tubes. These tubes were shipped to the laboratory in an ice chest cooled by dry ice and upon arrival were kept in a freezer until analyzed. The ends of the tubes were sealed with fiber tape from the time of collection until analysis.

Charcoal from each section of the large tubes was emptied into a cold 50 ml volumetric flask. Twenty-five ml of cold (6°C) CS, was added to each of the flasks to desorb the vinyl chloride. The flasks were placed in a freezer and left for 30 minutes to allow for complete desorption. An aliquot of each extract was then analyzed on a flameionization gas chromatograph held at the following conditions:

Oven temperature 50°C
Detector temperature 150°C
Injector temperature 100°C
Column 10' stainless steel, 6% OV-101 on 60/80 GCO

The desorption efficiency of vinyl chloride from the large tubes, at a level of 220  $\mu g$  on the tube, (each section contained 1.5 g of NuChar 14 x35) was 100%. Detection limit was 2.5  $\mu g$  VCM per section.

B. Small charcoal tubes. These tubes were shipped to the laboratory in an ice chest and, upon arrival, were kept in a freezer until analyzed. The ends of the tubes were closed with plastic caps from the time of collection until analysis.

The charcoal from the front section (100 mg) of each tube was emptied into a cold 2 ml vial. One ml of cold (6°C) CS, was added and the vial immediately sealed with a septum cap. The vial was then placed in a freezer for 30 minutes to effect complete desorption. An aliquot of the extract was then analyzed on a flame-ionization gas chromatograph under the conditions previously given.

The desorption efficiency for vinyl chloride from the small tubes at a level of 8.5  $\mu g$  of vinyl chloride on the tube, was found to be 91%. The data have not been corrected for desorption efficiency.

The back-up sections of charcoal (50 mg) for some of the tubes were also analyzed. The analysis is done in exactly the same manner as described above. In no case did the amount of vinyl chloride found on the back-up section exceed 30% of what was found on the front section. It therefore appears that breakthrough of vinyl chloride was not a problem in these samples. The amount reported is the sum of the two sections of the tube. Detection limit was 0.1  $\mu g$  VCM per section.

# GAS CHROMATOGRAPH/MASS SPECTROMETRY CONFIRMATION

The following are results from a sample analyzed for vinyl chloride by combined gas chromatography/mass spectrometry. The sample was a carbon disulfide extract of an activated charcoal tube sealed in a 2 ml vial, labeled as follows: Station 560, Hill Northeast of Plant on Barbed Wire Post, Sequence 16. The routine analysis had indicated a 0.3 ppm VCM concentration. Vinyl chloride was readily identified by comparing the mass spectrum of the sample to that of a standard vinyl chloride mass spectrum run on the same instrument. (Figure B-1 standard vinyl chloride and Figure B2-B sample.) There is some solvent interference at m/e 60 from a component peak that elutes a little earlier than vinyl chloride (Figure B2-B reconstructed gas chromatogram) but this small amount of interference did not preclude the positive identification and confirmation of vinyl chloride in the sample. The interference was not identifiable.

# SECTEM MUNEER 12 - 35

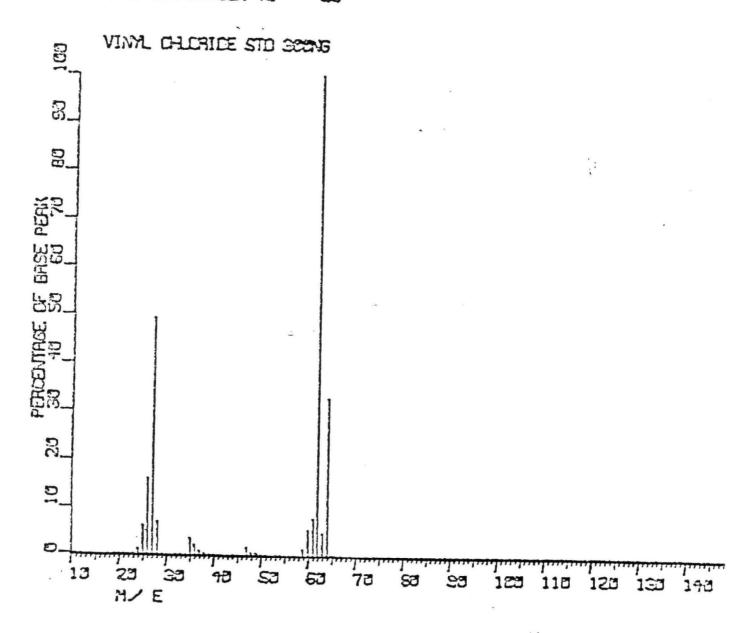
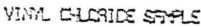
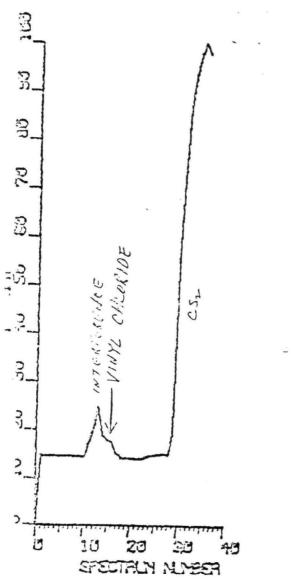
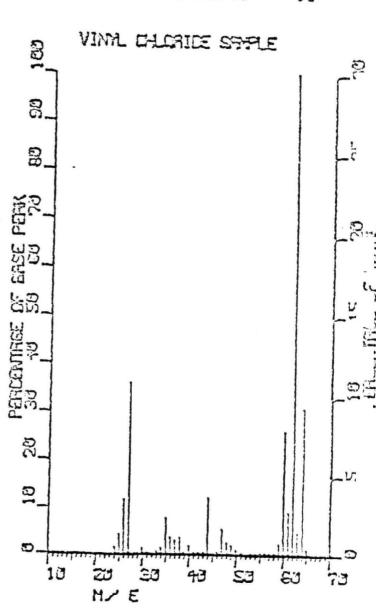


Figure B-1. Vinyl Chloride Standard





A. Reconstructed Chromatagram

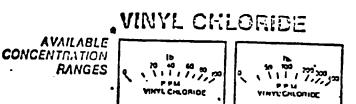


B. Sample

Figure B-2. Vinyl Chloride Sample

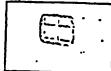
# Appendix C

IST Portable VC Monitor Specifications and Interference Data



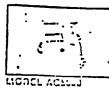
ÄVAILARILE • INSTRUMENT CONFIGURATIONS



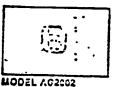


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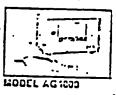


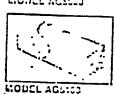


2 0 to 20 ppm range unit prepared for Engineering-Science, Inc.

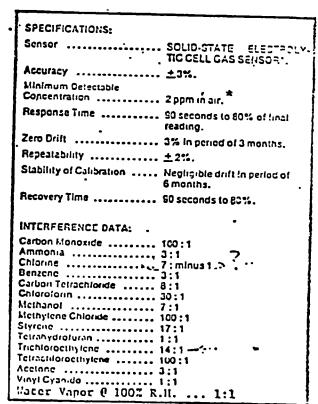








IST offers the only Vinyl Chloride sensor which has the advantages of the Solid-state Electrolytic Cell Sensor". The IST Vinyl Chloride instrument is more selective than instruments costing several times more. (See Interference Data.) The combination of solid-state circuitry and sensor results in an instrument that will provide years of trouble free operation.





3201 SOUTH HALLADAY STFEET EANTA ANA, CALIFORNIA 32705 • 714/646-0672 Appendix D

Medical Assessments

### DEPARTMENT OF HEALTH

2151 BERKELEY WAY
BERKELEY 94704
(415) 843-7900 Ext. 505

August 3, 1977

R.L. O'Connell, Director Enforcement Division United States Environmental Protection Agency, Region IX 100 California Street San Francisco, California 94111

> Re: E-3-2 Enf: 3-1-5

Dear Mr. O'Connell:

I have read your letter of July 15 concerning the question of whether there exists imminent or substantial endangerment to health of persons living near the Keysor-Century plant due to vinyl chloride monomer.

All the available data concerning health hazards from vinyl chloride relate to long-term exposure, and all the unequivocal data to long-term occupational exposures.

While the levels found by the NEIC study of 1977 seem excessively high, in light of what we know about the long-term hazards, it would not seem reasonable to use the term "imminent or substantial endangerment" of health status.

For imminent or substantial endangerment to be found it would in my view be necessary to have long-term exposures (years) to high average or repeated levels.

There are suggestive data of birth or pregnancy outcome abnormalities among residents near vinyl chloride plants in Ohio. No exposure data are known to me, so this type of hazard can hardly be put in quantitative terms.

Your letter enjoined haste, so the information provided above is based on memory rather than review of scientific reports.

Sincerely.

John R. Goldsmith, M.D.

oflick Gulmail

Medical Epidemiologist

Epidemiological Studies Laboratory



UNITED STATES ENVIRONM

ENVIRONM AL PROTECTION AGENC WASHINGTON, D.C. 20460

FROM:

Dr. Roy E. Albert Chairman, CAG

TO:

R. L. O'Connell, Region IX 8-556-1408

EBEARCH AND DEVELOPMEN

B. L. O'Connell, Director Enforcement Division, Region IX Environmental Protection Agency San Francisco, California 94111

AUG 8 1977

Dear Mr. O'Connell:

We have reviewed the NBIC monitoring report on the vinyl chloride concentrations near the Keysor-Century plant in Saugus, California. We have analyzed the monitoring data in such a way as to take into account as much as possible the measurements where VC was undetected as well as the concentrations detected. This was done by assuming that the measurements are distributed as a normal distribution as a function of the log of the dose, fitting the upper portion of the distribution to the measurements that were above the threshold for detection, and extrapolating the distribution to the 50 percent point, which is the median concentration. This median value is a rough estimate of the average concentration, and will of course be less than the measured values in this case, since only 37 of the 240 measurements are above the detection limit.

When this analysis was done, the following median values were obtained.

1) All composite samples combined: 0.33 ppb

2) All grab samples combined: 3.2 ppb

3) Grab samples in night-time hours: 3.0 ppb

4) Grab samples during daylight hours: 1.9 to 3.0 ppb. (This distribution was not closely log normal)

Therefore as a conservative (upper part of the range of uncertainty) estimate, the median concentration can be assumed to be 3 ppb, measured over a radius of 0.5 mile around the plant.

Before the vinyl chloride emission standards went into effect, the average concentration over a 5 mile radius of all plants combined was about 17 ppb, according to the evaluation of Kuzmack and McGaughy. The regulations had the effect of reducing the concentrations to 5 percent of their unregulated values, or to an average of about 1 ppb.

A continuous exposure to 1 ppb of vinyl chloride causes a life-time risk to the individual of about  $3 \times 10^{-5}$ , which is in the range of other government standards for carcinogen risks. Therefore it would seem logical to take action whenever the long-term average concentration exceeds 1 ppb.

Since the average level appears to be about 3 ppb near the plant, which includes the school yard, it would seem logical to take action sufficient to reduce the ambient concentrations to one third their current values in order to protect public health.

Sincerely yours,

Roy B. Albert, M.D.

Chairman

Carcinogen Assessment Group (RD-673)

Still a deman

cc: B. Gage W. Barber

J. Bonine

BERKELLEY . DAVIS . TRVINE . LOS ANCELES . RIVERSIDE . VAN DIEGO . SAN FRANCISCO



SANTA BARBARA · SANTA CRUZ

CM IFORMLY COLLEGE OF MEDICINE DEPARTMENT OF COMMENTEY AND LIMITED THE MEDICINE

IRVINE, CALIFORNIA 92717

July 21, 1977

Mr. Charles Eckerman
United States Environmental Protection Agency
Enforcement Division
Region IX
100 California Street
San Francisco, California 94111

RE: E-3-2 ENF-3-1-5

Dear Mr. Eckerman:

The following is in response to Mr. O'Connell's letter of July 15, 1977.

You requested that I give you an opinion as to the effect on human health of exposure to vinyl chloride in the ranges found by the National Field Investigation Center during the study of the Keysor-Century Plant in Saugus, California. Grab samples taken in the community near the plant were reported as having concentrations up to 0.50 ppm. A fifteen hour composite average value of 0.75 ppm was found and a peak value of 2.8 ppm recorded during a seven minute period by a continuous monitor located in the Saugus Elementary School.

The question of potential human hazard from such exposures has to take into consideration several points. First of all, the association between the vinyl chloride and the occurence of cancer in mr is so strong that today vinyl chloride is widely considered to be a carcinogen. Inhalation laboratory studies of animals in both this country and abroad have now shown the ability of vinyl chloride to produce cancer in several species of animals at the exposure level of 50 ppm. A further point to be taken into consideration is information from the animal work of Maltoni and Lefemine that the likelihood of development of angiosarcomas and nephroplastomas increases with the length of exposure. Maltoni and Lefemine have also demonstrated that vinyl chlorice is a transplacental carcinogen capable of producing cancer in the animal fetus. Another piece of vital information growing out of recent research work is that of Dr. Gehring's group at Dow Chemical in Midland, Michigan. This group has been able to show that the normal detoxification of vinyl chiroide through onjugation with hepatic glutathione may be saturated at high exposure levels has allowing for the formation of vinyl chloride epoxide. It is probable that the epoxide is the active carcinogen. The last piece of information is based on the work that has been done by many investigators over some long time to the effect that absorption of gases and vapors by the respiratory route increases with physical activity.

The relationship of these points to the present issue goes something like this: we are dealing with a well known carcinogen in which the length of exposure increases the likelihood of effect. The presence of such a compound is of increasing concern if children and young people are exposed since their potential length of exposure could be much greater than that of workers in the labor force. The ability of the compound to produce tumors in the fetus increases our concern for pregnant mothers in the community. The ability of the normal detoxification route in the liver to be saturated leads to concern for people in the community who have diseases which may limit their ability to detoxify vinyl chloride, consequently putting them in greater risk than healthy workers in the labor force. Lastly children, especially in school yard playgounds, may be exposed to greater absorbed doses for a given atmospheric concentration than workers in industry because of the greater physical activity of children during periods of play.

The above points argue very strongly for establishment of exposure limits well below the 1 ppm TLV set by the U.S. Department of Labor. The question of how far below the industrial TLV is one which can not be set with great precision. The June 1977 report from the National Enforcement Investigation Center sights as precedence for a community exposure 1/10 the industrial TLV, the National Bureau of Standards Handbooks 59 and 69 concerned with Ionizing Radiation. Other factors for the relation of community exposure levels to industrial TLV's can be found in standards for carbon monoxide, sulfur dioxide and beryllium. California Air Pollution Standards for carbon monoxide are 1/3 of the industrial TLV and for SO<sub>2</sub> are 1/25 of the industrial TLV. The long established community exposure limit for beryllium of .01 µg/M<sup>3</sup> averaged over a 30 day period is 1/200 of the industrial TLV of 2 µg/M<sup>3</sup>.

In view of the grave consequences of significant exposures to vinyl chloride and the potential for its far greater effect on people in the general population than those in the labor force, the community exposure level of vinyl chloride should probably be less than 1/10 of the industrial TLV. My recommendation would be at least 1/50 and more probably 1/100 of the industrial TLV based upon air sampling that averages concentration over periods of at least 24 hours.

In response to your request for a brief statement of my background and qualifications, please find enclosed a copy of my curriculum vitae.

Sincerely.

B. Dwight Culver, M.D.

Associate Clinical Professor

enc.

July 28, 1977

Charles Eckerman Senior Attorney Advisor United States Environmental Protection Agency Region IX 100 California Street San Francisco, California 94111

> Re: E-3-2 ENF-3-1-5

Dear Mr. Eckerman:

Enclosed is my report and opinion in connection with the  $\ensuremath{\mathtt{EPA}}$  Keysor-Century document.

Please let me know if I can be of additional help to you.

Sincerely yours,

Thomas H. Milly, M.D.
Thomas H. Milby, M.D.

THM/kh

Encl.

### STATEMENT

Prepared for the United States Environmental Protection Agency, in connection with the potential health consequences posed by vinyl chloride levels measured in the area around the Keysor-Century Plant at Saugus, California.

Statement of Qualifications.

See attached.

My opinion on the potential health effects of the vinyl chloride levels reported in the vicinity of the Keysor-Century Plant.

I have read the document entitled "Survey of Vinyl Chloride Levels in the Vicinity of Keysor-Century, Saugus, California," prepared by the U.S. Environmental Protection Agency Office of Enforcement (EPA-330/2-77-017). My comments and opinions will be limited to a consideration of the potential human health consequences of exposure to vinyl chloride air concentrations approximating those reported in this EPA document. I am not qualified to comment on the air sampling techniques, analytical methodologies, or meteorological considerations discussed in detail in this document. Accordingly, my opinions are based on the assumption that the reported levels are substantially representative of the actual levels present, and that these levels range from about one-half to

one parts per million, with at least one reading as high as

2.8 parts per million having been reported. In my opinion

these air concentrations represent a clear and imminent

danger to human health.

The basis for my opinion is as follows. There exists adequate experimental evidence to confirm that vinyl chloride is carcinogenic in mice and rats when administered by inhalation at doses as low as 50 parts per million. In man there is clear, sound scientific evidence to indicate that vinyl chloride is capable of producing uniformly fatal cancers of the liver (angiosarcoma), as well as strong evidence implicating the chemical as a cause of cancer of the central nervous system and possibly the lung. In man the least dose capable of producing cancer is not known. Based primarily on extrapolation from data obtained in studies of experimental animals, the Occupational Safety and Health Administration (OSHA), at the advice of scientists from a National Institute for Occupational Safety and Health (NIOSH) established a workplace permissible exposure level of one part per million vinyl chloride following extensive administrative hearings in June of 1974. In the course of these hearings testimony was given to the effect that, based on currently available information, no decision could be made concerning risk of exposure to vinyl chloride at concentrations less than 50 parts per million. However, testimony to the contrary, that is, a safe exposure concentration is not possible within the present

state of scientific knowledge, was also given by a number of scientists from both the public and private sectors. This latter argument prevailed and, as a result, the one part per million standard was established.

No national ambient air quality standard for vinyl chloride exists. In the EPA Keysor-Century report it was suggested that a factor of one-tenth be applied to OSHA standards to adapt them to general population exposures. is worth while noting here that, historically, it has been a practice to apply informally a factor of one-tenth the value of a sound scientifically based workplace exposure limit to exposures involving the general population. The rationale here has been that, although the work force is comprised of comparatively healthy adults, the general population contains substantial numbers of infants and children, elderly and infirm, any or all of whom may be reasonably expected to be more sensitive to the toxic effects of any chemical agent than their more healthy employed counterparts. Accordingly, the argument goes, a safety factor of ten should be applied to occupationally permissible air concentrations when such concentrations are applied to the general population as a whole. Although this tenfold safety factor appears reasonable when the hazardous substance involved is one that possesses conventional toxic properties (for example lead, mercury, strychnine, parathion), when the issue is carcinogenicity, the argument is substantially weakened. That is, one could

argue that exposure of a large number of the members of the general population could be expected to result in the causation of a substantial number of cancers even though the relative risk is extremely low. On the contrary, exposure to the same carcinogen even at a tenfold higher concentration would result in few if any cancers because the extremely low relative risk is unlikely to ever be expressed in a small (employed) population. The point of this whole discussion is that although the tenfold safety factor is reasonable in connection with conventionally toxic substances, it may not be reasonable when the toxic substance is a cancer producing agent. In the latter case a much greater safety factor than ten would in my opinion be justified.

Promas H. Milly, M.D.

Thomas H. Milby, M.D.

July 29, 1977