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INVENTORY OF CARCINOGENIC SUBSTANCES
RELEASED INTO THE AMBIENT AIR
OF CALIFORNIA: PHASE II

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ABSTRACT

The purpose of this research was to examine the significant sources of atmospheric transported carcinogenic emissions from a number of stationary sources in California. In the previous phase of this program substances and sites were identified for study and emissions were estimated based upon the available literature. In this phase principal emissions sources at each site were monitored and analyzed. Emission factors were computed and population exposure to the adjacent areas was determined by source and dispersion modeling. Concentrations predicted due to plant releases were compared with typical urban levels for each substance. Alternative control measures were described.

Sites measured were a secondary lead smelter (reverberatory furnace system stack), a primary steel mill (coke oven, tar decanter, and cooling tower), an asbestos-cement pipe plant (fiber baghouse and fugitive releases), a secondary lead smelter (reverberatory furnace) and four organic chemical manufacturing plants (stacks, storage tanks, wastewater streams, fugitive sources).

Compounds measured were cadmium, arsenic, polycyclic organic matter, asbestos, carbon tetrachloride, chloroform, perchloroethylene, benzene, and ethylene dichloride.

In general it was found that releases predicted from emissions factors published in the literature overestimated the measured emissions derived from source testing.

Releases from organic chemical manufacturing plants were due principally to storage tanks breathing and working losses. Such sources, although permitted by the local district, were exempt from stringent control requirements either because of their capacity, the fluid vapor pressure or the substance classification. The significance of plant releases was evaluated by computing the resultant incremental population exposure above background. Emissions from three of the four chemical plants were predicted to cause elevated population exposure to a level greater than 50% above typical urban background.

Releases of asbestos from the asbestos-cement pipe plant and arsenic from the secondary lead smelter were predicted not to elevate significantly general ambient concentrations of their respective substances.

The presence of five carcinogenic polycyclic aromatic hydrocarbon compounds was identified in the coke oven emissions from the primary steel mill. Their quantitative fractions of total emissions were determined by source measurements and their emission factors developed based upon the observed historical incidence of oven leaks coupled with a release factor per leak. Emissions were predicted to significantly elevate the typical ambient levels for the surrounding area. Although it is anticipated that the primary steel operation (coking) will cease, significant reduction of emissions will occur if the most leakprone coke oven batteries were closed.

Alternative control technology options exist and were delineated for all significant emission sources. Practical regulatory options are suggested including reduction of the minimum size for the requirement of storage tank emission controls.

FINDINGS AND CONCLUSIONS

1.1 Identification of Airborne Carcinogens

- (1) A framework was established in the previous phase of this study to prioritize the substances and emission sources of carcinogens within the state. It was by means of the derived rankings that sites were identified for further study and field testing in this program. In general it was concluded that this screening approach was effective in establishing appropriate priorities.
- (2) Where significant differences were observed between estimated plant emissions factors and those derived as a result of the field testing, the underlying cause for the disagreement was the adequacy of the information base upon which the emission factors were estimated. In several cases it was apparent that nationally based emission factors overpredicted California plant releases principally because local district or statewide regulation and/or inspection standards are more rigorous.
- (3) This study encompassed stationary source emissions identified by a statewide survey conducted as part of the previous phase of this study. Area and mobile sources were incorporated into the study framework as part of the urban background data base. An overall program objective was to identify any significant combinations of substances and sites which would induce so-called exposure "hot spots" where levels of exposure to the general population in the proximity could constitute a potential health risk. The program clearly delineated and prioritized several areas where background ambient concentrations of a particular substance are incrementally elevated by greater than 50%.

1.2 Emissions of Airborne Carcinogens

Emissions from plant processes and fugitive sources were quantified for each program site. Annual emissions predictions are listed:

- (a) Allied Chemical, El Segundo
chloroform: 23.5 to 325 lb (based upon year round chloroform feed operation)
carbon tetrachloride: 3669-5875 lb (based upon year round carbon tetrachloride feed operation)
chloroform and carbon tetrachloride: 1846-3100 (based upon equally divided feed operation)
- (b) Dow Chemical U.S.A., Pittsburg
carbon tetrachloride: 35,724 to 51,883 lb
perchloroethylene: 8,309 to 10,530 lb
(total plant emissions are sum)
- (c) Du Pont, Antioch
carbon tetrachloride: 16,515 to 21,467 lb
- (d) Johns Manville, Stockton
asbestos: <1 lb
- (e) Kaiser Steel, Fontana
five carcinogenic polycyclic aromatic compounds: 7420 lb
benzene: 315,000 lb
cadmium: negligible
arsenic: negligible
- (f) RSR Corp., City of Industry
arsenic: 8-32 lb
- (g) Stauffer Chemical, Carson and San Pedro
ethylene dichloride: 34,860 to 34,969 lb (Carson)
23,724 lb (San Pedro)

1.3

Control of Airborne Carcinogens

- (1) Emissions from the four synthetic organic chemical manufacturing plants are principally from storage tank breathing and working releases. Tanks are either feed or product storage and although permitted are exempt from stringent control for one of several reasons: because of their small capacity, the substance vapor pressure at permitted temperatures, or due to the fact that the substance is not classified as an organic liquid. A variety of

control options including vapor recovery systems are available to effectively reduce emissions.

- (2) Release of ethylene dichloride from the plant process wastewater stream at Stauffer was identified as a significant emission source. Emissions reduction could be achieved by modifications to improve the efficiency of the plant stripper processes or use of an activated carbon (or XAD-2 resin) system in the discharge stream.
- (3) Five carcinogenic polycyclic aromatic hydrocarbons were identified and quantified in the Kaiser coke oven gases. Leaks from coke ovens can be abated by rebuilding ovens or terminating operations on the most leakprone coke oven batteries.

1.4 Changes in the Emissions of Airborne Carcinogens

Coincident with this study a number of companies formally or informally announced changes in their operation which will directly influence plant emissions. Furthermore the trend in business activity at several sites is distinctly downward due to general market factors or the specific product market.

Specifically:

- (1) Kaiser Steel announced plans to terminate primary steel making operations. Projected closure will be in 1983. All emission sources identified in this site study pertain to such operations.
- (2) Stauffer Chemical Company formally announced plant closure in the near future due to market and plant economics.
- (3) The market for fluorocarbons has continued to decline and is expected to affect process activity at Dow, Du Pont and Allied.
- (4) Johns Manville announced the closing of its Carson asbestos-cement pipe plant asbestos related activity. Stockton plant activity is under production capacity due to the general economic situation.
- (5) Gould, a secondary lead smelter that was to be evaluated based upon testing results at RSR, has irreversibly discontinued operations at its original plant and built a new plant with

advanced control equipment. Baghouses are specified as 99.98% efficient for lead particulate.

- (6) Several plants indicated that they are planning to install emissions control systems on the storage tanks. No formal commitments were made.

1.5 Incremental Population Exposure Due to Stationary Sources

The four sites which were predicted to significantly elevate the typical urban background concentrations are listed below:

Site	Substance	Typical Urban Background Level	Population Exposed to Increment over Background	
			>100%	>50%
Allied+	Carbon Tetrachloride	0.15 ppb (942 ng/m ³)	<4,044 to 16,025	16,025 to 19,377
Dow	Carbon Tetrachloride	0.15 ppb (942 ng/m ³)	10,796 to 20,309	<20,309
Kaiser	PAH-5 compounds	3.5 ng/m ³	72,196	72,196
Stauffer	Ethylene Dichloride	0.51 ppb (2100 ng/m ³)	92,552	117,532

+ Assumes one half year operation using carbon tetrachloride feedstock

1.6 Regulatory Options

- (1) This study did not attempt to quantify or address the health effects or risk due to exposure from the predicted concentrations of any substance.
- (2) Each site and substance combination deserves to be considered individually. Regulatory options for emission sources at the four sites noted in Section 1.5 are as follows:
 - o Allied Chemical - Emissions are principally from feed storage tank working loss (displaced vapor volume). Tank is exempt due to minimum size requirements of SCAQMD Rule 463. The minimum tank capacity for control could be reduced. A closed loop feedback control system analogous to the existing adjacent chloroform tank would effectively reduce emissions.

- o Stauffer Chemical - Emissions from the offsite storage tanks (3) are due to normal tank breathing. Tanks are exempt since vapor pressure is slightly under the 1.5 psi threshold at storage conditions. One option is to amend Rule 463 and lower the vapor pressure threshold by less than 10%. Another is to consolidate the three tank contents.

Emissions of EDC from plant process wastewater account for the other principal source. Allowable concentration is stipulated in the discharge permit with the Los Angeles County Sanitation District. This permit would offer the most direct means of regulating EDC concentrations in wastewater. As previously noted the plant is discontinuing operations and currently has its vinyl chloride monomer process closed due to exceedances of the ambient VC standard. Thus regulatory options may be a moot discussion point.

- o Kaiser - Emissions of carcinogenic PAH compounds from coke oven leaks can be reduced by rebuilding ovens or discontinuing their operations. Several batteries (B-D) contribute 86% of the emissions. Sequential shutdown of these batteries as part of the planned primary steel mill closure would be logical. Currently the plant is operating under a variance due to carbon monoxide emissions. Conditions of operation under that variance could be imposed which would minimize oven leak emissions.
- o Dow - Emissions are predominantly working level vapor displacement from process check tanks and also breathing and working losses from product storage tanks. Currently the tanks are exempt under Rule 85300 of the Bay Area Air Quality Management District because the substance is not classified as an organic liquid. Furthermore check tank size as measured by working capacity is under the minimum regulatory threshold.

2.0

RECOMMENDATIONS

Given the findings and conclusions presented in Section 1, we make the following recommendations.

- (1) Discussions should be held with local air quality control district staff and representatives of the four firms whose emissions were computed to significantly increase the local urban background concentrations of specific substances. If plans are underway to close the plants, schedules should be confirmed and monitored. Discussions with Allied and Dow should explore the status of company plans to install control systems on storage tanks. In the absence of such activity regulatory alternatives should be assessed.
- (2) Although fugitive emissions from the synthetic organic chemical manufacturing plants studied were found to be of secondary importance, refineries have orders of magnitude greater numbers of baggable sources including seals, valves and flanges. Inspection leakage frequency data currently being collected by each firm or by others (e.g., ARB or regional Districts) should be used to compute the plant emission factors for benzene. As a sufficient body of historical data become available for each refinery results should be used as source terms to predict ambient concentrations and determine whether additional actions are needed.
- (3) Release of carcinogenic volatile organic compounds into wastewater was not comprehensively examined by this program. One such source was identified and raises the question of whether other such emission sources exist throughout the state. Examination of process wastewater standards in consultation with county sanitation districts would be a first step.
- (4) It is recommended that as additional substances are identified as suspected carcinogens they be screened for possible importance employing the prioritization methodology developed in these studies.

3.0

DESCRIPTION OF THE PROGRAM

The purpose of this program was to intensively examine the significant sources of atmospheric transported carcinogenic emissions which were identified and inventoried in a preceding CARB sponsored research program conducted by SAI (Margler et al., 1979) and its subcontractor KVB (Roberts, 1980). Before discussing the objectives and approach of this subsequent project, a review of the findings of the initial program stages is in order.

3.1 BACKGROUND

The CARB-sponsored studies were initiated to identify airborne carcinogens of potential concern to the general public for the purpose of examining the need to develop some form of state emission regulations for these substances. The program was constructed as a three stage study. The objective of the first stage was to identify roughly ten materials which, of the thousands of known or suspected airborne carcinogens, were most likely to be of greatest importance to the general population of California. Also of interest were those substances which, in order to satisfy occupational health and safety regulations, might be transferred from the workplace air to the outside environment. The second stage encompassed using existing data to pinpoint the emission sources for each carcinogen, estimating emissions, and developing preliminary designs of source tests to quantify emission factors. The final stage, which is the subject of this report, consisted of the design and conduct of source testing at the sites identified as the suspected principal sources of the carcinogens of greatest concern.

In the initial stage of the program it was necessary to screen a large number of candidate carcinogens. The screening process was conducted as follows:

- (1) Eight compilations of known and suspected carcinogens were reviewed and those substances which were not used in California, were highly

unstable in air, or were very doubtfully carcinogenic, were eliminated.

- (2) After more detailed information was obtained for the remaining 25 substances, candidates were rated by arithmetic and multiplicative methods.
- (3) An expert panel was convened to review information dossiers on the candidates and to rank them independently.
- (4) From the eight to eleven substances ranked highest by all three approaches, eleven were selected for the emission identification and source-testing design stages of the effort.

Each of these steps is described in Appendix A, the Air Pollution Control Association Journal article, "Rapid Screening and Identification of Airborne Carcinogens of Greatest Concern in California."

The eleven substances selected for further study at the end of the first stage of the program were:

Arsenic	Ethylene Dibromide
Asbestos	Ethylene Dichloride
Benzene	Nitrosamines
Cadmium	Perchloroethylene
Carbon Tetrachloride	Polycyclic Organic Matter (POM)
Chloroform	

Sites where the highest emissions of these substances might be expected as a result of their use or manufacture were identified. In nearly all cases no direct information with which to predict plant emissions was available. Rather, indirect data and engineering judgement were used to estimate releases. Preliminary test plans were drafted for important sources to enable a direct determination of the emission factors. Although area or

dispersed sources were identified for many of the carcinogens, tests were conducted only for the stationary sources. This was done in order to locate and accurately quantify sources of concentrated releases, i.e. "hot spots", which could later be superimposed with the more diffuse distribution of area sources. Area sources such as dry cleaning establishments and degreasing operations (perchloroethylene) and home fireplaces (POM) are typically coincident with population density distributions. Other area sources are distributed during vehicular travel (benzene, cadmium, ethylene dibromide, ethylene dichloride and POM). Still others are distributed in agricultural operations (arsenic, ethylene dibromide and ethylene dichloride).

Site visits to a number of the plants were conducted during this stage to become more familiar with plant processes and potential emission sources and to assist in the formulation of the test plans. Each individual substance released at every site was ranked according to a formula consisting of the product of the specific pollutant emissions (in tons per year), the population of a 10-km grid centered at the site, and rating factors reflecting growth in chemical use, atmospheric stability, dispersion potential and evidence of carcinogenicity. Each facility was then ranked according to this hazard scaling factor. Table 3.1-1 (Roberts, 1980) is a summary of the results of this hazard ranking. It was recognized that only by on-site emissions testing could estimates of releases be realistically used in conjunction with meteorological data and census information to provide meaningful source factors with which to compute population exposures.

3.1.1 Outline of the Current Program

The program was divided into three principal tasks. Task I encompassed all pretest activities, including reviewing preliminary site sampling plans and analytical methods, conducting pretest site surveys at all locations, and formulating final sampling and laboratory analysis plans. Task II comprised the emissions testing and laboratory analyses. In Task III, emission factors were determined and Gaussian dispersion modeling was used to estimate integrated community exposures around each stationary source. Resultant concentrations were compared with typical ambient levels and site emissions were compared with total statewide releases where possible.

Finally for those stationary source emissions found to be significant mitigation measures were proposed and guidelines for the development of air quality or emission standards were provided.

Table 3.1-1 Relative Hazard Scaling Among Stationary Sources Investigated (Roberts, 1980)

$$\text{Scaling Factor} = (\text{Emissions, tpy}) \times (\text{pop. dens.} \times 10^{-3}) \times R_2 \times R_4 \times R_5 \times e^{R_6}$$

Site	Pollutant	Estimated Annual Emissions, Tons	Pop. density around site 10^3 People/ 100 sq. km	Rating Factor [†] R ₂ R ₄ R ₅ R ₆	Scaling Factor $\times 10^{-6}$
Kaiser Steel Corp., Fontana	Benzene	112	43.7	3 5 5 5	54.5
	Cadmium	7.0	"	3 5 5 5	3.4
	Arsenic	1.6	"	3 5 5 5	0.5
	POM	27 §	"	4 5 5 5	17.5
				Plant Total	75.9
Stauffer Chemical, Carson	Ethylene dichloride	150 #	89.9	3 5 5 4	55.2
Dow Chemical USA Pittsburg	Carbon tetrachloride	160 †	63.8	3 5 5 4	41.8
	Perchloroethylene	22 †	63.8	3 5 5 4	5.7
				Plant Total	47.5
DuPont de Nemours & Co., Antioch	Carbon tetrachloride	250 **	63.8	3 5 5 4	41.8
Chevron USA, Richmond	Benzene	50	62.8	3 5 5 5	35.0
ARCO, Carson	Benzene	25	75.9	3 5 5 5	21.1
Allied Chemical, El Segundo	Carbon tetrachloride	133 **	32.7	3 5 5 4	17.8
Witco Chemical Co., Carson	Benzene	14	89.9	3 5 5 5	14.0
Chevron USA, El Segundo	Benzene	30	35.9	3 5 5 5	12.0

continued

Table 3.1-1 Relative Hazard Scaling Among Stationary Sources Investigated (Roberts, 1980) (Continued)

$$\text{Scaling Factor} = (\text{Emissions, tpy}) \times (\text{pop. dens.} \times 10^{-3}) \times R_2 \times R_4 \times R_5 \times e^{R_6}$$

Site	Pollutant	Estimated Annual Emissions, Tons	Pop. density around site* 10 ³ People/ 100 sq. km	Rating Factor [†]			Scaling Factor x 10 ⁻⁶
				R ₂	R ₄	R ₅	
Gould Inc., Vernon	Arsenic	22	23.6	3	5	3	3.5
RSR Corp., Industry	Arsenic	3.3	59.5	3	5	3	1.3
ALCO-Pacific, Carson	Arsenic	2.2	88.1	3	5	3	0.4
Pacific Gas & Elec., Pitts.	Arsenic	1.0	63.8	3	5	3	0.4
Johns-Manville, Stockton	Asbestos	2.9	28.5	1	5	5	0.3
Calavaras Asbestos, Copperopolis	Asbestos	148	0.5	1	5	5	0.3
So. Cal. Edison, Long Beach	Arsenic	0.8	50.0	3	5	3	0.3
Pacific Gas & Elec., Salinas	Arsenic	1.0	0.3	3	5	3	0.02

NOTES: * Point source geographically located in center of 100 sq. km

+ Rating factors defined in Margler, 1979 as R₂ = growth in use of pollutant in California; R₄ = stability of pollutant in air; R₅ = pollutant dispersion potential; R₆ = evidence of pollutant carcinogenicity

§ Assumes POM/benzo(a)pyrene (BaP) = 10; BaP actually measured

A minimum estimate

‡ Process factors suggest that the large difference between CT and perc emissions is suspect

** May be high by an order of magnitude

3.1.2 Pre-test Activities

The first subtask undertaken in this program was to closely review the findings from the previous stages, particularly in light of the need to allocate resources effectively. Some emissions estimates were found, upon reanalysis and incorporation of new information, to be unreasonable. Furthermore, one identified arsenic source (Gould Metals Division, Vernon) entered into the final planning and initial construction phase of building a new facility; the existing plant was to be razed. Site visits were made to all remaining sites considered for testing and all but one were incorporated into the field measurement program. The project resources dedicated to each plant were established to correspond with both the predicted priority as a significant source and the uncertainty in the existing emission data. The sites which were sampled in this program were:

<u>Site</u>	<u>Carcinogen Sampled</u>
Kaiser Steel, Fontana	Arsenic, cadmium, POM, benzene
Stauffer Chemical, Carson	Ethylene dichloride
Dupont, Antioch	Carbon tetrachloride
Allied Chemical, El Segundo	Carbon tetrachloride or chloroform
Johns Manville, Stockton	Asbestos
RSR, City of Industry	Arsenic
Dow Chemical, Pittsburg	Carbon tetrachloride and perchloroethylene

These are listed in order of descending priority based upon the revised assessments. These emission estimates are discussed in the corresponding report sections on the determination of emission factors for the sampled sites. For completeness, Appendix B contains summary reviews of the disposition of several sites considered in the previous study stages which for various reasons did not need to be considered further in this stage.

Task II, Source Testing, is described in Sections 4.0 through 10.0. Task III is discussed as part of these sections (Determination of Emission Factors) and in Sections 11.0 through 12.0.

SOURCE TESTS AT RSR/QUEMETCO, CITY OF INDUSTRY

4.1 FACILITY DESCRIPTION

RSR's City of Industry facility, Quemetco Inc., is one of five secondary lead smelters operated by the corporation. On 10 December 1980, representatives of SAI and its subcontractor, Certified Testing Laboratories (CTL), toured the plant and obtained the following information.

Lead and its alloys are the company's primary products. The plant consists of a raw materials storage and crushing facility, a cupola (blast furnace), a reverberatory furnace, and a refining facility. The cupola has been shut down for the past two years, and is not expected to be reactivated in the near future; the slag which it once processed is shipped to an RSR plant in another state. Lead production rates are proprietary.

The input material consists primarily of lead-acid automobile batteries, although sundry lead scrap is also processed. According to plant management, the lead in batteries contains less arsenic than in former days. RSR no longer deliberately adds arsenic to its products. However, trace amounts of arsenic probably remain in the continually recycled lead.

At the crushing facility, the battery cases are removed. The newer ones, made of polypropylene, are crushed and then sold to a reprocessor. Hard rubber cases and PVC separators are not reprocessed and are discarded. Sulfuric acid from the batteries is, after use in the crushing facility, neutralized with ammonium hydroxide, and discharged into the sanitary sewer.

The first step in smelting is to dry crushed lead in a rotary kiln. The lead is then fed directly into the reverberatory furnace, which operates at 2200 to 2300 °F. Molten lead is poured into "hogs," which are taken to the refinery room in a hardened state. In general, the reverberatory furnace is operated for about two weeks and then shut down while the refining is done, although there is sometimes an overlap between smelting and refining. The plant's schedule is quite irregular, and cannot be predicted more than a couple of days in advance. The lead market is currently down, and the plant does not operate every day.

Quemetco maintains four essentially complete and independent air pollutant control systems. The one for the blast furnace is presently shut down. A second system serves the reverberatory furnace, and consists of two cooling chambers, a baghouse, a scrubber and a stack. The baghouse uses Teflon bags and is rated at 200 °F. The scrubber was modified by RSR from a commercial system, and its description is proprietary. There is nothing in the scrubber system that would chemically bind arsenic. The other two control systems trap fugitive emissions from the rotary kiln, the refinery and various other sources; Quemetco refers to these as "sanitary systems."

During our pre-test site visit, we made a few observations. There is no great accumulation of lead dust, and workers were continually vacuuming and shoveling whatever dust had settled around the kiln and the furnace. The outdoor storage and crushing area was being hosed down as we toured it. One diked area contained pools of acidic wastes. Quemetco said that it was going to be resurfaced. All the major emission sources, such as furnace and kiln doors and refinery pots, were hooded. We did see a thick cloud of dust issue from a port as a worker added coke fines. These emissions ceased when the worker adjusted a damper on the hood. The stack associated with the reverberatory furnace emitted a visible steam plume. We could see a faint, dark particulate plume continuing on after the steam evanesced.

4.2 SAMPLING AND ANALYTICAL APPROACH

Arsenic was the only air pollutant of interest to this study. Because the reverberatory furnace was considered to be the largest potential source of arsenic emissions, we decided to collect air samples downstream from the pollution abatement system associated with it. Although a port was available for sampling emissions from the "sanitary systems" (see above), we confined our attention to the reverberatory furnace emissions. Our reasons were:

- o The reverberatory furnace emissions were expected to be significantly greater than those from fugitive sources;
- o Access to the sanitary system sampling port was difficult; and
- o There was not enough time to sample both sources. (The facility operator in effect limited our presence on site to two days.)

4.2.1 Stack Sampling

Stack gas samples were collected by proposed U.S. Environmental Protection Agency Method 108, "Determination of Particulate and Gaseous Arsenic Emission from Nonferrous Smelters", a copy of which is provided in Appendix C. In this method, air samples are drawn isokinetically from a stack and through a sampling train consisting of a probe, a heated filter and a series of impingers resting in an ice bath. (See Figure 4.2-1). The filter removes particulate matter, and any arsenic vapor is trapped in the impingers.

Our procedures departed from Method 108 in three respects. First, the probe and the Teflon line connecting it to the heated filter were maintained at 250 to 320 °F to prevent condensation of water vapor flowing through the duct. Second, the three impingers used in Method 108 for sulfur dioxide sample collection were eliminated, since we were interested only in arsenic. Finally, instead of distilled water, the first two impingers contained a KI/I₂ solution and a Na₂S₂O₃ solution, respectively. The purpose of the iodine solution which was included at the suggestion of the CARB project monitor, was to oxidize any arsine gas present in the exhaust. The sodium thiosulfate protected the sampling pump by reducing iodine vapors.

Samples were taken from a 0.89-m outside diameter horizontal duct which connects the SO₂ scrubber outlet to an exhaust stack. A duct rests on a two-foot high ledge running diagonally across the roof of a small control building, and is equipped with one horizontal and one vertical sampling port. A portable ladder was used to get onto and off of the roof. We used the ledge to support various equipment, including the box containing the filter and impinger train. An "umbilical cord" connected the filter/impinger box with a pump console at ground level.

Each sampling run consisted of a horizontal traverse followed by a vertical one. The first step was to check the system for leaks. In all cases (before and after runs) no leaks were detected. Then the probe was inserted as far as possible into the sampling port. A heavy paper rag was used to block off most of the flow around the probe, although some steam did escape. In between horizontal and vertical traverses, and after the latter, the probe was held horizontal for five minutes, so that it could be purged with ambient air.

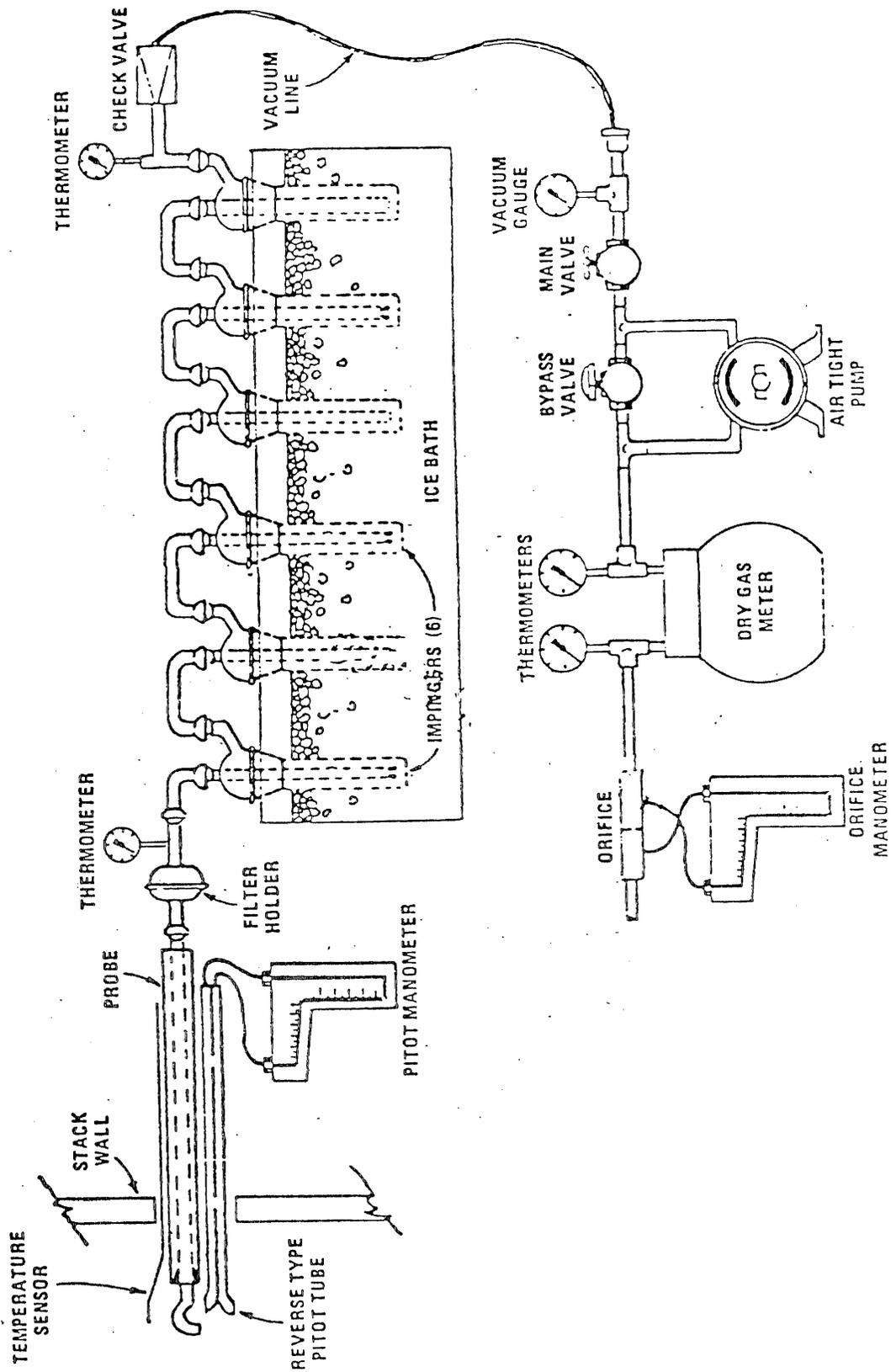


Figure 4.2.1 Arsenic Sampling Train

After the two traverses and the purging, the system was shut down. The nozzle was unscrewed from the probe, brushed and washed with 0.1 N NaOH. The Teflon line was laid out along a metal beam that ran alongside the roof, was taped securely in position, and then was washed with a brush attached to several sections of thin aluminum tubing. Great care was taken to avoid touching the brush to any contaminated surface. It was impossible to avoid contamination of the aluminum tubing. To minimize contaminating the washing from the Teflon tube, therefore, we wiped the aluminum tubing with a NaOH-soaked paper towel just before inserting each section into the Teflon line. After the brushing, additional NaOH was poured into the line. All washings were collected into a polyethylene bottle. The probe and a stainless steel pipe connecting the sampling line to the filter apparatus were washed in similar fashion. Finally, the impinger solutions were poured into sampling bottles, and the impingers were then washed with the corresponding matrices (iodine and sodium thiosulfate).

4.2.2 Analysis for Arsenic

Filters were cut into ribbons and digested in hot redistilled HNO_3 and H_2O_2 . Impinger solutions were acidified with redistilled HNO_3 . All samples were then analyzed by graphite furnace atomic absorption spectrophotometry.

4.3 DETERMINATION OF EMISSION FACTORS

4.3.1 Emission Test Results

Tests were performed on 10 and 11 February 1981 by SAI and CTL personnel. We originally planned to conduct three test runs. Test set-up and preliminary measurements took much longer than anticipated, however, and we did not begin the first run until about 1400 hours on 10 February. The horizontal traverse was conducted with no problem. At the start of the vertical traverse, however, a great deal of water was sucked into the system. We believe that this water had been lying on the bottom of the horizontal duct. The duct is drained by two pipes, but these were either clogged or at an improper angle for good drainage. The test was aborted. Since it was now late in the afternoon and extensive cleanup of equipment would be necessary, we decided to postpone further testing until the next day. During the evening, Quemetco personnel drilled two holes in the bottom of the duct to drain

out the water. On 11 February, we conducted two successful test runs. Filters and sample bottles were sent by air freight to SAI's La Jolla laboratory and were delivered within 18 hours of completion of Run 3.

After both runs the filter was very clean. No particulate matter was visible. A considerable amount of material was recovered from the nozzle and probe wash. Since these fine particles turned reddish-brown upon contact with the NaOH solution, we believe that they are primarily some form of iron hydroxide. After Run 2, three tiny clumps of yellowish material very similar in appearance to the substance covering the work area was found on the downstream end of the nozzle, just outside the orifice. We can only speculate on what this material is and how it got onto the nozzle. The most likely possibility is contamination during the probe assembly. Another is that the material coats the inside of the duct and that the nozzle touched it during a traverse. Another possibility is that the material was entrained by the flue gases somewhere in the system and collected by the nozzle. Material such as this was not observed after Run 3.

The results of our laboratory analyses were as follows:

<u>Sample</u>	<u>Arsenic Measured (micrograms)</u>	
	<u>Run 2</u>	<u>Run 3</u>
Filter	0.8	0.1
Impinger	0	0
Probe Assembly	86.4	28.3
Total	87.2	28.3

Arsenic concentrations in the iodine and sodium thiosulfate impingers were essentially the same as in the sample blanks for each impinger solution. Most of the difference in results for the two runs is due to the collection of the above-mentioned clumps of yellowish material by the probe in Run 2. Other test results cannot be furnished without violating a secrecy agreement between RSR and SAI. Total annual emissions, based upon proprietary information on lead processing rate and furnace operating hours, are estimated to be between 3.7 and 16 kg/yr (8.1 to 32 lb/yr). These emissions are quite low in comparison with those of other arsenic emission sources identified in the second stage of this study.

4.3.2 Estimation of Emission Factors

Emission factors for this plant cannot be stated without revealing proprietary information furnished by the plant.

SOURCE TESTS AT KAISER STEEL CORPORATION, FONTANA

5.1. FACILITY DESCRIPTION

Kaiser Steel Corporation's steel mill facilities at Fontana (San Bernardino County) have been described in detail in previous reports by the Air Resources Board (CARB, 1976) and KVB (Roberts, 1980). The purpose of this section is to describe conditions which have changed since those reports were written. Detailed descriptions of the emission sources we tested will be found in Section 5.2.

The coke oven complex at Kaiser consists of seven batteries of 45 ovens each. At the time of our first pre-test visit (28 October 1980), the status of Battery B was in doubt; it is presently in violation of South Coast Air Quality Management District (SCAQMD) regulations, and 27 of its ovens are out of service. The date of compliance with regulations had been postponed until December 1981. As of October 1980, 49 ovens (among all seven batteries) were "permanently out of service" (H. Rügge, personal communication).

During our October 1980 visit, dark particulate emissions from the stack associated with Batteries F and G were observed. According to Kaiser, the baghouse associated with these batteries had recently caught fire and was inoperable. Battery A had the least emission problems.

It should be noted that the Fontana operation has for the last several years been barely surviving economically. The inland location of the plant put it at a disadvantage with respect to other steel-making facilities, especially those of Japan, while the switch from steel to aluminum in can manufacture has eliminated a major operation. Indeed, Kaiser management recently decided to terminate all the basic steelmaking operations, including the coke ovens and blast furnaces.

5.2 PRE-TEST REVIEW OF EMISSION SOURCES AND RATES

Before formulating a test plan for the Kaiser facility, we reviewed the literature on pollutant emissions from coking operations and integrated steel mills, discussed previous sampling work with federal and local air pollution control officials, and visited Kaiser twice. The purposes of these

activities were (1) to identify specific sources of polycyclic organic material (POM)⁺, benzene and cadmium at steel mills in general and at Kaiser in particular; (2) to review methods used by previous researchers; and (3) to estimate likely ranges of pollutant concentrations in emissions of various types, so that appropriate sampling techniques could be developed. A major finding of our review was that very little work had been done to quantify emissions of the carcinogens of interest from coke ovens and other major sources within steel mills. Because the bulk of these emissions are fugitive, measuring their emission rates has been and will continue to be a challenge.

Table 5.2-1 summarizes SAI's preliminary, pre-testing estimate of the sources and rates of emissions of polycyclic organic materials (POM), benzene, arsenic and cadmium from major discrete sources in the Kaiser plant. The derivation of these estimates is discussed in detail in the sections to follow. Some comments are in order now, however. First, given the great uncertainty in the data, some of the estimates may be "incorrect" by a factor of two or three. While an estimate from the literature was available for benzene emissions from coke oven charging, it was too speculative to merit reporting; unfortunately, charging may be a significant source of this carcinogen. Field measurement data were also lacking for POM emissions from coke byproduct recovery plants. All we could say at this point was that the operating conditions in these facilities are less conducive to POM formation and emission than are those associated with coke processing.

5.2.1 POM Emission Sources

Since the bituminous coal used in coking is composed essentially of polycyclic aromatic compounds, a potential exists for the generation of POM during coke production and byproduct recovery. We now review what is known about POM emissions from various steel mill operations.

Coke Oven Emissions of POM

The following discussion is based primarily upon a recent environmental impact statement prepared by the EPA to support national emission standards for hazardous air pollutants (NESHAPS) for coke oven emissions (EPA, 1980). Information provided by supporting documentation for the EIS, including a review by Tronholm and Beck (1978) and emission factor estimates by Allan (1980a and 1980b), was also used. Data are presented here for each of the major coke-processing operations.

⁺ The term polycyclic aromatic hydrocarbons (PAH) will also be used in the text when referring to that specific subclass of POM

Table 5.2-1
 SUMMARY OF PRE-TEST ESTIMATES OF CARCINOGEN
 EMISSIONS FROM KAISER STEEL CORPORATION, FONTANA
 (All values in tons/year)

Source	POM ^a	Benzene	Arsenic	Cadmium
<u>Coking</u>				
Charging	1.4	c	0.82 - 4.3	0.011 - 0.27
Pushing	b	6		
Topside	0.8	5		
Doors	1.2	20		
Battery Stack	0.03	0.04		
Quenching	0.2	0.3		
<u>Byproduct Plant</u>				
Tar Decanter	d	24		
Primary Cooler	d	14		
Tar Storage	d	0.01		
Ammonia Handling	d	b		
Final Cooling Tower	d	79		
Light Oil Storage	d	25		
<u>Sintering Plant</u>	0.015	b		

^a Values reported are for benzo(a)pyrene only; total POM emissions could be higher.

^b Negligible emissions.

^c A potentially importance source; unfortunately no reliable data are available.

^d Emissions believed to be negligible; field data nonexistent (Kemner, 1978).

Wet-Coal Charging. Figure 5.2-1 is a schematic of the topside of a coke oven battery. Coal is fed through the charging ports from a "larry car," which moves along the top of the battery. Coke ovens are always at a high enough temperature to rapidly volatilize coal constituents. When coal is introduced into an incandescent oven, the large volume of steam, gases and smoke that forms is forced from the oven by the pressure of the expanding gases. Emissions may flow at high velocity from any opening, including the charging ports (of which there are three per oven at Kaiser), feed hoppers, ascension pipes, standpipe caps, and the collection main. Emissions are intermittent and relatively short in duration; however, the large number of potential release points may, in concert, constitute a major source.

POM may be emitted from charging operations in both particulate and gaseous forms. Known or suspected carcinogens identified in particulate samples from one plant included benzo(a)pyrene (BaP), benz(c)phenanthrene, benz(a)anthracene, a benzfluoranthene isomer, and cholanthrene (Bee et al., 1974). Particle sizes are bimodally distributed. Roughly half the particles have a mass mean diameter of 8.5 microns; most of the POM is associated with this fraction. POM can also be emitted in gaseous form (Smith, 1970), although emission data of this sort are lacking.

According to Tronholm and Beck (1973), "no reliable, quantitative measurements for POMs or benzene soluble organics (BSO) are known to be available" for this source. Estimated emission factors in the literature vary by at least an order of magnitude. By considering total particulate matter emissions and limited data on percentages of BSO in the total mass, and percent BaP in the BSO, EPA has estimated an uncontrolled emission factor of 5.5×10^{-3} kg of BaP per Mg of coal (0.011 lb/ton).

Pushing. When coke is pushed from a coke oven, convective currents entrain loose coke dust and volatile materials. Emissions can include any and all of the byproducts produced upon destructive distillation of the coal during the coking cycle. Coal near the doors of the oven gets heated the least, so that emissions from "uncoked material" may result; pollutants in this category may include ammonia, coke oven gas, tar, phenol, light oil, benzene, toluene, xylene, and pyridine, as well as a variety of POM, including BaP. Trenholm and Beck (1978) summarized emissions measurements at two steel mills in 1973 and 1974. Care had to be taken to distinguish between emissions

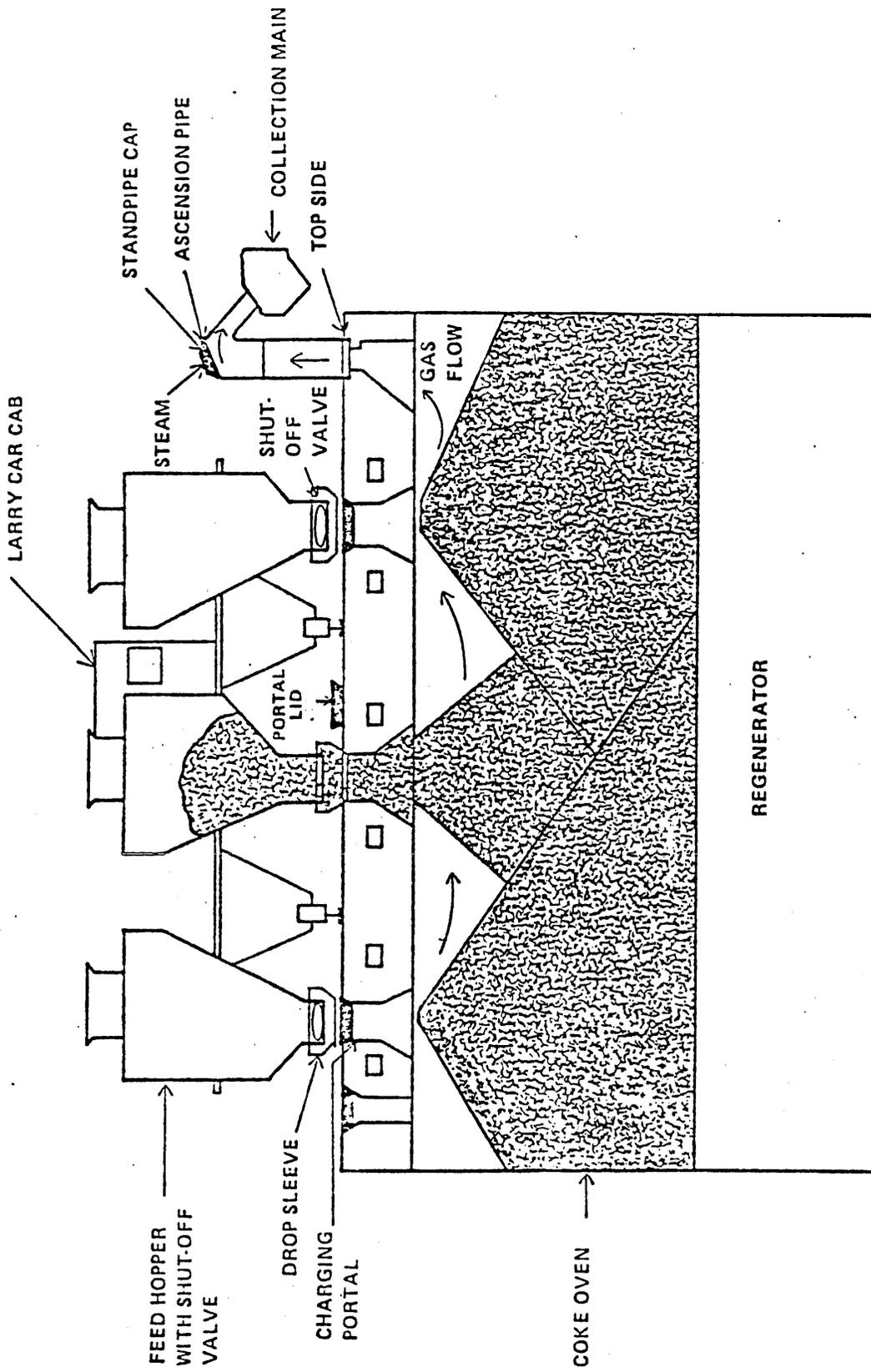


Figure 5.2-1 Schematic of Coke Oven Topside

from pushing and those from door leaks, since some ovens were in the coking phase while others were being pushed. Their conclusions were that BaP emissions from pushing alone were "negligible," and that BSU emissions were about 0.02 lb per ton of coal charged.

Topside Leaks. During the coking portion of the coking cycle, leaks may occur through improperly seated or distorted charging ports and standpipe lids; through cracks in the standpipes, or through broken seals at the base of the standpipes. Emissions would tend to be similar in quality to those occurring during charging, although particle sizes would, in this case, tend to be smaller. EPA's (1980) in-house estimate of topside emissions is 0.04 kg of BSU per ton of coal, which is equivalent to 0.08 lb/ton. If we assume, as EPA does, that BaP constitutes 1 percent of the BSU, then the emission factor for BaP from topside leaks would be 8×10^{-4} lb/ton. It should be emphasized that this estimate was not based upon any measurements of mass emissions.

Coke Oven Doors. During coking, fugitive emissions of yellow-brown coke oven gas and smoke particles can occur through any gap between the oven doors and their jambs. Emissions can also occur around the small chuck door on the pushing side of the oven. Coke oven emissions consist of over 10,000 compounds, including many POMs. Table 5.2-2 lists POMs identified in coke oven door leak samples collected at one steel mill. The rate and composition of the emissions vary with time. Generally, emissions are highest during the first hour of coking; they then decline as volatile tars condense and seal the doors from the inside, and internal pressure decreases.

The fugitive nature of door leaks has posed sampling problems. Mass emission rates of particulate matter may vary by three orders of magnitude (Barrett et al., 1977). After reviewing the scarce data on emission rates, EPA (1980) estimated an emission factor of 2.5g of BaP per tonne of coal (0.005 lb/ton), assuming that 30 to 65 percent of the doors are leaking at any given time.

Allen (1980a) has developed a model relating oven pressure and percent leaking doors to emissions. This model will be discussed below.

Battery Stacks. The gases used to heat the coke oven batteries (cleaned coke oven gas or blast furnace gas) are relatively free of particulate organic matter. However, organic gases and particles may leak

Table 5.2-2

POMS IDENTIFIED IN COKE OVEN DOOR LEAKS *

POM Species	Carcinogenicity Rating **	Emission Rate (mg/hr)
Naphthalene	-	387
Fluoranthene	-	428
Pyrene	-	184
Benz(c)phenanthrene	+++	17
Chrysene	±	124
Benz(a)anthracene	+	114
7,12-Dimethylbenz(a)anthracene	++++	1
Benz fluoranthenes	++	154
Benz(a)pyrene	+++	43
Benz(e)pyrene	-	95
Cholanthrene	++	<0.04
Indeno (1,2,3-cd)pyrene	+	46
Dibenz(a,h)anthracene	+++	48
Dibenz acridines	++	<0.04
Dibenz(c,g)carbazole	+++	<0.04
Dibenz pyrenes	+++	43
3-Methyl cholanthrene	++++	<0.04

Source: Barrett and Webb, 1978.

* Coke side doors only.

** Carcinogenicity reported by Public Health Service (NAS, 1972) where
 +++++, +++, ++ Strongly carcinogenic
 + Carcinogenic
 ± Uncertain or weakly carcinogenic
 - Not carcinogenic

from the ovens into the flue which removes combustion products from the ovens. According to the EPA (Tronholm and Beck, 1978), uncontrolled emissions of BSO would be 3.2×10^{-3} lb per ton of coal. Measured BaP emissions at four plants ranged from 0.4 to 4.2×10^{-5} lb/ton of coal, with an average of 2.4×10^{-5} lb/ton. This value is consistent with the previous assumption of 1 percent BaP in the BSO. These rates will be compared with those derived from measurement work at Kaiser later in this report.

Quench Tower Emissions of POM

The following discussion is based upon the findings of a quench tower emission testing program conducted by York Research Corporation (YRC) for the EPA (Buonicore, 1979; Ertel, 1979; Laube and Drummond, 1979). Incandescent coke is pushed from the ovens into rail cars which are conveyed to a hollow tower. There, water is sprayed rapidly onto the coke, generating thereby huge billowing clouds of steam, water droplets and particles which exit the top of the tower. Towers frequently have baffles to reduce losses of large droplets. The water not evaporated or entrained is collected in a sump and recycled. Losses are compensated for with makeup water, which may be relatively clean river water, or (as is the case with Kaiser), process water contaminated with organic pollutants.

The chemical and physical interactions between the hot coke and the water (and contaminants therein) are complex and poorly understood. Particulate matter can enter the air through entrainment of fine coke particles, shattering of rapidly-quenched coke, condensation of gaseous molecules, and transport of dissolved solids in aerosolized water droplets. It is clear from all reported emissions test results that the quench water itself is a major source of airborne pollutants. Since the composition of this water varies from plant to plant, it is impossible to describe "typical" emissions. Merely for sake of illustration, we list in Table 5.2-3 the results of quench tower measurements made by YRC at an Ohio steel mill in 1976. Note that benzo(a)pyrene was not detected in these emissions, although it was found in both "clean" and contaminated quench water. YRC cites Hendriks et al. (1979):

"There appears to be no correlation between concentrations of BaP and other organics, hence, it does not seem to be a good indicator of the concentration of other organics in the quench tower emissions."

Table 5.2-3

POLYCYCLIC AROMATIC HYDROCARBONS DETECTED IN QUENCH TOWER WATER AND EMISSIONS AT AN OHIO STEEL PLANT, 1976

	Contaminated Water				Clean Water		
	Stack Emissions		Inlet Water		Stack Emissions*		Water (Composite)
	lbs/ton of coal (x10 ⁻⁵)	µg/m ³	lbs/ton of coal (x10 ⁻⁵)	µg/l	lbs/ton of coal (x10 ⁻⁵)	µg/m ³	lbs/ton of coal (x10 ⁻⁵)
Anthracene/Phenanthrene	0.24	0.9	0.26	0.5	0.13	0.6	0.03
Methyl Anthracenes	0.10	0.4	0.07	0.1	0.07	0.3	0.02
Fluoranthene	0.12	0.5	0.28	0.5	0.07	0.3	0.03
Pyrene	0.09	0.4	0.16	0.3	0.05	0.2	0.02
Methyl Pyrene/ Fluoranthene	0.07	0.3	0.10	0.2	0.04	0.2	0.02
Benzo (c) phenanthrene	0.07	0.3	0.06	0.1	0.04	0.2	
Chrysenes/benz (a) - anthracene	0.10	0.4	0.17	0.3	0.05	0.2	0.03
Methyl chrysenes			0.09	0.2	0.004	0.2	
Dimethyl benz (a) - anthracene					0.05		
Benzo Fluoranthenes			0.12	0.2			
Benz (a) pyrene			0.02	0.04			
Benz (e) pyrene			0.04	0.08			
Indene (1,2,3-cd) pyrene			0.04	0.06			
Total	0.79	3.2	1.4	2.58	0.50	2.4	0.15
							0.27

Source: Buonicore, 1980

* Average of two tests.

In 1977 tests at the same mill, BaP was found in emissions from some, but not all, quenches. YRC estimated emission factors of 3.8×10^{-5} and 1.62×10^{-4} lb BaP per ton of coal when clean and contaminated quench water, respectively, is used. Recognizing the above caveat, we will use the latter value (as a worse case) solely for comparison with other BaP emission sources.

It is also instructive to estimate total polynuclear aromatic hydrocarbon (PAH) emissions. As seen in Table 5.2-3 total stack emissions of PAH in YRC's 1976 test were 5.0 to 7.9×10^{-6} lb per ton of coal, depending upon the quench water source.

Coke Byproduct Plant Emissions of POM

The coke oven gas evolved during coking is collected and piped to a byproduct plant, where it is purified for re-use as combustion gas in the coke ovens. Commercially valuable byproducts, such as ammonia, are also recovered. Emissions of benzene, the chief pollutant of concern in these facilities, are discussed below.

Van Usdell et al. (1979) have identified four potential sources of POM emissions in coke byproduct recovery plants: tar decanters, tar dewatering and storage facilities, ammonia processing, and the final cooling tower. The only species for which any measurements have been made is naphthalene, a noncarcinogen (NAS, 1972). Since all POM emissions from coke byproduct plants are fugitive, mass emission rates cannot be estimated at this point.

Sintering Plant Emissions of POM

The purpose of a sintering plant is to recover ore fines and/or waste products from various steelmaking processes. The fines are blended with coke breeze, limestone and dolomitic lime and conveyed on a belt through a furnace. EPA-sponsored measurements of uncontrolled emissions at two plants showed relatively high particulate loading (Westbrook, 1979a). Organic matter of all types constituted from 0.6 to 1.8 percent of the particulate matter generated. Fused aromatics having molecular weights above 216 comprised less than 0.2 percent of the total. While a low-resolution mass spectrograph analysis revealed compounds having molecular weights associated with carcinogens, a gas chromatography-mass spectrometry run on one sample did not confirm the presence of any carcinogen.

Pre-Test Estimate of POM Emissions at Kaiser

In estimating emissions, we have assumed that 266 ovens operate continuously and that 1.97×10^6 tons of coal are processed per year. BaP emissions were estimated as follows:

Charging: The 0.011 lb/ton emission factor given above was for uncontrolled emissions. South Coast Air Quality Management District Rule 477 sets the following limitations on emissions during charging:

477(b)(1) - "There shall be no visible emission of air contaminants into the atmosphere for a total accumulated time equal to or greater than seventy-five (75) seconds from any charge port, offtake system and larry car on a coke oven during five (5) consecutive charging operations."

According to the SCAQMD, the typical time to charge 5 ovens is 600 seconds. If Rule 477 (b)(1) is not violated, then controlled emissions would be 75/600 or 12.5 percent of the uncontrolled emissions, and the BaP emission factor would be 0.0014 lb/ton of coal. Total BaP emissions at Kaiser would then be $(0.0014 \text{ lb/ton})(1.97 \times 10^6 \text{ ton/yr}) / (2000 \text{ lb/ton}) = 1.4 \text{ tons/yr}$ or 0.04 g/sec.

Pushing: Negligible.

Topside: $(8 \times 10^{-4} \text{ lb/ton})(1.97 \times 10^6 \text{ ton/yr})(0.0005 \text{ ton/lb})$
= 0.79 tons/yr
= 0.02 g/sec

Coke Oven Doors: Emissions of BaP were estimated in two ways, each based upon a model formulated by Allen (1980a). First, Allen derived a theoretical equation to relate changes in coke open door emissions to changes in the percentage of doors leaking at any given time:

$$\frac{E_1}{E_2} = \left(\frac{PLD_1}{PLD_2} \right)^{2.5} \quad (5.2-1)$$

where PLD_1 and PLD_2 are different percentages of leaking doors and E_1 and E_2 are the corresponding total mass emission rates. Rearranging the equation yields

$$E_1 = E_2 \left(\frac{PLD_1}{PLD_2} \right)^{2.5} \quad (5.2-2)$$

As noted above, EPA estimated an emission factor of 0.005 lb BaP per ton, assuming that 30 to 65 percent of the doors are leaking. Rule 477 of the

South Coast Air Quality Management District limits visible emissions to 10 percent of the total number of doors on all operating batteries. If this rule is complied with, then emissions would lie between the following two values:

$$\begin{aligned}
 E &= 0.005 \text{ lb/ton} \left(\frac{10}{65} \right)^{2.5} (1.97 \times 10^6 \text{ ton/yr})(0.0005 \text{ lb/ton}) \\
 &= 0.046 \text{ ton/yr} \\
 &= 0.001 \text{ g/sec} \\
 E &= 0.005 \text{ lb/ton} \left(\frac{10}{30} \right)^{2.5} (1.97 \times 10^6 \text{ ton/yr})(0.0005 \text{ lb/ton}) \\
 &= 0.32 \text{ ton/yr} \\
 &= 0.009 \text{ g/sec}
 \end{aligned}$$

An alternative way of estimating coke oven door emissions at Kaiser was suggested to SAI by the developer of the model (C.C. Allen, personal communication). Figure 5.2-2 which is reproduced from Allen's report, shows the theoretical relationship between PLD and total emissions for an oven having a 9.6 m perimeter. The oven doors at Kaiser are 14 ft high by 22 inches wide (4.2 m by 0.559 m) (CARB, 1976), so that their perimeter is also about 9.6 m. From the figure, it is estimated that a 10-percent leaking door rate would result in total emissions of approximately 8 kg per door per cycle. If we assume 18 hours per cycle, then total emissions would be about 1142 tons per year. Allen (1980a) estimates that 0.106 percent of these emissions consist of BaP. Therefore BaP emissions would be 1.2 tons/yr or 0.03 g/sec. This estimate is an order of magnitude higher than the ones based upon EPA's NESHAP emission factor. In order to consider a "worst case" we shall use the 1.2 ton/yr value.

Battery Stacks: If the EPA estimate of 2.4×10^{-5} lb BaP per ton of coal presented above is realistic, then emissions at Kaiser would be 0.024 tons/yr or 0.0007 g/sec. According to the SCAQMD, measurements of particulates in the flue gases (after the baghouse) in the stack associated with Battery A were made in March 1973 (C. Anderson, personal communication). The total suspended particulate emission rate was estimated to be 14.3 kg/hr. Using a median percent BSO of 0.45 in the particulate matter (Tronholm and Beck, 1978) and an average of 1 percent of BaP in the BSO, BaP emissions would be $(14.3 \text{ kg/hr})(1000 \text{ g/kg})(\text{hr}/3600 \text{ sec})(0.0045)(0.01) = 0.0002 \text{ g/sec}$. Battery A is fully operational. Total emissions would be found by multiplying the

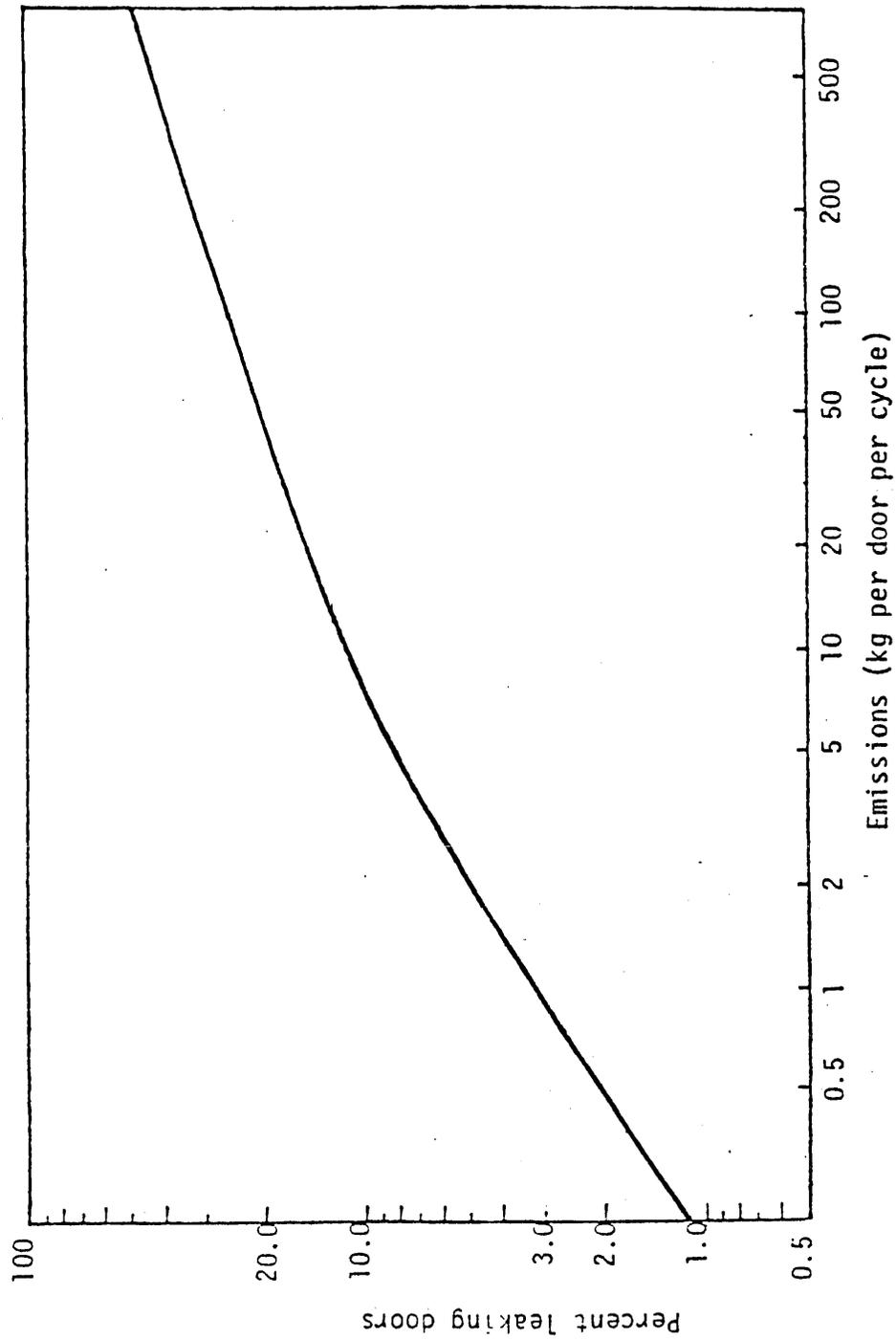


Figure 5.2-2 Theoretical Relationship Between Percentage of Leaking Doors and Coke Oven Door Leak Rate (Allen, 1980a).

rate just calculated by the fraction (266 operating ovens/45 ovens in Battery A); thus BaP emissions would be about 0.001 g/sec. The two estimates are therefore fairly close. It is also seen that stack emissions are much lower than those from other coke oven sources. Finally, according to an EPA scientist who has analyzed for BaP in Kaiser battery stack exhaust, BaP emissions would be far lower than those estimated here (F. Clay, personal communication).

Quench Towers: As noted above, BaP is probably not a good indicator of organic, or even POM, emissions from quench towers. For comparison purposes we use an emission factor of 0.000162 lb/ton of coal. Resulting emissions would be 0.16 tons/yr, or 0.005 g/sec.

Sintering Plant: Limited measurement data have not confirmed the presence of carcinogens in uncontrolled sintering plant emissions. We did, however, attempt a very rough quantification of these emissions at Kaiser, in order to judge whether they should be considered seriously in a measurement program. In the studies reported by Westbrook (1979a), organic particulate matter comprised a maximum of 1.8 percent of the uncontrolled particulate emissions of 450 kg/hr. From analysis of Westbrook's results, it may be estimated that roughly half of these organic compounds are BSO.

Recent measurements at Kaiser showed total controlled particulate emissions of 5.44 to 8.5 kg/hr at Sintering Plants 1 and 2 (C. Anderson, personal communication). Since the POM would probably be associated with relatively fine particles, the fraction escaping the baghouses would be higher than for particulate matter in general. However, we have no data on the size fractionation at Kaiser.

If we now assume that BaP constitutes 1 percent of the BSO, then the maximum emissions of BaP per sintering plant at Kaiser would be: $(0.018)(8.5 \text{ kg/hr})(0.01)(2.205 \text{ lb/kg})(0.0005 \text{ ton/lb})(8760 \text{ hr/yr}) = 0.015 \text{ tons/yr}$ per sintering plant. This rate is equivalent to 0.0004 g/sec. Compared to other potential POM sources, then, the sintering plants are relatively unimportant.

5.2.2 Benzene Emission Sources

Coke Oven Emissions of Benzene

In a study sponsored by the EPA's Industrial Environmental Research Laboratory, Kemner (1979) reviewed a wide variety of technical data on benzene

emissions from different parts of the coking cycle. Table 5.2-4 lists the emission factors which he derived. Note that, given the great variability among coke ovens, and the paucity of test data, none of these emission factors may be considered to be highly reliable. Kemner's evaluation of the confidence of each estimate is included in the table.

Larry Car Charging. No measurements of benzene emissions during this operation have been made. It is assumed that some emissions will occur, since benzene may be volatilized instantaneously when the coal is loaded into the red-hot ovens. The emission factor reported in Table 5.2-4 is based upon the unsupported assumption that benzene mass emissions are equal to half the total suspended particulate emissions from oven charging.

Coke Pushing. The factor reported in Table 5.2-4 is based upon several tests at one coking plant. In four tests, emissions of compounds with the formula C_6H_6 averaged 0.008 lb/ton of coal; Kemner estimates that benzene accounted for 0.006 lb/ton. In a very clean operation, emissions could be as low as 0.0005 to 0.001 lb/ton.

Quenching. For his emission factor estimate, Kemner cites a study by Dowling et al. (1978), in which two grab samples of benzene were taken at one quench tower. The reliability of the estimate is "extremely poor."

Coke Oven Door Leaks. During coking, a considerable amount of benzene is generated and drawn off for processing in the coke byproduct plant. It is to be expected that benzene vapors constitute part of the fugitive leaks from coke oven doors. Again, field measurement data are scarce. Kemner cites EPA-sponsored tests of a coke oven door (Barrett et al., 1977) and of a coke side enclosure (GLCC, 1977). In reviewing the coke oven door study, we were unable to derive an emission factor estimate since the rate at which the oven was charged with coal is not reported; furthermore the reported gas flow, upon which one may base an estimate of benzene mass emissions, is roughly approximated. Kemner's estimate of 0.02 lb benzene per ton of coal must therefore have been based upon the coke side enclosure tests.

Topside Leaks. The value reported in Table 5.2-4 is based upon the assumption that topside emissions are roughly half those from oven doors, since the area through which gases may escape is half that of the doors, the oven pressure is generally lower, and emissions are more easily controlled by coke

Table 5.2-4

ESTIMATED UNCONTROLLED BENZENE EMISSIONS FROM
THE COKING CYCLE

Emission Source	Emission Factor (lb/ton coal)	Confidence in Estimate
Larry Car Charging	0.5	Very Low
Coke Pushing	0.006	Good
Quenching ^a	3×10^{-5} - 2.6×10^{-4}	Very low
Door Leaks	0.02	Moderate
Topside Leaks	0.005	Very Low
Battery Stack ^b	4×10^{-6} - 4×10^{-5}	

Source: Kemner, 1979 unless otherwise noted.

^a Low Estimate is for clean water quench; high estimate is for dirty (recycled) water quench.

^b Estimated from test data reported by Taback, 1978.

oven workers (Kemner, 1979). Indeed, we observed at Kaiser that workers were continually applying luting compounds to visible leak points. Unfortunately, the topside source test performed by TRW at U.S. Steel's Clairton Coke Ovens (Hartman, 1979) was unable to quantify benzene emissions, since the gas chromatographic column used to analyze an integrated bag sample was unable to separate benzene adequately from other volatile organic compounds.

Battery Stack. Kemner found no data for benzene emissions from combustion of fuel gases in coke ovens. From data reported by KVB on stack gas measurements performed at Kaiser (Taback, 1978), a benzene emission factor of 4×10^{-6} to 4×10^{-5} lb/ton coal may be estimated.

Coke Byproduct Plant Emissions of Benzene

When coal is converted to coke, hundreds of its chemical constituents are converted to vapor. This vapor is drawn off of the coke ovens by standpipes and collector mains, which transport it to a coke byproduct plant. The purpose of the byproduct plant is to remove and process coke gas constituents which have commercial value. The remaining gas, which has a heating value of about 500 to 600 Btu/scf, is then returned to the coke battery and burned to supply heat to the ovens. Table 5.2-5 shows the manner by which the original coal is partitioned among the various products, byproducts, and cleaned gas. No two steel mills produce the same set of byproducts, nor is there a standard way to process any of the coke oven gas constituents. To our knowledge, Kaiser Steel recovers crude tar from the ovens but does not process it on site. Recovered ammonia is used for ammonium sulfate and ammonium phosphate production. Finally, light oil is recovered and stored, but not refined.

Research Triangle Institute recently reviewed the problem of hazardous air pollutant emissions from coke byproduct plants and performed an EPA Level 1 assessment at a steel mill in Alabama (Allen, 1980c; Van Osdell et al., 1979). One of their main findings was that most of the organic vapor emissions were from fugitive sources, so that estimation of total emissions from their point source measurement data is problematical. Table 5.2-6 lists estimates of benzene emission rates from the six coke byproduct plant components common to the Alabama mill and Kaiser.

Table 5.2-5

PARTITIONING OF COAL MASS AMONG COKE
PRODUCTS AND BYPRODUCTS

Material	Weight Percent		Product Volume ^a
	Mean	Range	
Coke	68.5	62.3 - 72.8	
Coke Oven Gas	16.0	14.3 - 20.3	10,860 scf
Breeze	5.2	2.8 - 8.1	
Crude Tar	3.8	2.9 - 4.7	7.8 gal
Crude Light Oil	0.9	0.6 - 1.1	2.4 gal
Ammonia ^b	0.8	0.7 - 0.9	

Source: U.S. Bureau of Mines data, summarized by Van Osdell et al. (1979).

^a Per ton of coal.

^b As ammonium sulfate.

Table 5.2-6

ESTIMATES OF BENZENE EMISSIONS FROM COKE
BYPRODUCT PLANT COMPONENTS^a

Component	Emission Rate ^b (g benzene/1000 kg coke)
Tar Decanter	15.66
Primary Cooler Condensate Tank Vent	8.89
Tar Storage	0.01
Ammonia Handling	c
Final Cooler Cooling Tower	51.03
Light Oil Storage	16.22
Total	91.81

^a Only those byproduct plant components found at Kaiser are listed

^b Estimated by Van Osdell et al. (1979) for one plant in Alabama.

^c Negligible emissions.

Because the tar decanter and the final cooling tower are believed to be the two largest sources of benzene emissions in the coke byproduct plant, they merit further discussion. The tar decanters at Kaiser are long, rectangular, multicompartment tanks. Their purpose is to separate tar from the flushing liquor which forms as the hot coke oven gases are sprayed with water in the collection mains. Tar settles to the bottom of the tanks and the flushing liquor is decanted off the top. The temperature of the flushing liquor in the decanters is around 80 °C (Allen, 1980c). Volatile benzene is emitted both deliberately through vents and unintentionally through poorly sealed hatches. One of the tar decanters we observed at Kaiser had one completely open hatch and one whose cover was so warped that a good seal was impossible.

In the final cooler, water at about 25 °C is sprayed onto hot coke oven gas. The purpose of the cooler is to cool the gas and to recover naphthalene, which condenses in the water and settles to the bottom. The water, whose temperature is raised by the heat exchange, is then sent to a cooling tower, where it is cooled and recycled. Since the final cooler is a closed system, gaseous emissions from it are negligible. However, the water going to the cooling tower may be rich in benzene, and considerable air stripping may occur. Field data on these cooling tower emissions are limited. Research Triangle Institute estimated, but apparently did not measure, a rate of 51.6 g of benzene per 1000 kg of coke produced. The only actual measurements of which we are aware were those done by EPA's Emissions Measurement Branch at an undisclosed site. In that case, benzene emissions were estimated at 18 lb/hr from each of four cells in a mechanical draft cooling tower (D. Bivens, personal communication).

Pre-Test Estimate of Benzene Emissions at Kaiser

To estimate benzene emissions, we assume that 1.97×10^6 tons of coal are processed per year. The ratio of coke produced to coal used is 0.66:1 (Roberts, 1980), so coke production is assumed to be 1.30×10^6 tons/yr, or 1.18×10^9 kg/year. Benzene emissions are estimated as follows, using the upper value where a range of factors is reported.

Coke Ovens

Larry car charging: $(0.5 \text{ lb/ton coal})(1.97 \times 10^6 \text{ tons/yr})$
 $= 1 \times 10^6 \text{ lb/yr}$
 $= 14 \text{ g/sec}$

Coke pushing: $(0.006 \text{ lb/ton coal})(1.97 \times 10^6 \text{ tons/yr})$
 $= 1 \times 10^4 \text{ lb/yr}$
 $= 0.2 \text{ g/sec}$

Quenching: $(2.6 \times 10^{-4} \text{ lb/ton coal})(1.97 \times 10^6 \text{ tons/yr})$
 $= 510 \text{ lb/yr}$
 $= 0.0074 \text{ g/sec}$

Door leaks: $(0.02 \text{ lb/ton coal})(1.97 \times 10^6 \text{ tons/yr})$
 $= 4 \times 10^4 \text{ lb/yr}$
 $= 0.6 \text{ g/sec}$

Topside leaks: $(0.005 \text{ lb/ton coal})(1.97 \times 10^6 \text{ tons/yr})$
 $= 1 \times 10^4 \text{ lb/yr}$
 $= 0.1 \text{ g/sec}$

Battery stacks: $(4 \times 10^{-5} \text{ lb/ton coal})(1.97 \times 10^6 \text{ tons/yr})$
 $= 80 \text{ lb/yr}$
 $= 0.001 \text{ g/sec}$

Byproduct Plant

Tar decanter: $(15.66 \text{ g/1000 kg coke})(1.18 \times 10^9 \text{ kg/yr})(0.0022 \text{ lb/g})$
 $= 4.07 \times 10^4 \text{ lb/yr}$
 $= 0.58 \text{ g/sec}$

Primary cooler: $(8.89 \text{ g/1000 kg coke})(1.18 \times 10^9 \text{ kg/yr})(0.0022 \text{ lb/g})$
 $= 2.31 \times 10^4 \text{ lb/yr}$
 $= 0.33 \text{ g/sec}$

Tar storage: $(0.01 \text{ g/1000 kg coke})(1.18 \times 10^9 \text{ kg/yr})(0.0022 \text{ lb/g})$
 $= 26.0 \text{ lb/yr}$
 $= 3.7 \times 10^{-4} \text{ g/sec}$

Final cooler cooling

Tower: (51.03 g/1000 kg coke)(1.18 x 10⁹ kg/yr)(0.0022 lb/g)
= 1.32 x 10⁵ lb/yr
= 1.9 g/sec

Light oil storage: (16.22 g/1000 kg coke)(1.18 x 10⁹ kg/yr) (0.0022 lb/g)
= 4.21 x 10⁴ lb/yr
= 0.61 g/sec

Summary

Total estimated benzene emissions from Kaiser would be 649 tons per year. It should be noted that the largest single source would be larry car charging, which would account for 492 tons/year. The emission factor for this operation is not based on measurement and is judged to have very low reliability (Kemner, 1979). Without the larry car emission component, our estimate for the total would be comparable to the 112 tons/year estimated by KVB (Roberts, 1980). In turn, the latter estimate is based upon national averages of questionable validity.

5.2.3 Arsenic Emission Sources

According to KVB, 3,115 lb/yr of arsenic are emitted from iron ore reduction, foundry operations and coking at Kaiser (Roberts, 1980). The estimates for the first two processes were made by assuming that emissions at Kaiser were in the same proportion to national emissions as the plant's iron and steel production was to national totals. We could find no field data on arsenic emissions from iron ore reduction and foundry operations, so we can neither verify nor dispute these figures.

KVB estimated that coking accounted for 1,635 lb/yr of the total arsenic emission. An upper bound on emissions from this source may be estimated by assuming that all the arsenic in the coal is emitted to the atmosphere somewhere along the line. The most likely emission points would be the coke oven, since volatile arsenic trioxide would be expected to form therein. During our 26 January 1981 pre-test visit, we collected samples of coal, coke and baghouse dust. The coal and coke samples, according to our laboratory analyses, contained 6.18 and 7.28 ppm of arsenic, respectively. The

maximum emission rate would therefore be $(1.97 \times 10^6 \text{ tons/yr coal})(6.18 \times 10^{-6}) = 12.2 \text{ tons/yr}$.

The fraction of the As actually emitted is unknown. In a previous SAI study (Rogozen et al., 1976), we estimated that from 2 to 30 percent of the arsenic in coal is emitted in utility boiler combustion processes; power plants with modern controls would emit 2 to 6 percent. Since the potential for fugitive emissions is so much higher in the case of coke ovens, the fraction emitted would probably be toward the upper end of the range. KVB used 35 percent. An upper bound on As emission would thus be $(0.35)(12.2) = 4.3 \text{ tons/yr}$. A lower bound on the estimate may be obtained by considering only the losses during coking. From our measurement, the amount of arsenic remaining in the coke would be $(1.18 \times 10^9 \text{ kg/yr coke})(7.28 \times 10^{-6})(1.103 \times 10^{-3} \text{ ton/kg}) = 9.47 \text{ tons/yr}$. The loss during coking would then be $12.2 \text{ tons/yr} - 9.47 \text{ tons/yr}$ or 2.73 tons/yr . The amount actually emitted to the atmosphere would be $(0.3)(2.73)$ or 0.82 tons/yr .

To our knowledge, the only field test data are those reported by Battelle for their coke oven door emission tests at Republic Steel Corporation's plant in Youngstown, Ohio (Barrett et al., 1977). Arsenic concentrations in the coal and coke were 10 and 20 ppm, respectively. If we assume that, as in the case of Kaiser, 66 lb of coke are produced from every 100 lb of coal, then the mass of arsenic would appear to increase through the coking process; the uncertainty inherent in consideration of grab samples such as these is probably responsible for the paradoxical conclusion. One may, however, infer that losses (i.e. emissions) of arsenic for that plant would be low.

That arsenic emissions are probably low may also be supported by Battelle's data on particulate catch. Arsenic in the particulate matter trapped by the sampling train's filter ranged from 0.47 to $<3.5 \text{ ppm}$ by weight. Using data on total particulate emissions, one may estimate arsenic emissions of only 1.2 mg per coking cycle. It should be noted that volatile arsenic may have passed through the filters and gone on undetected; no data are given for trace element concentrations of materials collected by other parts of the sampling train.

Finally, even if none of the arsenic is emitted during coking, some may be volatilized later, when the coke is combusted in the blast furnace.

Since blast furnace gases are used as fuel in some of the coke oven batteries, volatilized arsenic could find its way into the battery stacks, via the baghouses associate with the coking operations. Indeed, our analysis shows an enrichment of arsenic (to 37.1 ppm) in the baghouse dust. Unfortunately, Kaiser could provide no data on baghouse dust generation and disposal rates. Thus no mass balance on arsenic could be performed.

5.2.4 Cadmium Emission Sources

Our analyses determined that the cadmium concentrations in the coal, coke and baghouse dust at Kaiser were 0.271, 0.024 and 46.0 ppm, respectively. The maximum emissions from the facility would therefore be $(1.97 \times 10^6 \text{ tons/yr coal})(2.71 \times 10^{-7}) = 0.534 \text{ tons/yr}$. Since $1.30 \times 10^6 \text{ tons/yr}$ of coke are produced, about $(1.30 \times 10^6 \text{ tons/yr})(2.4 \times 10^{-8}) = 0.0312 \text{ tons/yr}$ of cadmium ends up in the coke. As with arsenic, the amount of cadmium leaving the plant via baghouse dust cannot be determined from available data. The fact that only about six percent of the incoming Cd remains in the coke implies that most of it ends up in ash or is emitted to the atmosphere. Literature estimates of Cd emissions from coal combustion range from 2 to 50 percent (Rogozen et al., 1976). Our pre-test estimate of cadmium emissions from Kaiser would therefore be 0.011 to 0.27 tons/yr.

To our knowledge the only data on Cd emissions from coke ovens were obtained by Battelle-Columbus Laboratories in their abovementioned tests at Republic Steel Corporation's Poland Avenue coke plant in Youngstown, Ohio (Barrett et al., 1977). Cd concentrations in particulate matter collected by hi-vol samplers ranged from <0.079 to <0.87 ppm. Using Battelle's data for total particulate matter collected, we estimate Cd emissions of only 272 mg for the one oven, over a 13.2-hour coking cycle.

5.3 SAMPLING AND ANALYTICAL APPROACH

5.3.1 Selection of Sources to Test

Selection of appropriate sampling points at Kaiser presented us with several problems. As described in previous sections, 94 percent of the plant's POM emissions and most of its benzene emissions are fugitive. Relatively well-known sampling techniques such as EPA Method 5 are thus inapplicable to many of the most important emissions. Indeed, there are no "standard" procedures for measuring coke oven emissions. Furthermore, to characterize

coke oven emissions fully--an endeavor which has never been attempted--would be prohibitively expensive. For example, one thorough test of only one coke oven door by Battelle-Columbus Laboratories (Barrett et al., 1977) cost \$80,000 in 1976 dollars. Finally, the sampling environment at any integrated steel mill is quite dangerous. The sampling team would at minimum be exposed to heat, toxic gases, and the danger of explosion. Bearing these constraints in mind, we designed tests which would yield significant new information on emissions of the carcinogens of interest, would not duplicate previous work, and would be relatively safe.

After reviewing the literature and making two pre-test site visits we decided that it would be most cost-effective to sample a coke oven, a tar decanter, and a final cooler cooling tower associated with the coke oven gas byproduct recovery plant. Figure 5.3-1 shows the source locations and Table 5.3-1 summarizes the tests performed.

5.3.2 Coke Oven Tests

Sampling Protocol

As was noted in Section 5.2.1 the quantity of total mass emission from coke ovens may be estimated by means of a model developed by Research Triangle Institute for the U.S. Environmental Protection Agency. Our use of this model is described in Section 5.4. In order to calculate the fraction of those emissions represented by POM, benzene, arsenic and cadmium, it was necessary to determine the composition of the gases and particulates emitted by the ovens. After discussions with ARB and EPA officials, it was decided that the best approach would be to create a controlled leak from the one of the topside ports of a coke oven. After choosing this approach, we learned that it had already been taken by an EPA contractor in a study of emissions from a coke oven in Pennsylvania (Hartman, 1980).

It should be noted that Kaiser was not using its normal coal blend during the testing. Shortly before we were to begin the tests, the plant management informed us that a strike at the mine in Colorado which supplies 12 percent of the coal used for coking had begun and would last for several more weeks. The Colorado coal is of medium-volatile bituminous rank and is the "key" ingredient as far as resulting coke properties are concerned. During our tests, the facility was using a mixture comprised of 5 percent Colorado coal, 5

Table 5.3-1
SUMMARY OF SAMPLING PERFORMED AT KAISER

Sampling Point	Pollutants	Sampling Technique
Coal Storage		
Coke Storage	As, Cd	Grab Samples (Pre-test)
Battery Baghouse		
Charge Port on End Oven	POM, Benzene, As, Cd	Steel pipe with ball valve, impingers; charcoal adsorbent for benzene
Coke Byproduct Plant Tar Decanter	Benzene	Glass bulb; isobutane tracer
Coke Byproduct Plant Final Cooling Tower	Benzene	Velocity traverse, collection on charcoal
Plant Boundary (upwind, downwind)	As, Cd	Collected by SCAQMD per Rule 403

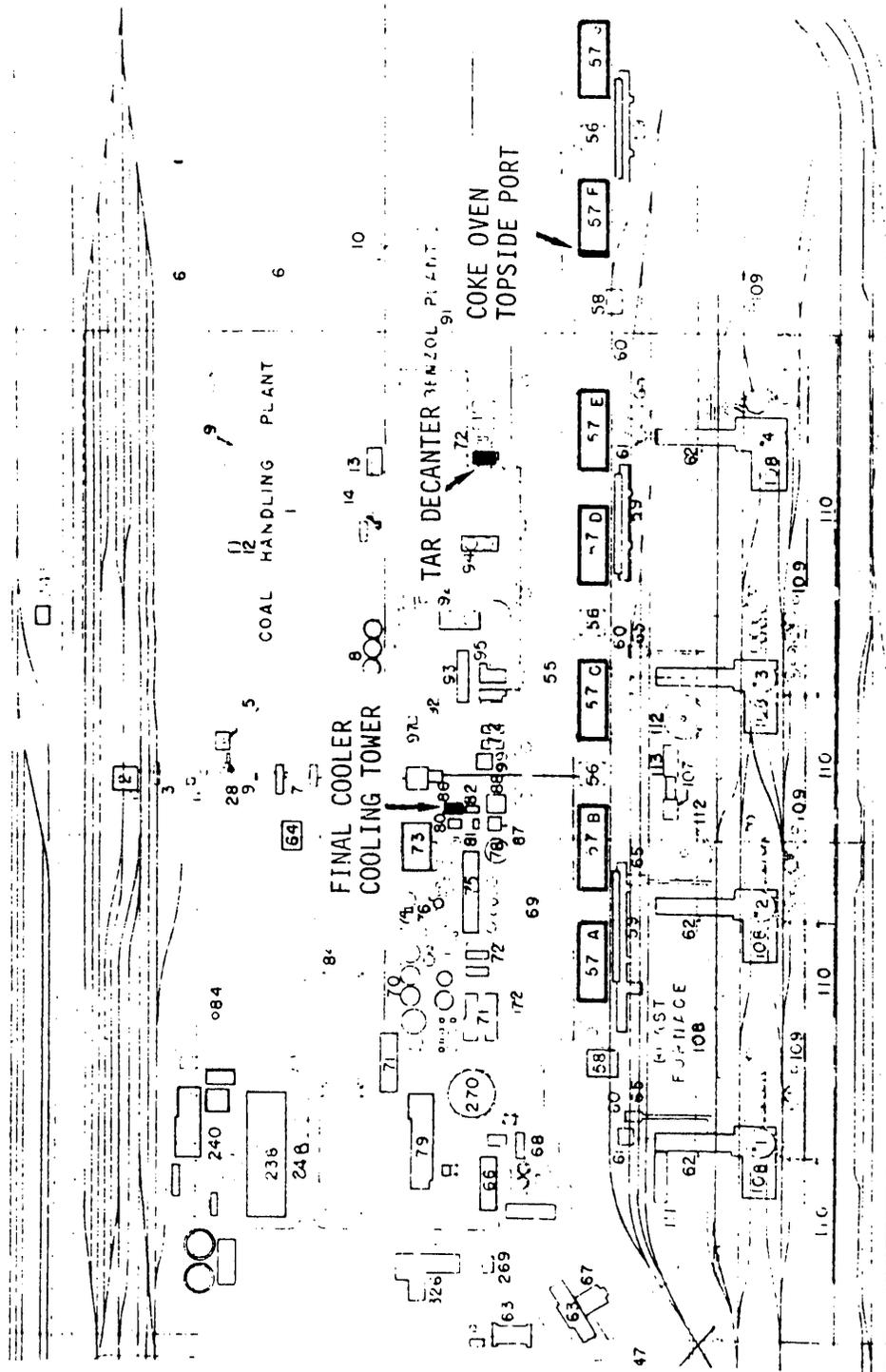


Figure 5.3-1 Sampling Sites at Kaiser Steel Corporation.

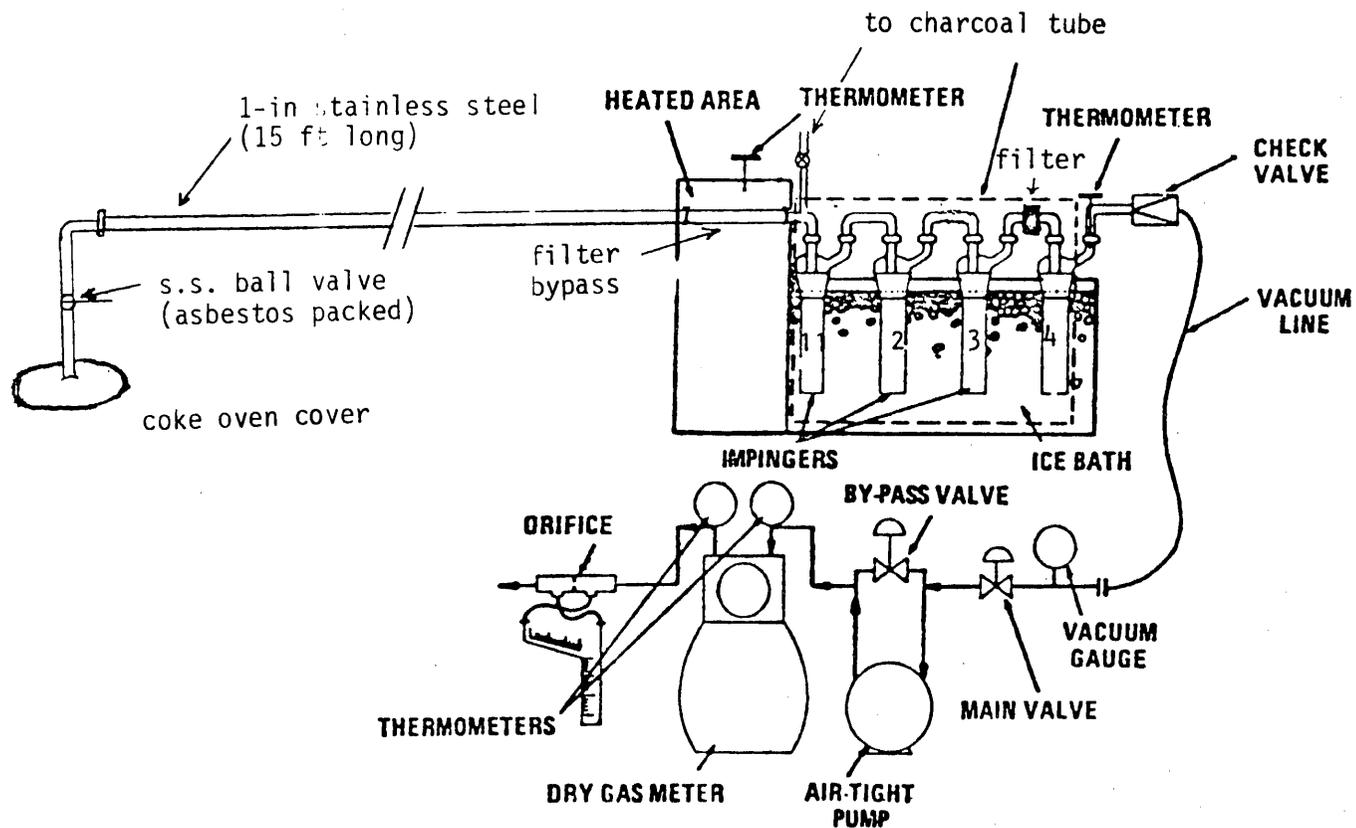
percent coal from the Sunnyside and York Canyon fields of Utah, petroleum coke, and "Chimney Rock" coal. We do not know the provenance of the last of the components, but Kaiser management informed us that it is of a lower coking quality than the Colorado coal and has a higher ash and sulfur content.

In order to avoid obstructing the operation of the larry car which charges the ovens with coal, an end oven was tested. Use of an end oven also allowed us to take advantage of a large empty space at the end of the battery roof. This space was considerably cooler than the rest of the battery topside and was near electrical outlets and the access stairs.

Figure 5.3-2 shows the sampling apparatus. Immediately after the oven was charged, the port lid on the south side was replaced with a lid drilled to accept a one-inch diameter stainless steel pipe. Six inches above the top of the lid was a one-inch, asbestos-packed stainless steel ball valve. Threaded to the ball valve was a 6-inch long, 90° elbow with a stainless steel threaded quick-disconnect fitting. The entire assembly was wrapped with heating tape and heated to a temperature of approximately 177 °C (350 °F). Running horizontally from the elbow was a 15-ft long, 1-inch diameter thin-walled schedule 316 stainless steel tube with a threaded quick-disconnect fitting on the end nearest the elbow and a fitting compatible with an impinger train on the other. During sampling, this tube was wrapped with heat tape and held at approximately 93 °C (200 °F).

The sampling train consisted of four impingers of the modified Greenberg-Smith type. Impingers 1 through 4 (see Figure 5.3-2) contained 100 ml of distilled water, 100 ml of distilled water, 225 g of XAD-2 resin, and 390 g of silica gel, respectively. The impinger assembly was in an ice bath throughout the testing. Although the impingers were originally believed capable of trapping all the particulate matter, a 8.2-mm glass fiber filter holder was placed in series between Impingers 3 and 4. This change was fortunate, inasmuch as considerable material was collected on the filters during the test.

An all-glass tee joint was installed in the line immediately upstream of Impinger 1, so that benzene could be sampled directly from the hot coke oven effluent. Samples for benzene analysis were pulled through an 0.25-inch Teflon valve, Teflon line and two charcoal traps in series by a diaphragm pump.



Impinger 1: 100 ml distilled water
 Impinger 2: 100 ml distilled water
 Impinger 3: 225 g XAD-2
 Impinger 4: 390 g silica gel

Figure 5.3-2 Schematic of Coke Oven Sampling Train.

Sampling was conducted by our subcontractor, Certified Testing Laboratories, Inc., as follows. For one minute out of each hour, the sampling train was run at a flow rate of approximately one ft³/min. After each sample was taken, a charcoal tube was connected to the Teflon valve upstream of Impinger 1 and a sample for benzene analysis was drawn through the charcoal tubes for 5 minutes at a rate of 200 ml/min. Upon completion of the benzene sampling, the stainless steel ball valve was closed until the next hourly sampling time. It was necessary to replace filters four times during the test because of excessive loading.

Sample Recovery and Analysis.

After completion of the sampling the entire coke oven sampling system was taken to Global Geochemistry Corporation (GGC) in Canoga Park for extraction and analysis. Figure 5.3-3 is a schematic of the treatment provided by GGC. As indicated at the bottom of the diagram, various extracts and filter halves were split with SAI for additional analysis and quality assurance.

Details of GGC's analytical protocols are presented in Appendix D. Connectors, tubing, impingers and the last filter remaining in the sampling train at the end of the test were extracted in dichloromethane (CH₂Cl₂). Impinger solutions and all washes were filtered. Filtrates were combined, split with SAI and then analyzed by high-performance liquid chromatography (HPLC). All filters were combined and extracted in a soxhlet apparatus with toluene. The XAD-2 resin from Impinger 3 was extracted in CH₂Cl₂ and split with SAI.

Splits SAI I, SAI II and SAI III (See Figure 5.3-3) were analyzed by combined gas chromatography and mass spectrometry (GC/MS). Details of our procedures are provided in Appendix E.

Benzene was recovered from the charcoal traps using carbon disulfide extraction and quantified by flame ionization detection gas chromatography. Extraction efficiency was determined by spiking the charcoal traps with known amounts of benzene; the average efficiency was 36 percent. Results of our analyses of field samples were corrected to take this efficiency into account; only corrected values are reported.

Water from Impingers 1 and 2 (Split SAI VIII) was wet digested with HNO_3 and H_2O_2 and subsequently analyzed by graphite furnace atomic absorption spectroscopy for total arsenic and cadmium. An attempt was made to digest the particulate matter collected on filters, connectors and steel tubing in the coke oven sampling train (Split SAI IV, V, VI, and VII). Since the digestion was incomplete, a reanalysis was attempted by low-temperature ashing the particulate matter prior to the nitric acid/hydrogen peroxide digestion. Once again the sample residue could not be completely dissolved. The residue was therefore separated from the digestate by centrifugation. The samples were adjusted to known volume with deionized water and were analyzed by graphite furnace atomic absorption spectroscopy for As and Cd.

5.3.3 Coke Byproduct Plant Tar Decanter Tests

Sampling Protocol

The tar decanter we sampled contained several fugitive emission sources, the largest of which was a permanently open hatch in the southwest corner of the decanter's "roof." Our original plan was to use the integrated bag sampling train described in EPA Method 110 (45 Federal Register 26677). Indeed, a complete sampling train was constructed and brought to the site. Due to an equipment malfunction, however, it was necessary to change our means of sample collection on the spot. Our final procedure was as follows.

Figure 5.3-4 shows the deployment of our test equipment. In order to determine a mass emission rate from this fugitive source, we injected isobutane gas into the tar decanter at a known rate. The gas was injected through a 0.25-inch i.d. copper tube whose outlet was placed about 15 cm above the rolling surface of the hot tar. Isobutane injection continued without interruption through the entire test. The sampling probe consisted of two 1.83-m (6-ft) sections of 1.9-cm (0.75-in) O.D. stainless steel tubing connected with Swagelok fittings. Swagelok fittings at the downstream end of the tubing reduced the diameter for connection to 0.63-cm (0.25-inch) Teflon tubing. Because of the extreme danger of explosion, the sampling pump had to be located about 20 m from the base of the tar decanter. Air was drawn at 6.48 L/min through a glass/Teflon gas sampling bulb for approximately 10 minutes, so that steady-state flow conditions could be achieved. The bulbs were then sealed at each end and returned to the laboratory for analysis.

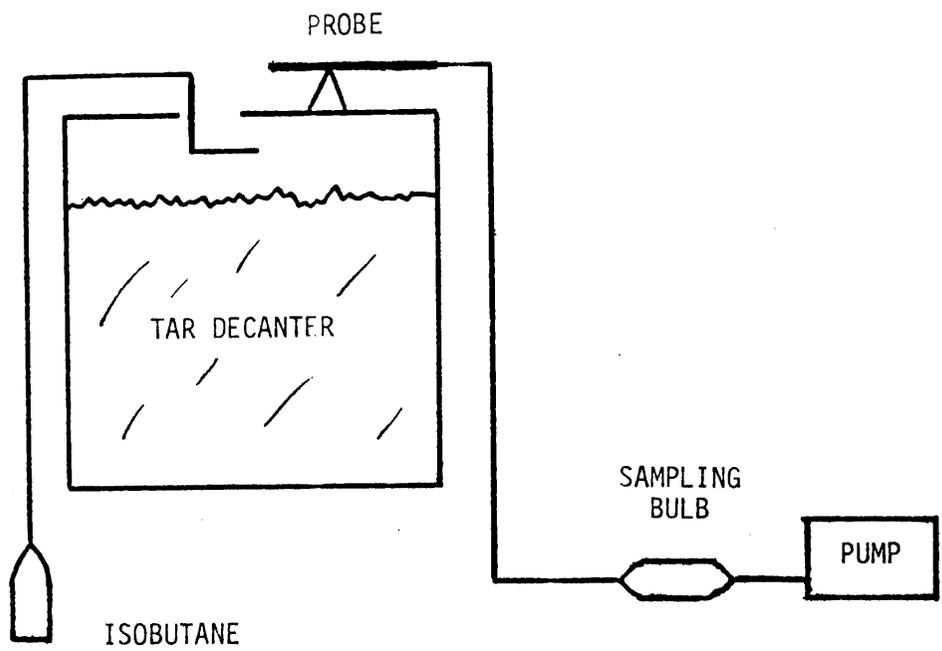


Figure 5.3-4 Arrangement of Equipment for Sampling Fugitive Benzene Emissions From the Tar Decanter. (Drawing not to scale.)

Analysis

Sampling bulb contents were analyzed directly for benzene and isobutane using packed column flame ionization gas chromatography.

5.3.4 Final Cooler Cooling Tower Tests

Sampling

The tower sampled was an octagonal mechanical forced-draft crossflow type which was in extremely poor repair. Numerous leaks from the hot water trough down the sides of the tower were observed. Our first step was to make a velocity traverse across the east-west axis of the tower, which measured 4.1 m. To do this, the vane of an Ota Keiki Model 29-DGDC digital air velocity meter was suspended at various points. Air flow was fairly uniform, so that average air flows (all of which were upward) could be determined. Readings were accurate to 0.1 m/s. Air samples for benzene analysis were collected with the same stainless steel probe used for the tar decanter sampling. An 18-m length of Teflon tubing connected the probe with charcoal traps in series and the sampling pump. Samples were taken at the center of the tower and at 30 cm from each side. In each case 1.02 liters of air were collected. (Although a longitudinal velocity traverse would have been helpful, extremely hazardous conditions atop the tower forced us to minimize our sampling time.)

Analysis

Charcoal traps were extracted in CS₂ and analyzed by the same means as for the coke oven samples.

5.4 DETERMINATION OF EMISSION FACTORS

5.4.1 Estimation of Coke Oven Mass Emission Rate

Records of visible emission inspections performed by the South Coast Air Quality Management District's Colton office from October 1979 through 1980 were obtained from that agency (Camarena and Stiles, 1980). Since the inspectors counted leaks from the push side and the coking side doors as separate emissions, the percentage of leaking doors (PLD) was computed by dividing the number of observed leaks at a battery on a given day by 90. Table 5.4-1 shows the mean PLD for each battery, as observed on 63 sampling occasions. The mean PLD, as well as the lower and upper limits of the 95-percent confidence interval, were then used in conjunction with Figure 5.2-2

Table 5.4-1
 ESTIMATION OF TOTAL ANNUAL MASS EMISSIONS FROM DOOR LEAKS
 AT KAISER STEEL CORPORATION COKING FACILITIES

Battery	Percent Leaking Doors 95-Pct Conf. Int.	Mean	Emission Rates* 95-Pct Conf. Int	Annual Emissions** 95-Pct Conf. Int.
B ^a	11.2 - 15.6	12.4	10.0 - 30.5	26.2
C	8.3 - 12.2	6.4	5.0 - 11.5	26.0
D	8.6 - 12.0	6.4	5.2 - 11.5	26.0
E	6.3 - 8.8	3.8	3.1 - 5.2	11.5
F	2.4 - 4.1	0.91	0.63 - 1.5	1.63
G	1.6 - 2.1	0.28	0.33 - 0.50	0.26
TOTAL				

^a Emission estimate based upon 18 operating ovens.

* kg/door-cycle

** metric tons/yr

to estimate the total mass emission rate per door per cycle. For each battery, then, total annual emission were calculated from:

$$\frac{\text{Total Emissions}}{\text{(kg/yr)}} = \frac{(90 \text{ doors})(8760 \text{ hr/yr})}{(18 \text{ hr/cycle})} \times \frac{(\text{PLD})}{100} \times E_d \quad (5.4-1)$$

where PLD is the percentage of leaking doors and E_d is the emission rate (kg per door per cycle), obtained from Figure 5.2-2. Note that, in the case of Battery B, only 18 of the 45 ovens were assumed to be operating.

Table 5.4-1 also shows the estimated mean and 95-percent confidence interval for the emissions from each battery. That the means are toward the low end of the confidence intervals is due to the nonlinear relationship between PLD and emissions. Total emissions from the coke oven doors are estimated to be 91.6 metric tons/yr (101 tons/yr).

5.4.2 Estimation of Total Mass Collected

Processing of the samples by the methods shown in Figure 5.3-3 resulted in the following recovery:

XAD-2 resin = 1.35 g
 Dichloromethane extract = 20.84 g
 Toluene extract = 3.04 g
 Nonextractable solids = 5.79 g
 Total = 31.02 g

The total mass of benzene emitted during the test day was estimated as follows. As will be discussed in Section 5.4.4, 586.6 mg of benzene were collected on charcoal traps. The total volume collected, corrected to standard conditions, was 0.0101 m^3 (0.357 scf). Now, according to Certified Testing Laboratories (Salot, 1981), the total metered volume of gas collected through the impinger and filter train was 0.405 standard cubic meters (14.3 dry standard cubic feet). If we assume that the concentration of benzene in the sidestream sample was the same as in the main air stream flowing through the sampling train, then the mass of benzene which would have flowed through the train would be $(0.5866\text{g})(0.405 \text{ m}^3)/(0.0101 \text{ m}^3) = 23.52 \text{ g}$.

As will be discussed below, the mass of arsenic and cadmium collected was less than 1 milligram, and can therefore be omitted from total mass

estimations. The total mass emitted during the sampling periods was therefore 31.02 g + 23.52 g = 54.54 g. This value will be used as the basis for determining fractional emissions of various chemical species.

5.4.3 Polycyclic Organic Materials

Estimation of Emissions

Table 5.4-2 shows the extent to which POM present in the various extracts from the coke oven sampling train could be identified. Global Geochemistry Corporation (GGC) was able to identify species responsible for approximately 36 percent of the total extract. Note that, although the XAD-2 resin was extracted in dichloromethane in a Soxhlet apparatus, the extractables were too volatile to be determined by evaporation and weighing. It is unlikely that significant amounts of POM were collected on the XAD-2.

The results of GGC's analyses by HPLC and GC and SAI's analyses by GC/MS are shown in Table 5.4-3. Polycyclic aromatic hydrocarbon species are listed in order of increasing molecular weight. The XAD-2 resin was analyzed only for naphthalene. GGC analyzed for chrysene and benz(a)anthracene individually by GC and in combination by HPLC. Benzo(ghi)perylene and indeno(1,2,3-cd)pyrene were also analyzed for by the two methods. The total masses of the species pairs were as follows:

	<u>HPLC</u>	<u>GC</u>
Chrysene/Benz(a)anthracene	0.0890 g	0.755 g
Benzo(ghi)perylene/ Indeno(1,2,3-cd)pyrene	0.660 g	0.423 g

In order to be able to report species-specific emissions, we used the results of the gas chromatographic analyses in these cases.

Since it was our intention to estimate total mass emissions, no attempt was made to associate chemical species found with location in the sampling train or with solid or liquid media. Dichloromethane and toluene extraction appeared to be about equally effective in recovering PAH from the samples processed by each method.

Table 5.4-4 shows how PAH emissions from coke oven doors were estimated for the entire facility. Except for species for which GC/MS analyses were not performed, we averaged the results of the HPLC and GC/MS analyses.

Table 5.4-2
 RECOVERY OF POLYCYCLIC ORGANIC MATERIALS FROM COKE OVEN SAMPLES
 (All masses are in grams)

Mass	CH ₂ Cl ₂	Toluene Extract	XAD-2 Resin	Totals
Identifiable	6.83 (32.8%)	0.966 (31.8%)	1.35 (<100%)	9.15 (<36.3)
Unidentifiable	14.01 (67.2%)	2.07 (68.2%)	a	16.08 (<63.7)

^a XAD-2 extractables were too volatile to be determined gravimetrically.

Table 5.4-3
 MASS OF POLYCYCLIC AROMATIC HYDROCARBONS IDENTIFIED IN
 EXTRACTS FROM COKE OVEN SAMPLING TRAIN
 (All masses are in grams)

Compound	CH ₂ Cl ₂ HPLC	Extract GC/MS	Toluene HPLC	Extract GC/MS	XAD-2 HPLC	Extract GC/MS
Naphthalene	0.917	0.996	0.070	0.122	1.35	0.123
Fluoranthene	0.441	0.365	0.050	0.097		ND ^a
Phenanthrene	1.40	0.635	0.236	0.150		ND
Anthracene	0.613	0.205	0.056	0.048		ND
Pyrene	1.12	0.325	0.146	0.080		ND
Chrysene	0.355 ^b	0.173	0.076 ^b	0.038		ND
Benz(a)anthracene	0.274	0.091	0.050	0.024		NA ^c
Perylene	0.184	NA	0.060	NA		NA
Benzo(e)pyrene	0.716	NA	0.110	NA		NA
Benzo(a)pyrene	0.370	0.357	0.062	0.026		ND
Benzo(ghi)perylene	0.169 ^b	0.189	0.030 ^b	0.036		ND
Indeno(1,2,3-cd)pyrene	0.188	0.109	0.036 ^b	0.027		ND
Coronene	0.080	NA	0.014	NA		NA
TOTALS	6.83		0.996		1.35	

^a ND = Analyzed for but not detected by GC/MS.

^b Analyzed for by GC (see text).

^c NA = Not analyzed for by GC/MS.

Table 5.4-4
 CALCULATION OF POLYCYCLIC AROMATIC HYDROCARBON
 EMISSION ESTIMATES

Compound	HPLC Total (g)	GC/MS Total (g)	Mean (g)	Fraction of Total Estimated Mass Emissions	Estimated Annual Emissions ^c	Metric tons/yr tons
Naphtnalene	2.337	1.241	1.789	0.0328	3.00	3.31
Fluoranthene	0.491	0.462	0.477	0.0087	0.80	0.088
Phenanthrene	1.636	0.785	1.211	0.0222	2.03	2.24
Anthracene	0.669	0.253	0.461	0.0085	0.78	0.86
Pyrene	1.264	0.405	0.835	0.0153	1.40	1.54
*Chrysene	0.431 ^d	0.211	0.321	0.0059	0.54	0.60
*Benz(a)anthracene	0.324	0.115	0.220	0.0040	0.37	0.40
Perylene	0.244	b	0.224	0.0041	0.38	0.41
*Benzo(e)pyrene	0.826	b	0.826	0.0151	1.38	1.52
*benzo(a)pyrene	0.432	0.383	0.408	0.0075	0.69	0.76
Benzo(ghi)perylene	0.119 ^d	0.225 ^d	0.212	0.0039	0.36	0.39
*Indeno(1,2,3-cd)pyrene	0.224 ^d	0.136 ^d	0.180	0.0033	0.39	0.43
Coronene	0.094	b	0.094	0.0017	0.16	0.17
TOTAL	9.17	-	7.26	0.155	12.3	13.5

* Mammalian carcinogen.

^d Done by GC

^b Not analyzed by GC/MS

^c Assuming mean value from Table 3.3-2

PAH collected and identified constituted 15.5 percent of the total mass collected by the sampling train, as estimated above. From Table 5.4-1, we see that our mean estimate of annual emissions of all substances from coke oven doors is 91.59 metric tons/yr (101 tons/yr). Annual emissions for each species were calculated by multiplying this figure by the species' fraction of total mass emissions. Results are presented in the last two columns of Table 5.4-4.

According to our calculations, 12.3 tonnes (13.5 tons) per year of identifiable polycyclic aromatic hydrocarbon compounds are emitted from the coke oven door leaks. It is interesting to note that the estimate for benzo(a)pyrene, 0.69 tonne/yr (0.76 ton/yr), is within a factor of 2 of the pre-test estimate (1.2 tons/yr). PAH compounds which have been identified as mammalian carcinogens (Rinkus and Legator, 1979) are indicated by asterisks in Table 5.4-4. Estimated emissions of these compounds total 3.37 tonnes/yr (3.71 tons/yr).

SAI's GC/MS analyses of coke oven samples identified numerous additional compounds. Tables 5.4-5 through 5.4-7 list the species identified in the three sample extracts. Mass spectra for the samples are shown in Figures 5.4-1 through 5.4-3.

Emission Factors for PUM

Emission factors for the five carcinogens identified and quantified were determined by dividing the emissions estimates by the mass of coal used annually to make coke (1.97×10^6 tons/yr). Results are shown in Table 5.4-8.

5.4.4 Benzene

Coke Ovens

Table 5.4-9 shows the results of our gas chromatographic analyses for benzene on the 17 charcoal trap samples. At least 0.586 g of benzene were collected on the traps. As seen in the last column of the table, the benzene concentration in the emitted gas stream was generally greater than 1 percent during the first 11 hours of the coking cycle. At 0030 hours it began declining, reaching 0.08 percent at 0430 hours.

As estimated above, the mass of benzene which would have flowed through the sampling train was 23.52 g, or 43.1 percent of the total mass emission during the test. Annual emissions would therefore be $(0.431)(91.59$

Table 5.4-5
COMPOUNDS FOUND BY GC/MS TO BE PRESENT
IN DICHLOROMETHANE EXTRACT OF COKE OVEN SAMPLES

benzonitrile
1-ethynyl-4-methyl benzene
azulene
benzothiazole
isoquinoline
2-methyl naphthalene
1h-indole
4-methyl-3,5-pyridine dicarbonitrile
1-1'biphenyl
1,2-dihydro acenaphthylene
benzophenylene
2-methyl-1,1'biphenyl
dibenzofuran
1h-phenalene
9h-fluorene
[1,1'biphenyl]-4-carboxaldehyde
dibenzothiophene
anthracene
acridine
9h-carbazole
1-phenyl naphthalene
2-methyl phenanthrene
4h-cyclopenta[def]phenanthrene
2-methyl-9h-carbazole
2-phenyl naphthalene
pyrene
3,7-dithiabicyclo[7.3.1]trideca-1(13),9,11-triene
fluoranthene
pyrene
1,4-dihydro-1,4-ethenoanthracene
9-anthracenecarbonitrile
1-methyl pyrene
9h-fluorene-9-carbonitrile
11h-benzo[a]fluorene
benzo[b]naphtho[2,1-d]thiophene
benzo[ghi]fluoranthene
benz[a]anthracene
triphenylene
benzo[c]phenanthrene
7h-benz[de]anthracen-7-one
benzo[k]fluoranthene
dibenz[a,h]anthracene
indeno[1,2,3-cd]pyrene

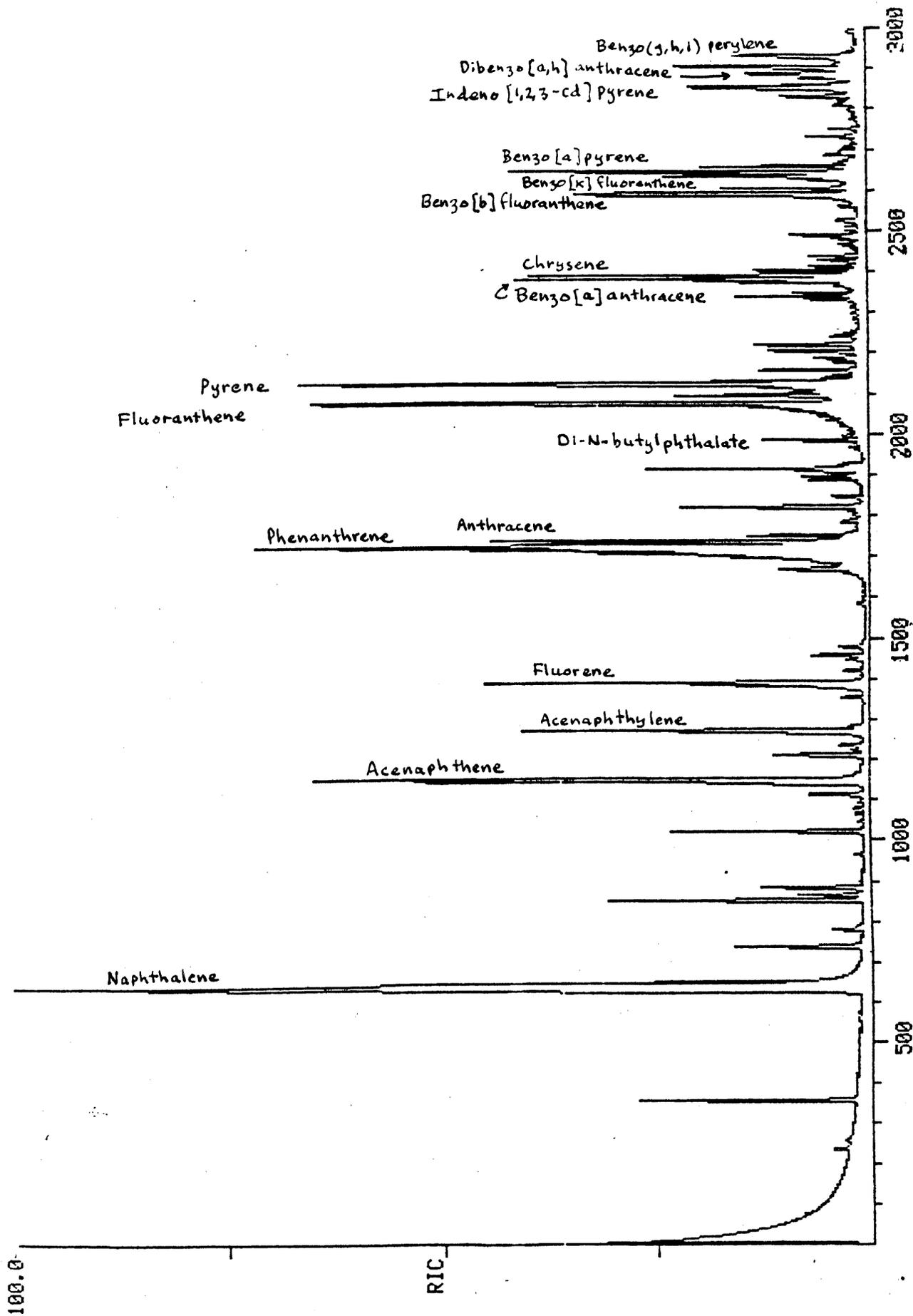
Table 5.4-6
COMPOUNDS FOUND BY GC/MS TO BE PRESENT IN
TOLUENE EXTRACT OF COKE OVEN SAMPLES

1h-indene
azulene
benzothiazole
isoquinoline
2-methyl naphthalene
1h-indole
1,1-biphenyl
biphenylene
1,2-dihydroacenaphthylene
dibenzofuran
1h-phenalene
9h-fluorene
4-methyl dibenzofuran
dibenzothiophene
d-10 phenanthrene (i.s.)
anthracene
benzo[h]quinoline
9h-carbazole
2-methyl phenanthrene
2-phenyl naphthalene
pyrene
fluoranthene
1-iodo-4-methyl benzene
1-methyl pyrene
9h-fluorene-9-carbonitrile
11-h-benzo[a]fluorene
benzo[b]naphtho[2,1-d]thiophene
benzo[ghi]fluoranthene
benz[a]anthracene
benzo[a]phenanthrene
benzo[c]phenanthrene
7h-benz[de]anthracen-7-one
benzo[k]fluoranthene
benzo[b]chrysene
ideno[1,2,3-cd]pyrene
dibenz[a,h]anthracene

Table 5.4-7

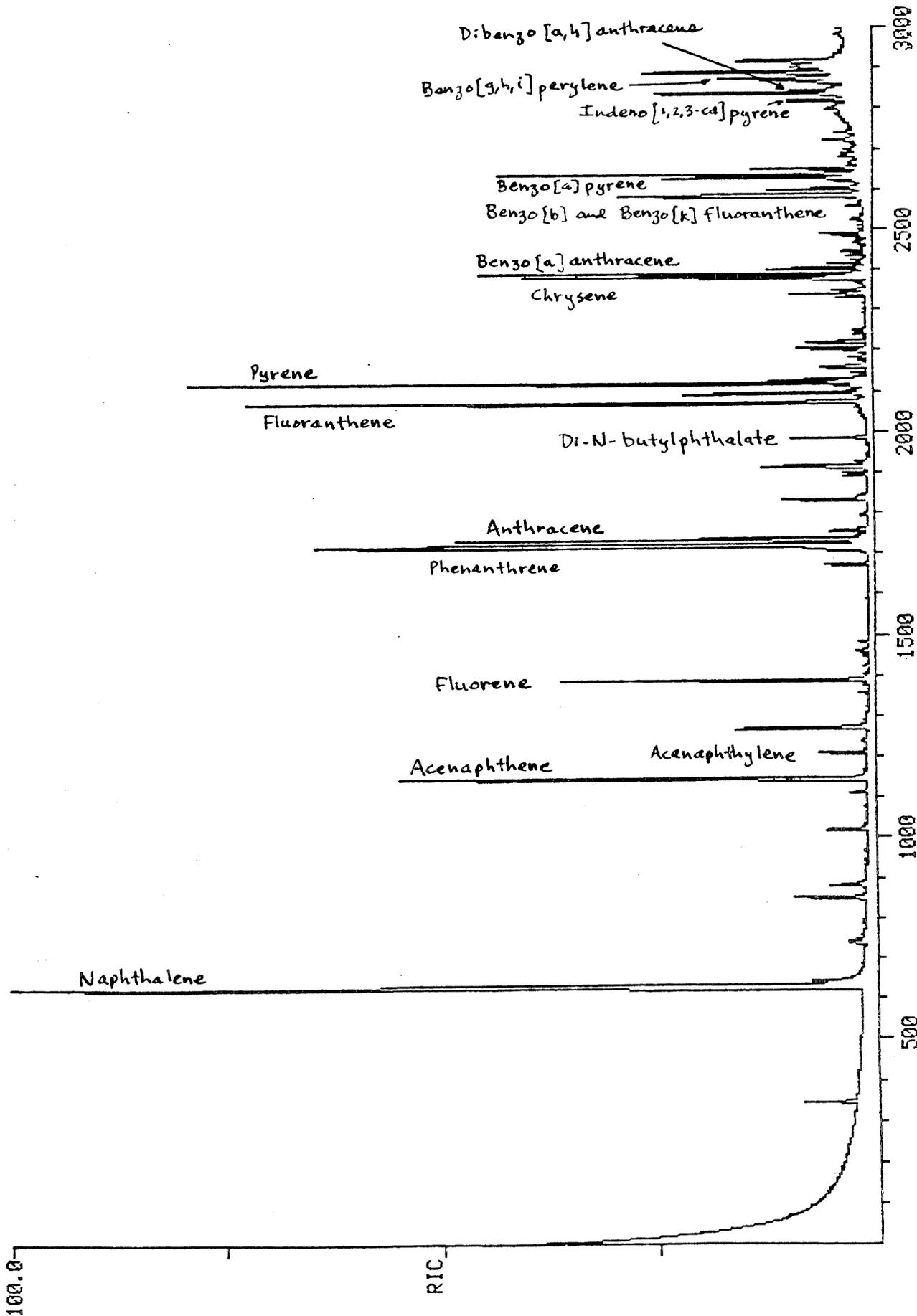
COMPOUNDS FOUND BY GC/MS TO BE PRESENT
IN EXTRACT FROM XAD-2 RESIN

ethynyl benzene
bicyclo[4.2.0]octa-1,3,5-triene
benzonitrile
benzofuran
2,3-dihydro-1h-indene
1-ethynyl-4-methyl benzene
2-chloro-1-phenyl ethanone
azulene
isoquinoline
2-methyl naphthalene
biphenylene
dibenzofuran
d-10 phenanthracene
butyl-2-methylpropolyester 1,2-benzene dicarboxylic acid
3-ethyl-2-methyl heptane
2-(9-octadecenyloxy)-(z)ethanol
octadecylester 9-octadecenoic acid (z)
4,6,8-trimethyl-1-nonene
1,1-oxybis octane



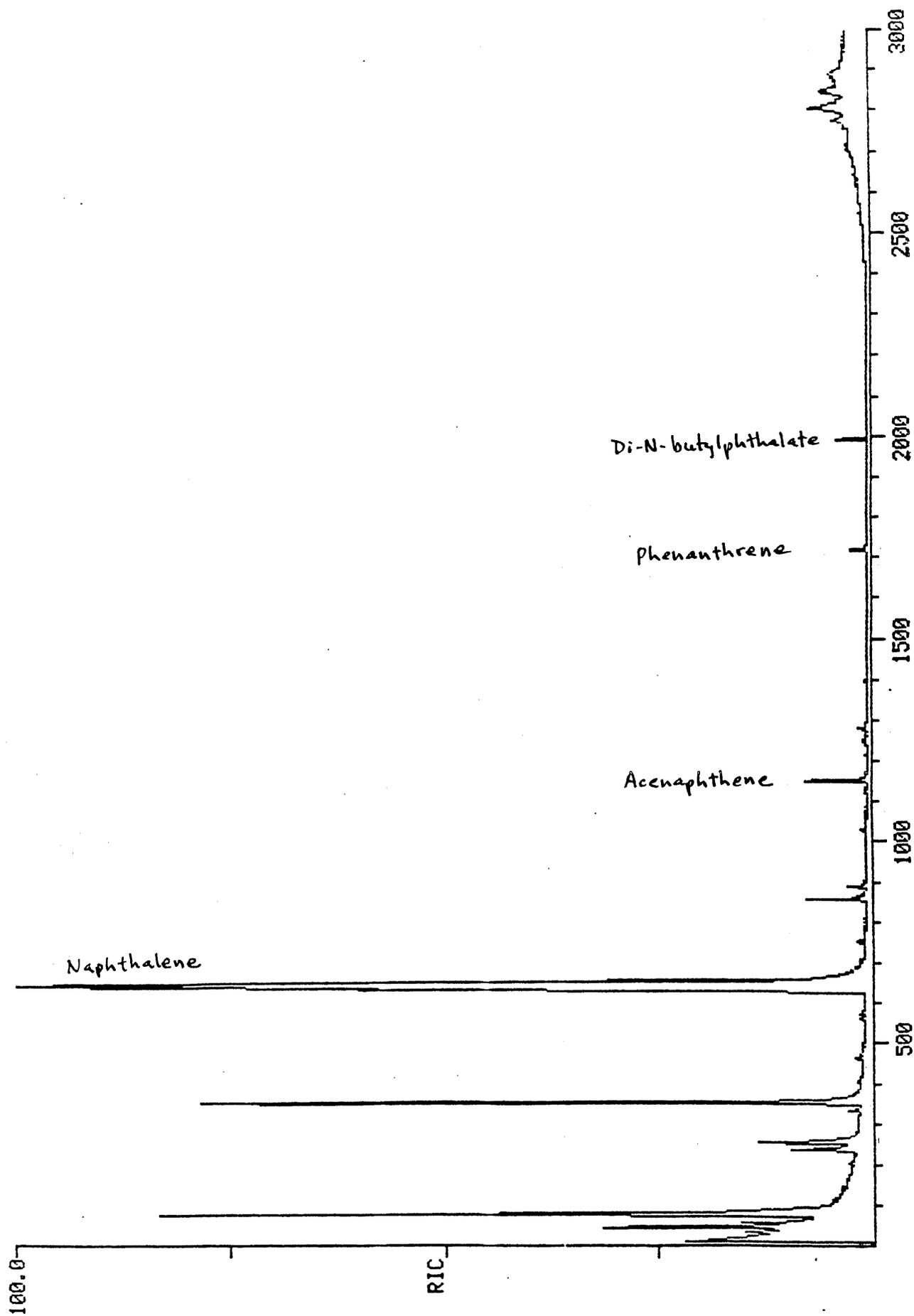
Mass Spectrum of Dichloromethane Extract of Coke Oven Emission Sample

Figure 5.4-1



Mass Spectrum of Toluene Extract of Coke Oven Emission Sample.

Figure 5.4-2



Mass Spectrum of Dichloromethane Extract of XAD-2 Sample of Coke Oven Emissions.

Figure 5.4-3

Table 5.4-8
EMISSION FACTORS FOR CARCINOGENIC POLYCYCLIC
AROMATIC COMPOUNDS IN COKE OVEN DOOR EXHAUST

Compound	Emission Rate (tons/yr)	Emission Factor (lb/ton coal)
Chrysene	0.60	6.1×10^{-4}
Benz(a)anthracene	0.40	4.1×10^{-4}
Benzo(e)pyrene	1.52	1.5×10^{-3}
Benzo(a)pyrene	0.76	7.7×10^{-4}
Indeno (1,2,3-cd)pyrene	0.43	4.4×10^{-4}
TOTALS	3.71	3.7×10^{-3}

Table 5.4-9
RESULTS OF GAS CHROMATOGRAPHIC ANALYSIS OF
BENZENE COLLECTED FROM COKE OVENS AT KAISER

Sampling Time Date Hour	Mass on Trap ^a (mg)	Gas Volume Sampled (liters) ^b	Concentration in Sample (Pct. by Volume) ^c
15 July 1450	45.3	1.000	1.51
15 July 1530	23.6	1.000	0.79
15 July 1630	>52.8	1.000	>1.76
15 July 1730	>51.6	1.000	>1.72
15 July 1830	>56.7	1.000	>1.89
15 July 2000	>67.2	1.000	>2.24
15 July 2030	>30.3	1.000	>1.01
15 July 2130	>47.5	1.000	>1.58
15 July 2230	>58.6	1.000	>1.95
15 July 2330	>68.0	1.000	>2.26
16 July 0030	>33.9	1.000	>1.13
16 July 0130	23.5	1.000	0.78
16 July 0230	9.7	1.000	0.322
16 July 0330	3.3	1.115	0.10
16 July 0430	>2.3	0.925	>0.08
16 July 0530	9.2	0.575	0.53
16 July 0630	2.1	0.385	0.18

^a Mass reported as an inequality when the backup trap contained an amount of benzene greater than 20 percent of that measured on the front trap.

^b Not corrected to standard temperature and pressure.

^c For T = 350 °F (450 °K), P = 1 atm.

metric tons/yr) = 39.4 tonnes/yr (43.5 tons/yr). This figure is slightly more than twice our pre-test estimate of 20 tons/yr.

Tar Decanter

Isobutane was injected into the tar decanter at the rate of 7.3 ml/sec. Since the isobutane gas bottle was at ambient temperature (about 100 °F), it can be estimated that each liter of isobutane comprised about 0.04 moles. The injection rate was therefore $(0.0073 \text{ L/sec})(0.04 \text{ moles/L})(58.12 \text{ g/mole}) = 0.017 \text{ g/sec}$. Table 5.4-10 shows the concentrations of benzene and isobutane in the three glass bulb samples taken. Assuming that the ratio of benzene to isobutane in the glass bulb was the same as in the decanter, (i.e. that the two gases were sampled in the same proportions), we estimated benzene emission by multiplying the isobutane injection rate by the benzene/isobutane ratio. Results are also shown in Table 5.4-10. The mean emission rate would be only about 10 kg/yr, with a 95-percent confidence interval of $\pm 24 \text{ kg/yr}$. The tar decanter is thus a minor source compared to the coke ovens and the final cooler cooling tower.

Our pre-test estimate, which was based upon a grab sample at a steel mill in Alabama, was about 20 tons/yr. Some of the possible reasons for the great difference between the estimate and the field sampling result are:

- The Alabama site test measured tar decanter emission composition only; since the decanter is a fugitive emission source, the mass emission rate could only be estimated.
- Isobutane did not mix thoroughly enough with the vapors in the tar decanter.
- Shifting winds resulted in a non-representative sample.

Final Cooler Cooling Tower

Upward air flow from the tower was estimated from velocity traverse data to be $96.1 \text{ m}^3/\text{s}$ (204,000 cfm). The mean exhaust air velocity was 2.7 m/s. The average concentration of benzene in the three air samples collected from the tower exhaust was 0.0113 g/m^3 . The mean emission rate was therefore $(0.0113 \text{ g/m}^3)(96.1 \text{ m}^3/\text{s}) = 1.09 \text{ g/s}$. Annual emissions are estimated to be 34 metric tons (38 tons). Since three cooling towers are associated with the final cooler, total benzene emissions would be about 102 tonnes/yr (114 tons/yr).

Table 5.4-10
ESTIMATION OF BENZENE EMISSION FROM THE TAR DECANTER

Sampling Time	Concentrations in Bulb (ppmv)		Benzene/ Isobutane Ratio	Benzene Mass Emission Rate		
	Isobutane	Benzene		(g/sec)	(kg/yr)	(lb/yr)
1535	65.7	0.18	0.0027	4.6×10^{-5}	1.4	3.2
1545	5.0	0.19	0.038	6.5×10^{-4}	20	45
1555	57.3	0.84	0.015	2.0×10^{-4}	6.4	14
Mean			0.019	3.2×10^{-4}	10	22

Emission Factors for Benzene

Emission factors for benzene were determined by dividing the coke oven and cooling tower estimates by the mass of coal used annually by the facility (1.97×10^6 tons/yr). They are:

- o Coke Ovens: 0.044 lb/ton
- o Cooling Towers: 0.12 lb/ton

5.4.5 Arsenic and Cadmium

Estimation of Emissions

Table 5.4-11 shows the results of our analyses of impinger liquids and particulate matter from the impingers, filters, tubing and connectors for arsenic and cadmium. Only 48 and 28 μg of the two metals, respectively, were detected. If this finding is representative of coke oven emissions, then less than a kilogram of each metal would be emitted annually. These measured emission rates are far below our pre-test estimates. However, as noted in Sections 5.2.3 and 5.2.4, our pre-test estimates were subject to considerable uncertainty.

Emission Factors for Arsenic and Cadmium

Emission factors for arsenic and cadmium were determined by dividing the coke oven emission estimates by the mass of coal used annually by the facility (1.97×10^6 tons/yr). They are:

- Arsenic: 9.1×10^{-8} lb/ton
- Cadmium: 5.4×10^{-8} lb/ton

5.5 RESULTS OF AMBIENT MEASUREMENTS AROUND THE FACILITY

As part of an independent sampling program, the South Coast Air Quality Management District (SCAQMD) collected hi-vol air samples on 1 July 1981 at 12 sites on the boundaries of the steel mill complex. Figure 5.4-4 shows the average wind speed and direction at each point during the five-hour test. Filter pad cuttings provided to SAI by the SCAQMD were wet digested with HNO_3 and H_2O_2 and then analyzed by graphite furnace atomic absorption spectroscopy for total arsenic and cadmium. Table 5.4-12 presents the results of our analyses. Except for Station 10, arsenic concentrations appear to be similar to the background concentration of 4 to 6 ng/m^3 reported in the first stage study (Margler et al., 1979). Cadmium levels were all below the average reported for 18 California cities between 1970 and 1974 (15 ng/m^3).

Table 5.4-11
ARSENIC AND CADMIUM EMISSIONS FROM COKE OVENS

Sample	Mass Collected (μg)	
	Arsenic	Cadmium
Impinger liquid	23.8	9.0
Sample train filters (SAI IV and V)	4.56	1.20
Particulate matter from tubing and connectors	14.3	13.3
Particulate matters from impingers	5.56	4.96
Total	48.22	28.46
Fraction of total mass collected	8.84×10^{-7}	5.22×10^{-7}
Estimated emission rate (kg/yr)	0.081	0.048

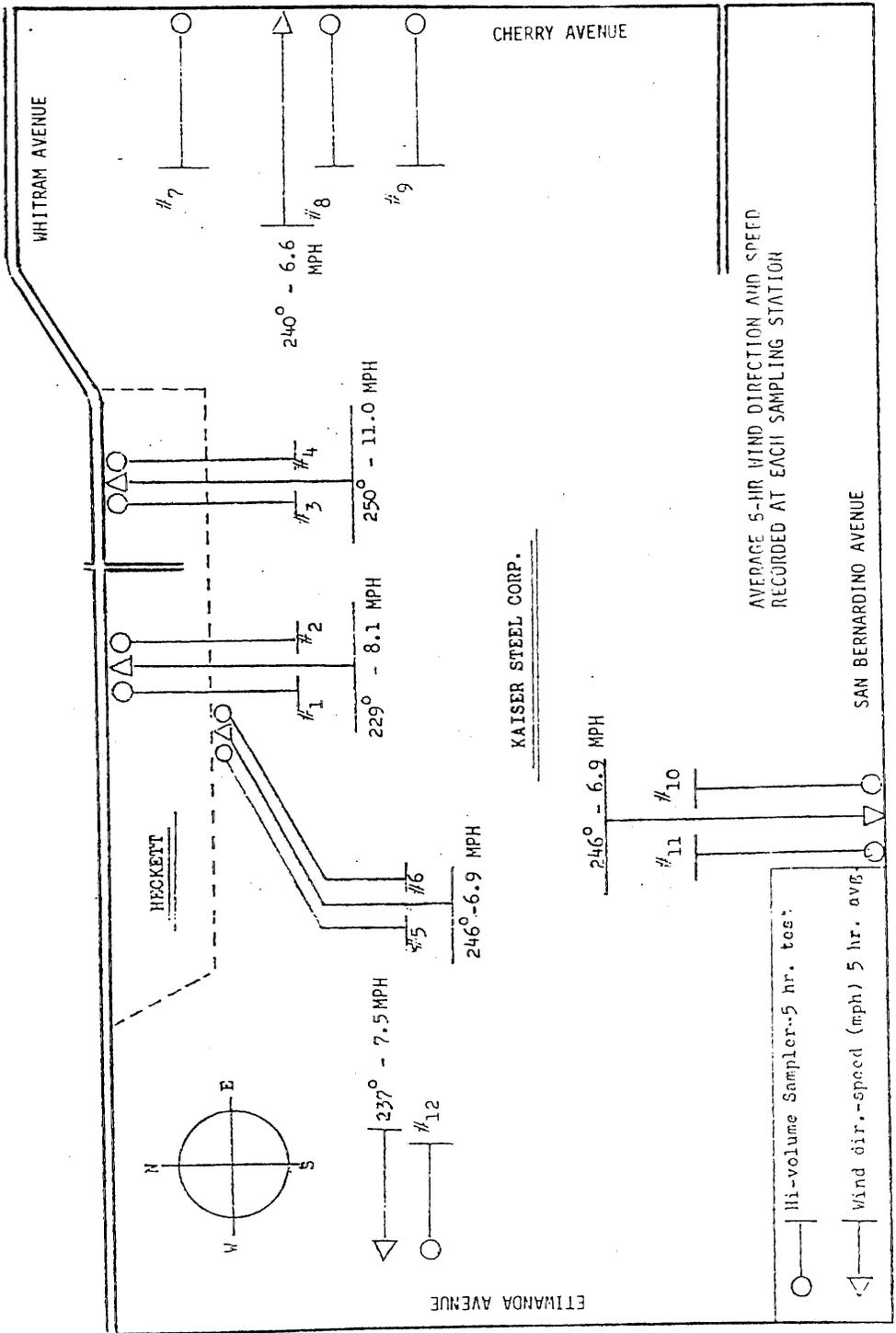


Figure 5.4-4 Ambient Air Sampling Points for South Coast Air Quality Management District Tests at Kaiser Steel Corporation, 1 July 1981

Table 5.4-12
 AMBIENT ARSENIC AND CADMIUM CONCENTRATIONS AT
 THE KAISER PLANT BOUNDARIES

Sampling Station	Direction From Coke Ovens	Arsenic Concentration ^a (ng/m ³)	Cadmium Concentration ^a (ng/m ³)
1	Upwind	<3.6	<0.02
2	Upwind	3.0	<0.02
3	Upwind	<4.8	0.5
4	Upwind	<5.0	0.4
5	Upwind	<4.6	0.3
6	Upwind	<4.4	0.5
7	Downwind	<5.4	1.3
8	Downwind	<4.9	2.5
9	Downwind	<3.4	1.7
10	Upwind	144	5.1
11	upwind	<5.2	1.1
12	Upwind	<4.9	<0.02

^a Determined from analysis of hi-vol samples collected by the South Coast Air Quality Management District.

Upwind and downwind concentrations of arsenic appear to be comparable. The concentrations of cadmium at Stations 7, 8, and 9, on the other hand, were higher than for any of the upwind sites except Station 10. The reason for the unusually high arsenic and cadmium concentrations at Station 10 is unknown.

SOURCE TESTS - JOHNS MANVILLE SALES CORPORATION

6.1 SITE OVERVIEW - JOHNS MANVILLE SALES CORPORATION

Johns Manville, Stockton, was identified as the largest asbestos user in the state (Margler, 1979) excluding mining and milling operations. Total suspended particle emissions from this plant are 19 tons per year, according to the CARB Emission Data System (EDS); the proportion of these emissions represented by asbestos is not stated. The applicable NESHAPS regulation stipulates zero visibility asbestos emissions. In order to determine the relative importance of various potential emission sources within the plant and develop a first-hand familiarity with plant operation, program staff conducted a literature review, made a pre-test site visit, and held discussions with plant and company personnel and researchers at several state and federal agencies. In conversations with company personnel it was determined that the EDS quantity should be considered an estimate with great uncertainty.

6.1.1 Facility Description

On 5 December 1980 program staff met with Johns Manville (JM) personnel to conduct a pre-test review of plant activities and processes, a plant inspection, and particulate monitoring. Basic operation and emission controls are described below.

JM purchases a variety of grades of asbestos from its Quebec mines and other suppliers to produce asbestos-cement pipe. Asbestos bags, shown in Figure 6.1-1, are slit and dry loaded into a willow which performs a fiber separation. Fiber storage, ingredient blending (asbestos, sand, cement) and formation of a water slurry follow. Slurry is transported on wide belts and deposited in thin layers onto a mandrel. After a sufficient thickness is built-up the mandrel is withdrawn, the pipe is usually kiln dried, cut, its ends are machined and other finishing and warehousing operations are performed. Composition of the product material is approximately 15 percent asbestos. Waste, baghouse dust and broken pipe are recycled. Previously, large pipe rejects were broken by earthmoving equipment and accumulated in an onsite refuse pile prior to recycle. However, a larger pipe crusher is now used to break up large pieces for recycling.

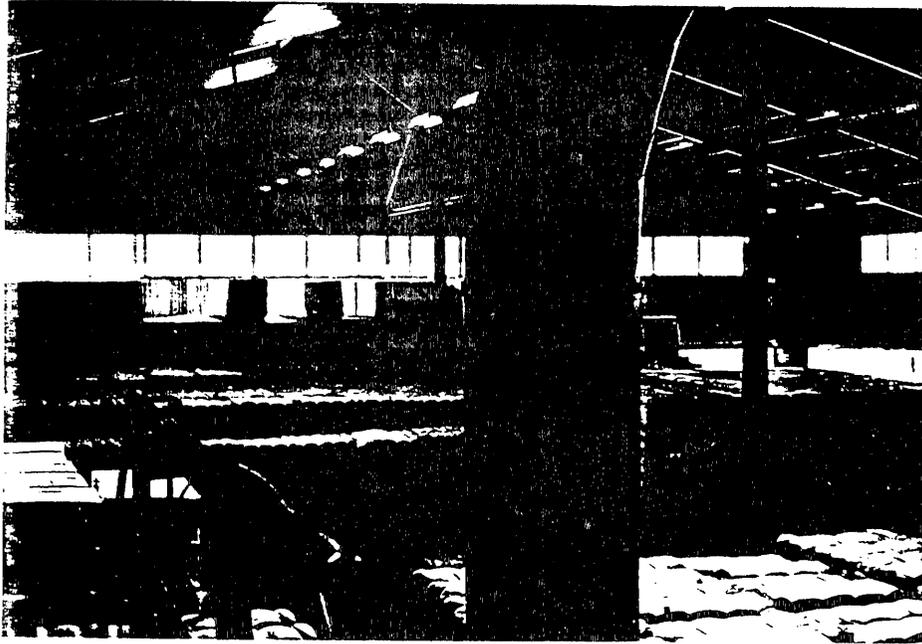


Figure 6.1-1 Johns Manville, Stockton, Asbestos Feed Warehousing Area

6.1.2 Emission Sources

All major processes and plant areas are tied into one of nine baghouses. These are delineated below along with their primary function and specified air flow rates in cubic feet per minute (cfm).

<u>System</u>	<u>Process</u>	<u>Flow</u>
D-1	No. 1 - No. 3 Willow (Fiber)	18,000
D-2	No. 1 - No. 3 Pipe Machines	26,000
D-3	No. 4 Willow (Fiber)	8,000
D-4	No. 4 Pipe Machine	13,000
D-5	Cutoff Machinery	53,000
D-6	Pipe Lathes	32,000
	Silica Grinding No. 1 Mill	2,500
	Silica Grinding No. 2 Mill	3,600
	Ball Mill Scrap Silex Unloading	8,500

Each baghouse vents through separate ducts to the atmosphere. Figure 6.2-1 illustrates the plant location of each baghouse.

There are no significant process operations not tied into bag houses. Area intakes are located throughout the plant. However, the facility is neither sealed nor operated under a pressure differential with respect to the outside.

Figure 6.1-2 to 6.1-4 illustrate several views of the D-1 bag-house. Figure 6.1-2 shows the upper level with the exhaust manifolds for the four individual baghouse compartments. Dampers which permit facility air to enter a baghouse compartment during the mechanical shake cycle are at the underside of each exit duct. Shake cycles for each baghouse compartment occur at roughly four-hour intervals and last less than one minute. Figure 6.1-3 illustrates the lower baghouse level where material is picked up by a worm gear train and transferred for recycle. Figure 6.1-4 shows the clean air exhaust duct between the baghouse (above) and the fan.

6.2 EMISSION MEASUREMENT APPROACH

6.2.1 Choice of Measurement Points

Three basic potential emission sources were postulated: baghouses, fugitives from within the plant area, and the exterior scrap storage area. It



Figure 6.1-2 Asbestos Fiber Baghouse, Upper Level



Figure 6.1-3 Asbestos Fiber Baghouse, Lower Level



Figure 6.1-4 Asbestos Fiber Baghouse, Clean Air Side
Exhaust Duct

was decided that the third source could be eliminated because use of a scrap storage area was to be discontinued and also because asbestos emissions should be relatively small from what little material might be present as part of the scrap recycle chain. (It was stated that no significant pipe crushing will be carried out by crushing with earth moving equipment). At the time of inspection a significant amount of material had been accumulated in the scrap storage area. After discussion with plant personnel, we assumed that this situation was temporary.

The three bag houses associated with the silica grinding and silex unloading are small and handle a relatively insignificant amount of fiber since approximately 10 percent of plant throughput is scrap recycle and, of that 10 percent, the asbestos content is 15 percent. Furthermore the asbestos present is no longer free fiber but rather is bound into a cement matrix.

Systems D-2 and D-4 are associated with wet process components, i.e. rolling of sheeted slurry onto steel mandrels, and were assigned secondary importance in comparison to dry process baghouses. Systems D-5 and D-6 are large airflow volume baghouses. However, they see only the 15 percent fiber content product. Furthermore, the material expected to comprise the D-5 and D-6 flows should be coarse since the fibers present are bound in the cement matrix. It was therefore expected that the D-1 and D-3 systems would carry nearly all of the asbestos fiber burden. D-1 receives the airflow from as many as three willows i.e. corresponding one-to-one with each of the three pipe machines. Typically, only one pipe machine is operating at a time and therefore only the corresponding willow is active. Results of asbestos measurements need only be scaled to the asbestos throughput handled during the collection period in order to develop a plant emission factor applicable to a specified production level.

In order to evaluate the importance of fugitive emissions from the plant and to assist another CARB sponsored program, "An Inventory of Asbestos Emissions in California," airborne asbestos sampling was planned immediately adjacent to the plant, simultaneously upwind and downwind, during periods of normal operation. The samplers were positioned to locate an upwind area at the border of the JM property line and the downwind site represented an area encompassing possible emissions from the transite pipe storage area and adjacent areas other than the baghouse plume itself. A 10 meter meteorological

tower was erected to provide continuous recording of wind speed, direction and temperature. Wet bulb temperature was manually taken. Figure 6.2-1 illustrates the spatial relationship among the detectors and the plant. The baghouse exhaust duct releases material at approximately 100 feet elevation and emissions were not expected to be detected at the ground level downwind detector.

Particle counter readings were taken at all sampling locations as part of our internal program to examine the relationship between asbestos fiber counts and particle counts for several size ranges. A Royco Model 225 light scattering particle counter was used with a paper tape recorder.

Summary

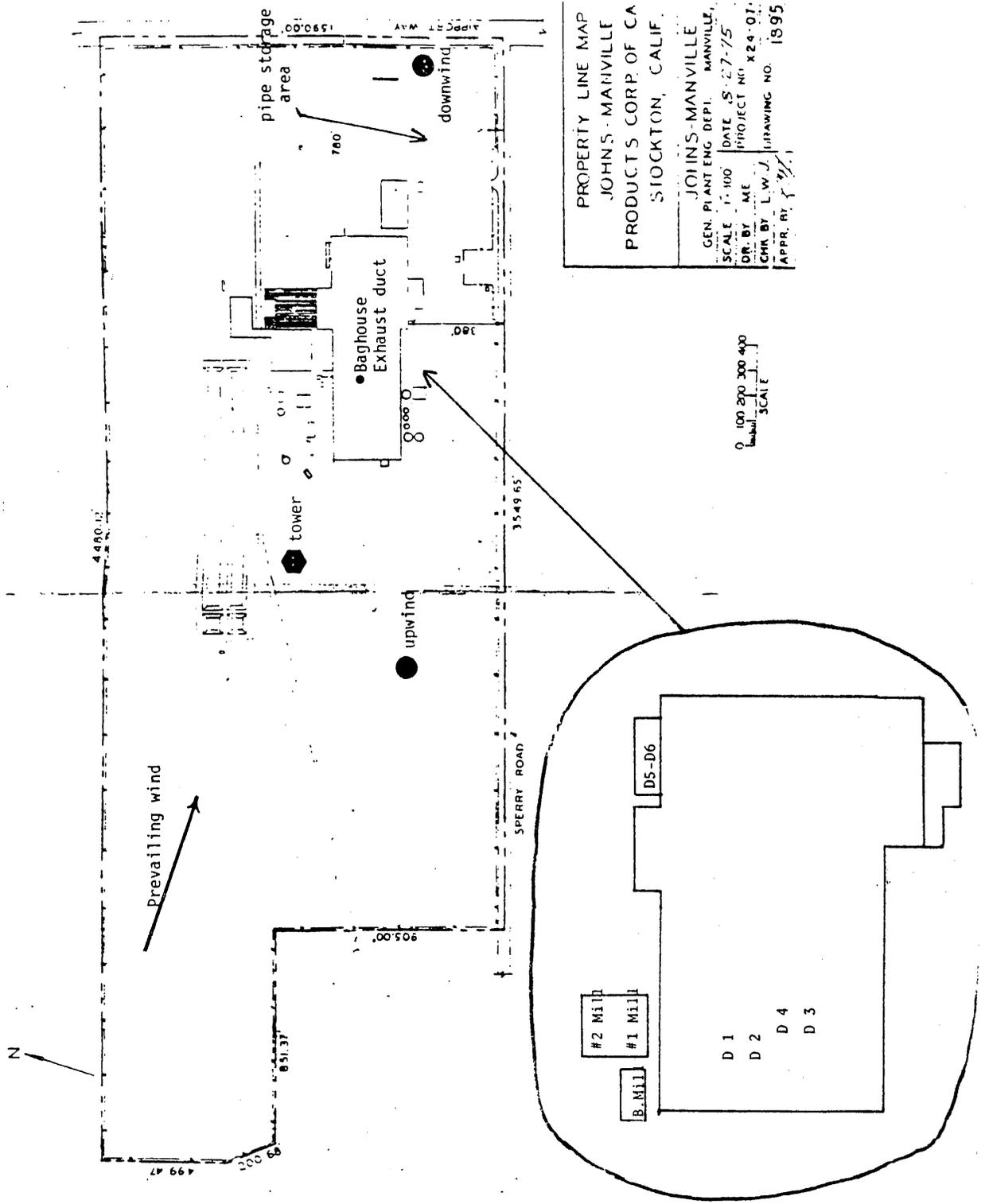
In this study the highest priority was given to determining the emissions of respirable fibers. Baghouse D-1 (or D-3) has the highest priority for measurement. Asbestos emissions leaving the baghouse should account for greater than 90% of total respirable fibers from processes since they are the only baghouses which handle fiber before it is combined into a slurry and becomes part of a blended matrix. Ten percent will be assumed as a conservative bound for miscellaneous process emissions. Although it is expected that most airflow within the main plant passes through a controlled ventilation system, it is still necessary to estimate the importance of miscellaneous fugitive sources by performing close-in area ambient sampling. Specifically, ground based simultaneous upwind and downwind ambient samples were taken adjacent to the plant with the latter detector established to see direct fugitive emissions from key plant access and material storage areas.

6.2.2 Measurement Approach

6.2.2.1 Baghouse

Samples were taken on polycarbonate membrane filters using a cyclonic pre-filter separator as specified by Dr. W. John of the California Air Industrial Hygiene Laboratory. The cyclone effectively eliminates the contribution of the larger nonfibrous materials (aerodynamic diameters ≥ 3.5 micrometers). The sampler is designed to run at a constant flow rate of 15.5 liters/minute to provide a 50 percent deposition of particles in the 2.5 to 3.5 micrometer aerodynamic size range. The filter collection media consisted of a 47 mm diameter Nuclepore filter of 0.2 micrometer pore size with a Millipore

Figure 6.2-1 Meteorological Tower and Asbestos Sampling Locations at Johns Manville



PROPERTY LINE MAP
 JOHNS-MANVILLE
 PRODUCTS CORP. OF CA
 STOCKTON, CALIF.

JOHNS-MANVILLE
 GEN. PLANT ENG. DEPT. MANVILLE,
 SCALE 1"=100' DATE 5/27/75
 DR. BY ME PROJECT NO. X24-07
 CHK. BY L.W.J. DRAWING NO. 1895
 APPR. BY

0 100 200 300 400
 Feet
 SCALE

backing filter. Each collector is enclosed as a filter cassette and is self contained in its own sealed box and stored in a specially constructed box designed to transport 50 samples in an upright position with a minimum of vibration. All loading and changing of filter cassettes in the field were conducted under a portable clean bench with HEPA^{*}-filtered air. The cyclone filter assemblies were totally disassembled and cleaned with Freon 113 between each sample run. Figure 6.2-2 illustrates the cyclone sampler. Air is drawn in through the underside of the protective hat down the duct and up through the cone shaped-cyclone. The filter cassette is situated horizontally at the cyclone top and the flow controller/pump rests on the ground at the bottom of the exit tube. Thus the cyclone acts to perform a separation process for coarse particle removal and those fibers remaining will have a sufficiently small aerodynamic diameter to be respirable.

Samples were taken from within the baghouse on the clean air side. The plant was operating in a normal condition somewhat under full capacity and samples were taken over a time expected to produce optimal filter loadings. The sampling time was chosen to be compatible with plant operation and observed baghouse particulate concentrations as determined by the Royco particle counter. Asbestos feed was observed during sampling in order to verify the level of plant activity. The number of willows and/or pipe machines operating is readily observed and directly confirms the level of plant activity.

Figure 6.2-3 shows the monitoring apparatus, which is on the catwalk outside the baghouse. NIOSH Method P & CAM 239 (phase contrast microscopy at 400 X magnification) was used in parallel with electron microscopy. The NIOSH method pumps were placed both on the replacement door and on the SIERRA pump. Sampling lines extend into the clean air side of the baghouse by passing through sealed openings in the substitute door. NIOSH sampling was conducted as specified by the method at a flow rate of 1.5 L/min with a 0.8 micrometer Millipore filter material. The SIERRA pump/flow controller was used to drive the cyclone separator sampling apparatus.

Samples were obtained by replacing the baghouse door with a fabricated substitute (see Figure 6.2-3) having sampling probe access. The cyclonic filter holder and all NIOSH filters were placed centrally inside the baghouse and all pumps and flow meters remained outside of the baghouse. The airflow velocity in the exhaust duct from baghouse D-1 was measured with a standard

* High efficiency particulate air filter

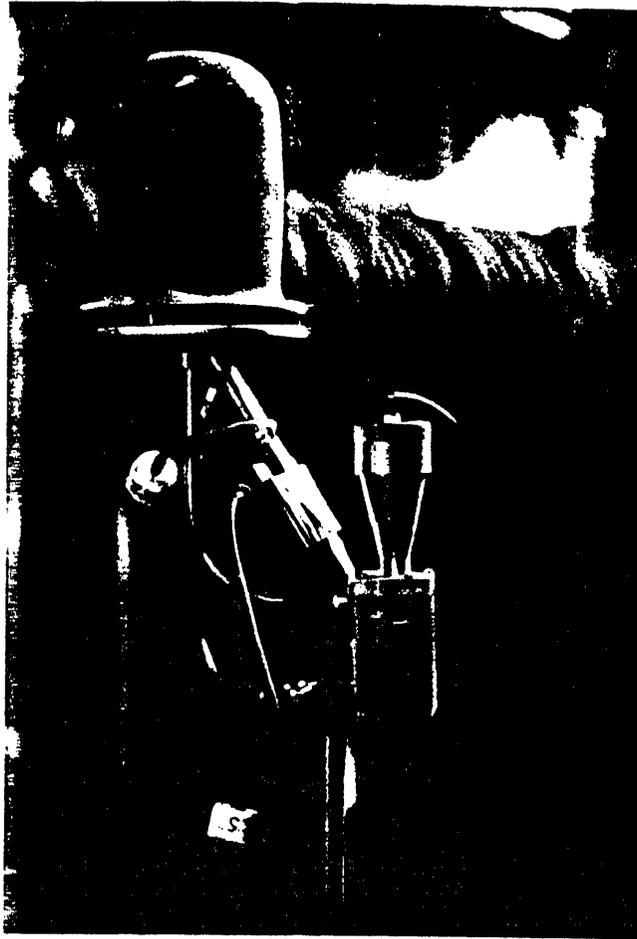


Figure 6.2-2 Asbestos Cyclone Sampling Apparatus

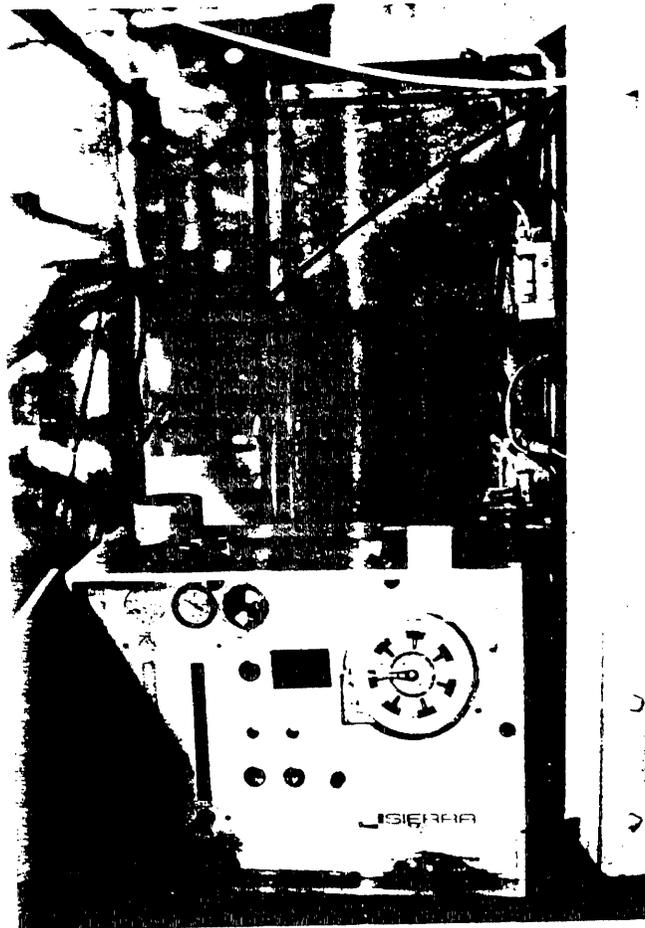


Figure 6.2-3 Asbestos Sampling Equipment Pumps

stainless steel pitot tube and a slant tube manometer. The temperature of the duct was measured with a mercury-in-glass thermometer. The average velocity of the stack gas was 39.071 ft/s and the actual flow at stack conditions was determined to be 14,781 acfm. Velocity traverses were made in the exit duct at eight points in each of two directions in conformance with EPA Methods 1 and 2. The exhaust stack area was 6.3 ft². The exhaust had a temperature of 111⁰F, and barometric pressure 29.9 in. Hg.

6.2.2.2 Upwind/Downwind Plant Area

For ambient sampling, we used the same cyclonic head and pump/flow controller equipment as for the baghouse approach. Samples were simultaneously upwind and downwind for about four hours to assure adequate filter loading and steadiness of meteorological conditions. Filters were handled only in the field laboratory and were thus protected from ambient contamination. Sampling sites were isolated from vehicular activity and other emission sources.

Weather conditions during the sampling period are shown in Figure 6.2-4. Skies were clear and humidity was low. The wind was consistently from the northwest (approximately 290 degrees). Wind speeds reached a maximum of 5 to 10 m/s by mid-afternoon. The temperature ranged from 10 to 30⁰C. the steadiness of the wind direction validated the choice of upwind and downwind sampling locations.

Ambient sampling was conducted on 23 July 1981 by placing the sampling pump assembly on the ground with the cyclone filter assembly fastened directly above. Both upwind and downwind samples were taken essentially at eye level. The upwind sample A-7 (See Table 6.2-1) was taken between 8:31 a.m. and 12:18 p.m. at a flow rate of close to 15.5 L/min. The downwind sample, which was located approximately 75 feet east of the transite pipe yard, was taken between 9:56 a.m. and 1:30 p.m. for 3331.7 L at the same flow.

6.3 DETERMINATION OF EMISSION FACTORS

Sampling was performed on 22-23 July 1981. Plant operations were close to normal although it was estimated that the effects of a labor dispute reduced the level of activity and caused recycle material to accumulate in the outdoor storage yard. Since only one pipe machine was in operation it is appropriate to apply a scale factor of two to measured emission values to account for a more typical baseline operating level. Table 6.3-1 is a summary

Weather Data
for Ambient Air Sampling at
Johns - Manville Transite Pipe Plant

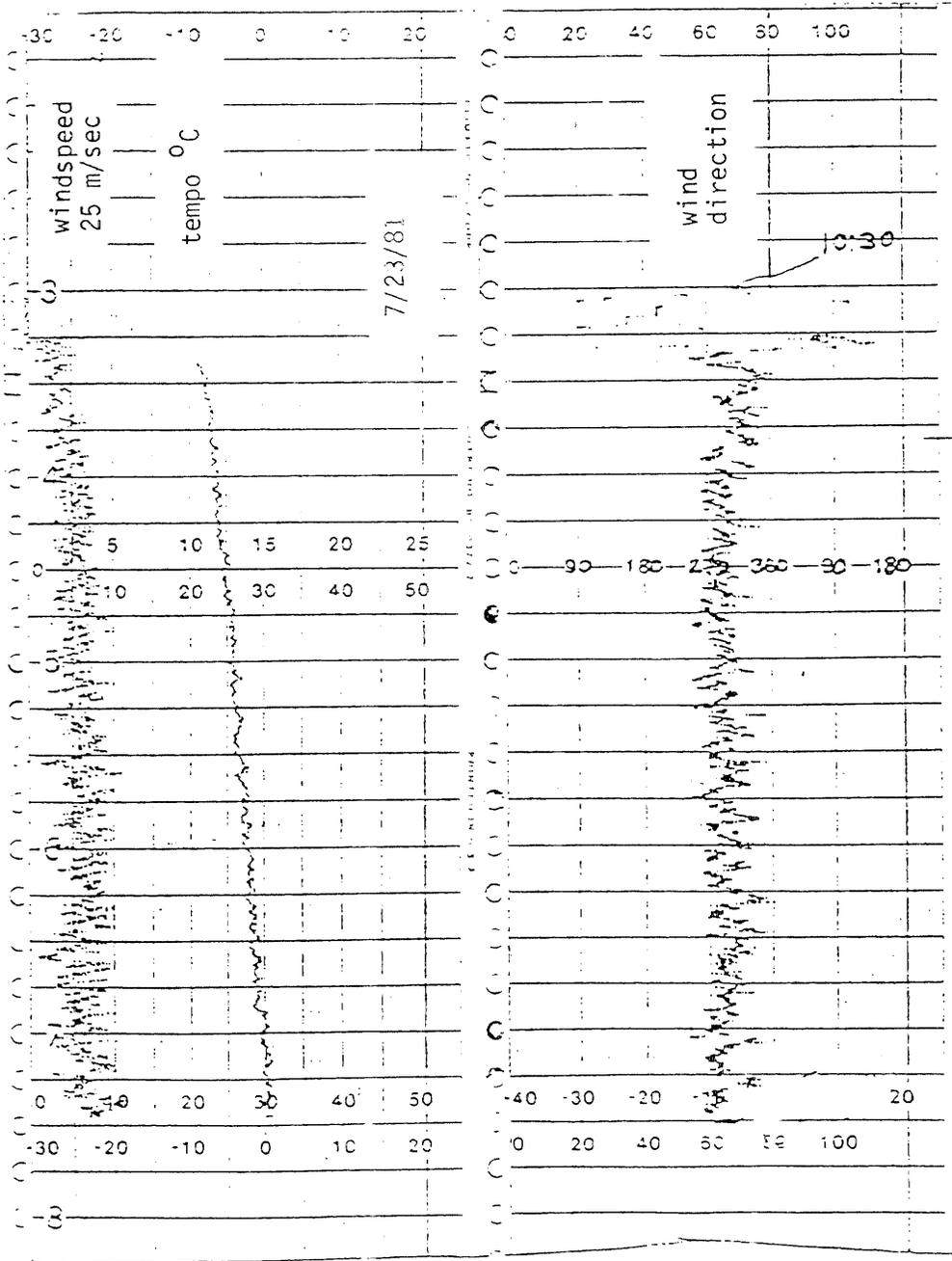


Figure 5.2-4

Table 6.2-1 JM Sample Collection Summary

<u>Sample #</u>	<u>Location</u>	<u>Date</u>	<u>Sample Start Time</u>	<u>Nuclepore Samples</u>		<u>Millipore Samples</u>	
				<u>Liters Sampled</u>	<u>Flow (ℓ/min)</u>	<u>Liters Sampled</u>	<u>Flow (ℓ/min)</u>
A-7	upwind	7/23/81	8:31 a.m.	3516	15.5		
A-8	downwind	7/23/81	9:56 a.m.	3331.7	15.5		
A-9	D-1 baghouse	7/23/81	1:41 p.m.	1497.3	15.5	144.9/140	1.5/1.45
A-10	D-1 baghouse	7/23/81	3:47 p.m.	2573	15.5	144.9/140	1.5/1.45

Table 6.3-1 Johns Manville Fiber Concentration Summary*

Sample#	Analysis Instrument	Location	Total Fibers/m ³			Non-Asbestos
			Chrysotile	Amphibole	Indeterminate	
A-7A	SEM	Upwind	---	---	2.7×10^5	8.9×10^4
A-7B	SEM	Upwind	---	---	1.3×10^5	1.8×10^5
A-7TEM	TEM	Upwind	---	2.5×10^3	7.5×10^3	2.2×10^4
A-8A	SEM	Downwind	1.0×10^5	---	1.0×10^5	1.0×10^5
A-8B	SEM	Downwind	1.0×10^5	---	1.0×10^5	---
A-8TEM	TEM	Downwind	1.8×10^4	3.7×10^3	3.3×10^4	3.7×10^3
A-9A	SEM	Baghouse	6.0×10^5	6.2×10^4	---	---
A-9B	SEM	Baghouse	5.7×10^5	---	---	---
A-9TEM	TEM	Baghouse	5.7×10^5	2.5×10^4	---	---
A-10A	SEM	Baghouse	4.4×10^5	5.1×10^4	---	---
A-10B	SEM	Baghouse	6.3×10^5	2.5×10^4	---	---
A-10TEM	TEM	Baghouse	4.4×10^5	5.0×10^4	1.9×10^4	---

* Any table entries less than approximately 5×10^4 should be considered below the practical limit of detection and assigned the inequality less-than-or-equal-to (\leq).

of the collection data. Only data taken on 23 July 1981 were used for determining emission factors. Baghouse measurement data from 22 July were archived because program staff had some concern that air flow from the plant may have mixed with the clean-side baghouse flow and would thus make differentiation of the latter's contribution impossible to quantify.

6.3.1 Electron Microscopic Analyses of Filter Samples

Measurement and verification of chrysotile fibers conformed to EPA procedure 600/2-77-178, Revised June, 1978. EM analyses were conducted on the Hitachi H-500 scanning transmission electron microscope at 100 KV beam voltage and calibrated with magnification standards. SEM (scanning electron microscope) analysis was performed on an International Scientific Instruments Super IIIA with a Kevex 5100 x-ray energy dispersive spectrometer.

The upwind, downwind, and D-1 baghouse samples were analyzed using both the Scanning Electron Microscope and the Transmission Electron Microscope to provide a comparison of both modes and also a quality control check on the primary (TEM) analysis.

6.3.2 SEM Analysis

The ambient upwind and downwind samples (A-7 and A-8) were coated with gold and a minimum of 100 fields were counted at a magnification of 10,000. Asbestos particles were confirmed using dispersive X-ray. The actual visual counting was conducted on the microscope using a slow raster scan rate (i.e. electron beam sweep rate) of approximately 4 seconds. A slow sweep rate was chosen to provide the best contrast for visual counting of fibers. The samples were analyzed according to the EPA counting procedure (EPA-600/2-77-178) with one modification involving the reporting of true fiber length. Due to the statistical calculation of mass, only the fiber length within the field of view is recorded using EPA's format. The partial length observation is correct in determining mass calculations but limits the recording of length data to the field of view when using the scanning electron microscope. Erroneous length data will be obtained unless another column of data is provided to note the true length of fibers when they extend beyond the field of view. When a fiber extends beyond the field of view the magnification is reduced so it is contained within the field. The true length is recorded along with a notation indicating that the process was performed. SAI's

computer program then accounts for this and the recording of mean length is calculated from the true length data. Mass calculations, on the other hand, are based upon dividing the true fiber length by a factor of two for this subgroup of fibers.

Two sections of filter were analyzed separately for each sample. The results are presented in Table 6.3-1. As noted in the table, fiber concentrations less than 5×10^4 fibers/m³ should be considered below the limit of detection. This limit is primarily a function of the air volume sampled and the number of fields counted in the analysis. It therefore varies from sample to sample and should be considered as the fiber concentration corresponding to finding less than one fiber among the prescribed number of fields counted. The D-1 baghouse samples (A-9 and A-10) were analyzed for 100 fibers and/or 100 fields at a magnification of 5000x. The reasons for the difference in the magnification in the baghouse analysis results stem from an attempt to increase the filter area being analyzed. Unlike the ambient samples, the baghouse asbestos fibers consist mainly of fiber bundles with mean diameters of 0.15 micrometers and mean lengths of 2.6 micrometers. These fibers are clearly visible at magnifications even lower than 5000x. Note that the Table 6.3-1 entry "indeterminate" applies to fibers which could not be positively identified and thus cannot be ruled out as asbestos. Sample notations A and B refer to analyses of independent sections of the same collected sample by SEM.

6.3.3 TEM Analysis

The filter sections for TEM analysis were prepared on 300 mesh copper grids using the modified Jaffe-Wick method outlined in the EPA provisional methodology EPA-600/2-77-178.

Both ambient and baghouse samples were counted at a magnification of 20,000. Ten grid holes per grid on three grids for each sample were counted for both ambient samples. A total of 100 fibers and/or 30 grid holes on 3 grids for each baghouse sample were counted. Confirmation of chrysotile and crocidolite (i.e. amphibole) asbestos was done using selected area electron diffraction.

6.3.4 Comparison of SEM and TEM Baghouse Analyses

The results of the SEM and TEM analyses are compared in Table 6.3-2. Fiber counts for both chrysotile and amphibole asbestos are well within

Table 6.3-2

JM BAGHOUSE ANALYSIS

Sample A-9 (7/23 @ 1:41 - 3:18) mid-point in baghouse

INSTRUMENT	MAGNIFICATION	Chrysotile		Amphibole	
		TOTAL FIBERS/m ³	MASS (pg/m ³) ⁺	TOTAL FIBERS/m ³	MASS (pg/m ³) ⁺
TEM	20,000x	5.7 x 10 ⁵	1.2 x 10 ⁵	2.5 x 10 ⁴	1.2 x 10 ⁴
SFM	5,000x	5.9 x 10 ⁵	3.1 x 10 ⁶	3.1 x 10 ⁴	2.3 x 10 ⁴

Sample A-10 (7/23 @ 3:47 - 6:33)

TEM	20,000x	4.4 x 10 ⁵	2.0 x 10 ⁵	5.0 x 10 ⁴	3.4 x 10 ³
SEM	5,000x	5.4 x 10 ⁵	3.4 x 10 ⁶	3.8 x 10 ⁴	6.0 x 10 ²

TOTAL STATISTICAL SUMMARY

INSTRUMENT	Chrysotile		Amphibole	
	FIBERS/m ³	pg/m ³ +	FIBERS/m ³	pg/m ³ +
TEM	5.1 x 10 ⁵	1.6 x 10 ⁵	3.8 x 10 ⁴	7.7x10 ³
SEM	5.7 x 10 ⁵	3.3 x 10 ⁶	3.5 x 10 ⁴	1.1x10 ⁴
		MEAN LENGTH*	MEAN LENGTH*	MEAN DIAMETER*
		2.6	.15	2.3
		12.3	.36	.18
				.16

* in microns

+ pg/m³, pico grams per cubic meter

statistical variation even for samples analyzed on the same instrument. The acceptable variation for an analysis of fiber counts is approximately 30 percent. The total statistical summary (average over A-9 and A-10) for the D-1 baghouse yield fiber count differences between the SEM and TEM of only 11% for both chrysotile and amphibole. The mass values are approximately one order of magnitude higher in the SEM analysis than the TEM analysis. The disagreement is somewhat to be expected due to the differences in sample preparation, lower resolution of the SEM (70 angstroms as compared to 2 angstroms in the TEM), and the way the electron image is actually generated. In TEM preparation, the samples are coated with carbon, but because the fibers are viewed in a transmitted fashion similar to an X-ray, the actual particle diameter is visible and accurately measured. In the SEM preparation, the filters are coated with gold and then analyzed on the SEM in an essentially reflected mode. The image measurement of the fiber diameter is a total of the actual fiber diameter and the thickness of the gold coating. In large diameter particles (0.5-1.0 micron) this is insignificant; but very small particle diameters can be significantly affected. It must be remembered that in calculating the mass of a fiber, the diameter measurement is squared and therefore mass value errors are drastically compounded.

6.3.5 Calculation of Mass Emission Rate

Fiber counts by SEM, TEM and optical microscopy (from the NIOSH samples) are compared in Table 6.3-3. Note that the optical sample analyses are of two separate filters taken simultaneously rather than of sections of one filter, as in the case of the SEM. Table 6.3-4 compares the fiber mass concentrations as a function of fiber size for SEM and TEM. The average TEM derived mass density for runs 9 and 10 is 1.6×10^5 pg/m³. This, coupled with the actual measured exit duct flow rate of 14,781 cfm (473 m³/min) yields an annual mass emission rate of approximately 40 g. Fiber concentration is in the neighborhood of 0.5×10^6 f/m³ at the release point. TEM, rather than SEM, measurements were used as the primary analysis tool for quantifying mass emissions, as discussed in the previous section on SEM analysis. Assuming the plant might typically operate at twice the activity level that was observed on 22-23 July (i.e. an average of two pipe machines rather than one) yields an emission rate of 80 g at a fiber concentration of approximately 1.0×10^6 fibers/m³. This is a conservative assumption since emissions would be less than doubled if the two pipe machines

Table 6.3-3
 COMPARISON OF FIBER COUNT CONCENTRATION AMONG ANALYTICAL METHODS
 (All concentration in fibers/cm³)

<u>Sample</u> ^a	<u>Fiber Size <5 micrometers</u>		<u>Fiber Size >5 micrometers</u>		
	<u>SEM</u>	<u>TEM</u>	<u>Optical</u>	<u>SEM</u>	<u>TEM</u>
9A	0.50		0.20	0.14	
9B	0.37	0.50	0.27	0.19	0.05
10A	0.33		0.12	0.11	
10B	0.58	0.42	0.14	0.05	0.02

^a See Table 6.2-1 and 6.3-1 for descriptions of the sample origins.

Table 6.3-4
 COMPARISON OF FIBER MASS CONCENTRATION AMONG ANALYTICAL METHODS
 (All concentration in pg/m^3)

<u>Fiber Size <5 micrometers</u>			<u>Fiber Size >5 micrometers</u>	
<u>Sample#</u>	<u>SEM</u>	<u>TEM</u>	<u>SEM</u>	<u>TEM</u>
9A	2.5×10^5		4.3×10^6	
9B	3.5×10^5	8.1×10^4	1.3×10^6	4.0×10^4
10A	1.9×10^5		3.3×10^6	
10B	1.1×10^5	3.3×10^4	3.8×10^6	1.62×10^5

operating were hooked up to the same baghouse, i.e. both to D-1 rather than one to D-1 and one to D-4.

Fiber counts for the upwind/downwind ambient measurements were listed in Table 6.3-1. Note that, by TEM, the chrysotile fiber density was zero and below the threshold of detection (1.8×10^4), respectively, for the upwind and downwind positions. These values, along with the particle counts by the Royco device and the CARB TSP Stockton monitors, will be incorporated into the analysis of ambient asbestos concentrations being undertaken in a separate CARB sponsored contract. The program findings do not support the determination of an emission factor from plant fugitive releases since TEM, the primary analytical tool, found upwind and downwind fiber densities to be below the practical limit of detection. Although SEM derived downwind concentrations were somewhat higher, so is the practical limit of detection by SEM since the area scanned in analysis is less than by TEM.

In summary, releases from the D-1 baghouse were determined to be equivalent to 80 g/year for average operating conditions. It was concluded previously that such emissions could be assumed to account for 90 percent of all plant ventilation system releases of respirable asbestos fibers and that miscellaneous fugitive emissions would be directly determined separately by simultaneous upwind/downwind ambient sampling. Therefore the overall plant emission rate will be taken to be 89 g/year in accordance with test findings. It is noteworthy that 19 tons/year of total particulate emissions were listed in the state emission inventory system data base.

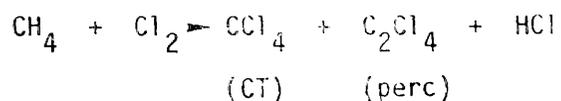
Detailed computer printouts of fiber and mass concentrations from TEM and SEM analyses are provided as Appendix F and may be consulted for examination of the raw data base.

7.0

SOURCE TESTS - DOW CHEMICAL U.S.A.

7.1 SITE OVERVIEW

The Dow facility in Pittsburg, California produces carbon tetrachloride (CT) and perchlorethylene (perc) by the same process. The yield of CT/perc can be varied as a function of feedstock composition. Products are produced by chlorination of methane according to:



After reaction, the process involves various stages of separation and purification and eventually storage and shipment.

Since the system is virtually closed to the atmosphere, it was anticipated that CT and perc would be emitted through fugitive losses from valves, flanges and pump compressor seals. Additionally, emissions from storage tanks and off-loading may be significant. Our recommended approach to determine a site emission factor was to conduct a leak survey of the plant and couple the results with an inventory of the components of interest in order to a mass emission rate. Emissions from storage and off-loading would be estimated from direct measurements (if possible) and calculations.

7.1.1 Facility Description

On 11 December 1980 a meeting was held at the site with Dow personnel. Although some plant information was obtained, it was not possible to tour the plant at that time. It was confirmed that the published process flow diagram of Phase I (Roberts, 1980) was, in fact, a useful representation of the process. Dow staff were sensitive to release of specific information concerning processes and production values. Dow estimated that fewer than 2000 valves, flanges, compressors and pumps exist in the systems which contain hydrocarbons. It was not known what percentage of these devices contain streams with greater than one percent CT or perc. However, no difficulty was anticipated in proceeding through the plant and identifying all such streams during testing. It was clear that numerous streams of CT and perc exist within

the process under a variety of physical states and in combination with other substances.

7.1.2 Emission Sources

Because we were unable to observe plant processes or obtain specifics on control system configurations, i.e., storage tank ventilation and turn-over rate, it was not possible to identify, at the time of the pretest visit, the most important emission measurement priorities beyond what was known in Phase I. The approach taken was to identify the system components of potentially greatest importance, i.e., to emphasize enriched stream compositions and historically important component types. If possible, 100 percent of streams containing greater than one percent product would be tested. It was not known whether storage systems would likely be of primary or secondary importance; we would however, measure only tank working emissions, i.e., displacement of product laden vapor during filling operations. Tank breathing emissions, i.e., equilibrium evaporative emissions, would be considered, if necessary, by calculation.

7.2 MEASUREMENT APPROACH

A secrecy agreement signed with Dow cleared the way for further information exchange and plant access. A protocol was developed which covered the proposed fugitive leak test procedure at Dow and three other synthetic organic chemical plants. This protocol is detailed below. The measurement approach at Dow was to leak test as large a sample as possible of CT- and perc- enriched lines and key component types with a Foxboro Systems Organic Vapor Analyzer (OVA) portable hydrocarbon vapor detector. A mass emission rate based upon knowledge of the leak rate, distribution of line compositions in the applicable sections of the plant, and a plant inventory of possible fugitive emission sources would then be derived. SAI developed OVA response functions for individual substances at various concentrations as well as for selected mixtures. These response functions were used to validate the approach to derive mass emission rates from observed OVA response. The field measurement approach, laboratory calibration and response function procedures, and determination of leak rate are described in Section 7.2.1 and apply to fugitive emission testing at Stauffer, DuPont and Allied as well as Dow.

It was our understanding that although emission from storage and check tanks are currently essentially uncontrolled, plans for future control are under way. Since the tanks are vented to the atmosphere, their emissions due to normal tank breathing was determined by calculation based upon their physical configuration, substance properties and the relationships given by AP-42. Off-loading procedures would be observed and if vented to the atmosphere, their emissions would be initially determined by calculation as follows:

$$L_w = 2.4 \times 10^{-2} M P K_n K_c$$

where: M = molecular weight
P = true vapor pressure at bulk liquid conditions (psia)
 K_n = turnover fraction (expressed as a function of the ratios of annual throughput to tank capacity)
 K_c = crude oil fraction (31 for CT and perc)
 L_w = working loss (lb)/10³ gal

Alternatively the working loss was calculated explicitly for each displacement transfer and combined to determine the annual working loss.

If the working loss was determined to be significant with respect to the normal tank breathing, direct measurement of working loss was planned, if practical, to validate calculational estimates. This would be done by obtaining and analyzing head space samples during off-loading. A sampling tube would be inserted into tank head space and a time integrated sample collected in a large 100L evacuated Tedlar bag. Contents of the Tedlar bag would be transferred to smaller glass bulbs, transported to the SAI laboratory and analyzed directly by gas chromatography. This is useful toward generating as accurate an emissions estimate as possible.

It is believed that the determination of emission factors by direct measurement and/or calculation is the method of choice. Despite the fact that a primary use of these emission factors would be to develop population exposure estimates in the offsite environment, it was concluded that direct ambient concentration determinations would be inappropriate. It was considered more important to unambiguously determine the emission source strength rather than establish, through an elaborate monitoring strategy, that, under a set of particular meteorological conditions, there is or is not a detectable concentration of CT or perc present downwind from the plant. Furthermore at

least two additional issues concerned us: low concentrations as expected off-site would present significantly greater problems to detect and having done so to calculate the emission source. All synthetic organic chemical plants were measured in this manner.

Finally it should be noted that all sites being studied are potential emission sources of substances currently known to be released by other point and area sources. In the case of Dow the clearest example is that of perc releases from dry cleaning operations. Emissions from each site were therefore evaluated within the perspective of other known sources and source types as their relative contribution to background levels.

7.2.1 Fugitive Emission Measurement Approach

Although the processes and even the substances of interest differ among the synthetic organic chemical plants, we were concerned, to some degree, with fugitive emissions from equipment sources including process valves, pump and compressor seals, flanges and relief valves. At some sites other potential emission sources were identified and testing proposed. A standardized approach used to sample fugitive releases is described below. Additional material specific to each plant is provided in corresponding sections. The screening approach is consistent both with previous studies (e.g. Radian Corp, Assessment of Atmospheric Emissions from Petroleum Refining EPA-600/2-80-075; Radian Corp., Frequency of Leak Occurrence for Fittings in Synthetic Organic Chemical Plant Process Units EPA-600/2-81-003) and with proposed standards (e.g. EPA Proposed National Emission Standard for Hazardous Air Pollutants - Benzene Fugitive Emissions 46 FR 1165, Jan. 5, 1981 and EPA Proposed VOC Fugitive Emission Standards for Synthetic Organic Chemicals Manufacturing 46 FR 1136, Jan. 5, 1981). The screening procedure utilizes a portable hydrocarbon detector in a prescribed manner to determine the maximum value of leak concentration at each potential leak site.

In all cases it was expected to be possible to survey nearly 100 percent of all potential equipment sources. Those accessible source types handling at least one weight percent of the substance are of interest. A range of emissions would be determined for each plant based upon the frequency of device leakage found and their magnitudes. Instrument response functions derived in the SAI laboratory would be used to calibrate each substance response to a hexane reference. Nomographs relating hexane (or methane)

response to mass emission would be used to develop a total plant fugitive emission value.

The Foxboro Model OVA-128 (formerly Century Systems) was proposed to determine emissions from plant devices of the following types:

- Process valves
- Pump seals
- Compressor seals
- Relief valves
- Process drains
- Open ended valve lines
- Selected flanges.

The instrument directly analyzes organic vapors in the 1-1000 ppm range and can be extended to 10,000 ppm by means of a dilution system. Additionally the OVA Model-128 optional gas chromatograph and strip chart recorder can be utilized for determining the composition of emissions from multicomponent streams.*

SAI staff met with plant personnel at each site and reviewed the plant processes and equipment components. A proposed test plan was submitted and approved by all parties. As cited above, only those components handling streams composed of greater than 1% content of the substance of interest were proposed to be monitored. Screening procedures to be followed were chosen to correspond to those employed in the Radian survey of thirteen petroleum refineries and twenty four synthetic organic chemical manufacturing plants in order to facilitate the use of nomographs to relate screening value (in ppmv) with total mass emissions.

* It has been our program experience in all sites but one that each plant operator has determined and is aware of, to an acceptable level of precision, the stream composition in nearly all lines of interest. Beyond this and GC characterization we proposed, where necessary, to take compositional samples on Tenax GC at high leakers and confirm composition by analysis at our La Jolla laboratory.

The OVA probe is held as closely as possible to the potential leak source. These locations differ for each device type. In general four points is taken at each source point corresponding to four compass points 90° apart. The probe is rotated around the circumference and if a leak is detected the location of its maximum screening value is taken as a reference for establishing the origin of the four compass points. Specific screening points are:

- valves (gate, globe, control)-stem and the packing gland
- valves (plug) - plug square and under the malleable gland
- flanges (note it is expected that only a fraction of flanges would be sampled from amongst those accessible) - the probe is rotated around the flange perimeter and four points chosen as indicated above
- pump and compressor seals - for single seal types the potential leak source is around the rotating shaft where it enters the pump (compressor) housing; for two seal types - inboard and outboard-each seal will be screened separately. If the seal area is enclosed and vented, the screening location is at a point just inside the end of the vent
- pressure-relief devices (vented to the atmosphere) screening points around the perimeter of the vent and at the center of the vent (as accessible)

Where highly variable leak rates are encountered, sufficient sampling time is allowed to obtain a representative average. Additionally where elevated ambient readings are suspected of contributing to the leak screening reading, average values of ambient hydrocarbon concentrations are determined by using the OVA at points in the proximity but removed from the influence of the source.

Based upon the Radian survey, screening values greater than 200 ppmv, calibrated to hexane,^{*} were defined as leaks and data recorded. However for carbon tetrachloride lines a screening leak threshold of 20 ppmv was defined. It was subsequently determined that leaks with screening values greater than 2000 ppmv contributed greater than 95% to the plant mass emission

* Note that the OVA instrument develops essentially the same response due to hexane and methane. Figure 7.2-1 provided by B. Tichenor of EPA from Radian Corp. documentation illustrates the relationship between the two gases is nearly linear and of unity slope.

Calibrated to Hexane @ 100ppm (Gas Select 393)

Gas Standard	9.5ppm	102ppm	983ppm
OVA 128 Reading	<u>9.2ppm</u>	<u>104ppm</u>	<u>1014ppm</u>
% Difference	3%	2%	3%

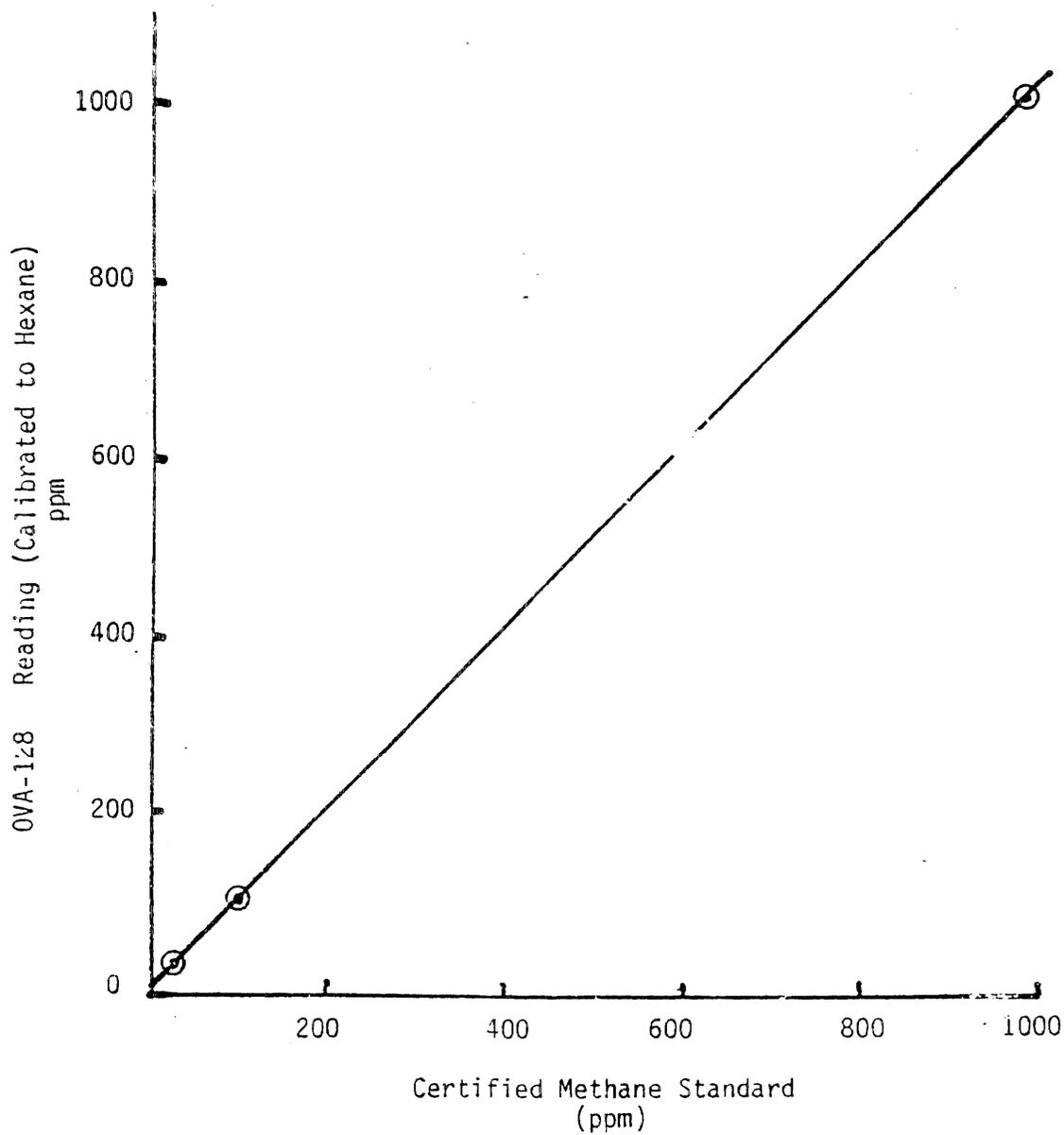


Figure 7.2-1

METHANE VERSUS HEXANE RESPONSE ON THE FOXBORO OVA 128

rate. Mass emissions calculated on both a per unit time basis and as an absolute quantity will be determined. These releases will be further broken out for each device type.

7.2.2 Analysis Approach

In order to determine the hexane response equivalent the OVA 128 was tested in the SAI Trace Environmental Chemistry Laboratory for its response relative to hexane for a number of volatile compounds targeted for measurement. Table 7.2-1 lists the basic data showing the concentration ranges measured, the standard deviations, and the response factors. Table 7.2-2 lists the regression statistics for the meter responses versus concentration. Concentration of each test substance were made by injecting a quantity of the compound into a clean 20 liter glass carboy. The mixture was shaken for 3-5 minutes. The response factor is defined as the ratio of the meter response to the actual concentration with the meter calibrated to read 100 with 100 ppm hexane. The data were taken to gain an appreciation of the absolute variation of response functions among substances and as a function of concentration of each substance in order to assist in field test planning.

Based on the data in Table 7.2-1 a number of multicomponent mixtures were made to determine how well the meter response could be predicted. The component mixtures and the predicted and actual meter responses are shown in Table 7.2-3. As the data indicates, the predicted values are approximately 10% higher than the actual meter responses assuming linear superposition. This is an acceptable error for the program application since the uncertainty, as expressed as 90% confidence interval, is typically greater than 10% and will likely be a greater source of uncertainty.

Figure 7.2-2 is a typical nomograph drawn from the Radian study of fugitive emissions from petroleum refining (Wetherold, 1980). We used such nomographs, after adjustment specific to each device category, as a key step in determining fugitive emission factors. In the EPA petroleum refining data base on the order of 6,000 devices were screened and approximately 700 were bagged to determine mass emission rates. Over 40,000 devices were screened in the EPA sponsored SOGMI surveys. Correlation coefficients between screened and leak rate measured parts were computed for each source type and ranged between 0.68 and 0.77. We recognize that the correlation between screening values and

TABLE 7.2-1
 OVA-128 METER RESPONSE AND G.C. RETENTION TIME - BASED ON METER RESPONSE OF 100 CALIBRATED
 WITH 100ppm HEXANE

Compound	Conc.	Meter Resp.	#Detn.	σ	% σ	Avg. GC Ret. Times T(°C)	RT	Response relative to a Calibration of 100 ppm Hexane
Hexane	10ppm	8.1	1			17°C	2.41min	0.81
	50	48	1			18	2.36	0.99
	100	100.7	8	2.0	2	20	2.10	1.0
	200	190	1			21	2.08	0.95
	300	420	1			22	1.92	1.40
	500	631	3	45	7	23	1.84	1.26
	700	850	1					1.21
	1000	1463	1					1.46
Benzene	10	30.5	2	3.5	11	19	3.35	3.05
	100	231	4	19	8	20	3.24	2.3
	300	822	1			21	3.23	2.74
	400	1040	1			22	2.85	2.60
	500	1145	1			23	2.79	2.29
CCl ₄	100	8.7	4	0.8	9	18	3.67	0.087
	1000	93	3	4.6	5	22	2.95	0.093
	10000	850	1			23	2.90	0.085
CHCl ₃	10	8.9	1			22	1.85	0.89
	100	77	3	0	0	23	1.85	0.77
	500	360	1					0.72
	1000	720	1					0.72
1,2-dichloroethane	10	13	1			21	2.56	1.3
	100	106	3	5.1	5	22	2.29	1.06
	500	572	2	3.5	<1	23	2.28	1.14
Styrene	10	12.2	1					1.2
	100	121	3	14	12			1.2
	500	845	2	35	4			1.69

Table 7.2-1 (Continued)

OVA-128 METER RESPONSE AND G.C. RETENTION TIME - BASED ON METER RESPONSE OF 100 CALIBRATED WITH 100ppm HEXANE (CONTINUED).

<u>Compound</u>	<u>Conc.</u>	<u>Meter Resp.</u>	<u>#Detn.</u>	<u>σ</u>	<u>%σ</u>	<u>Avg. GC Ret. Times T($^{\circ}$C)</u>	<u>RT</u>	<u>Response relative to a Calibration of 100 ppr Hexane</u>
Tetrachloroethylene	10	8.9	1					0.9
	100	101	2	2.8	3			0.9
	500	475	2	21.2	5			0.95
Methane	100	135	1			20	<15sec	1.35

TABLE 7.2-2
 OVA-128 LINEAR REGRESSION BASED ON CALIBRATION WITH 100ppm HEXANE

<u>Compound</u>	<u>Points Discarded</u>	<u>Slope (meter/ppm)</u>	<u>Y-Intercept (meter)</u>	<u>Corr. Coeff.</u>
Hexane	None	1.42	-51	0.9935
Hexane	300ppm, 500, 700, 1000	0.957	+0.53	0.9992
Benzene	None	2.41	+22	0.991
CCl ₄	None	0.0846	+4.1	1.0000
CHCl ₃	None	0.716	3.1	1.0000
1,2-Dichloroethane	None	1.15	-3.12	0.9998
Styrene	None	1.73	-26.3	0.9986
Tetrachloroethylene	None	0.946	2.5	0.9999

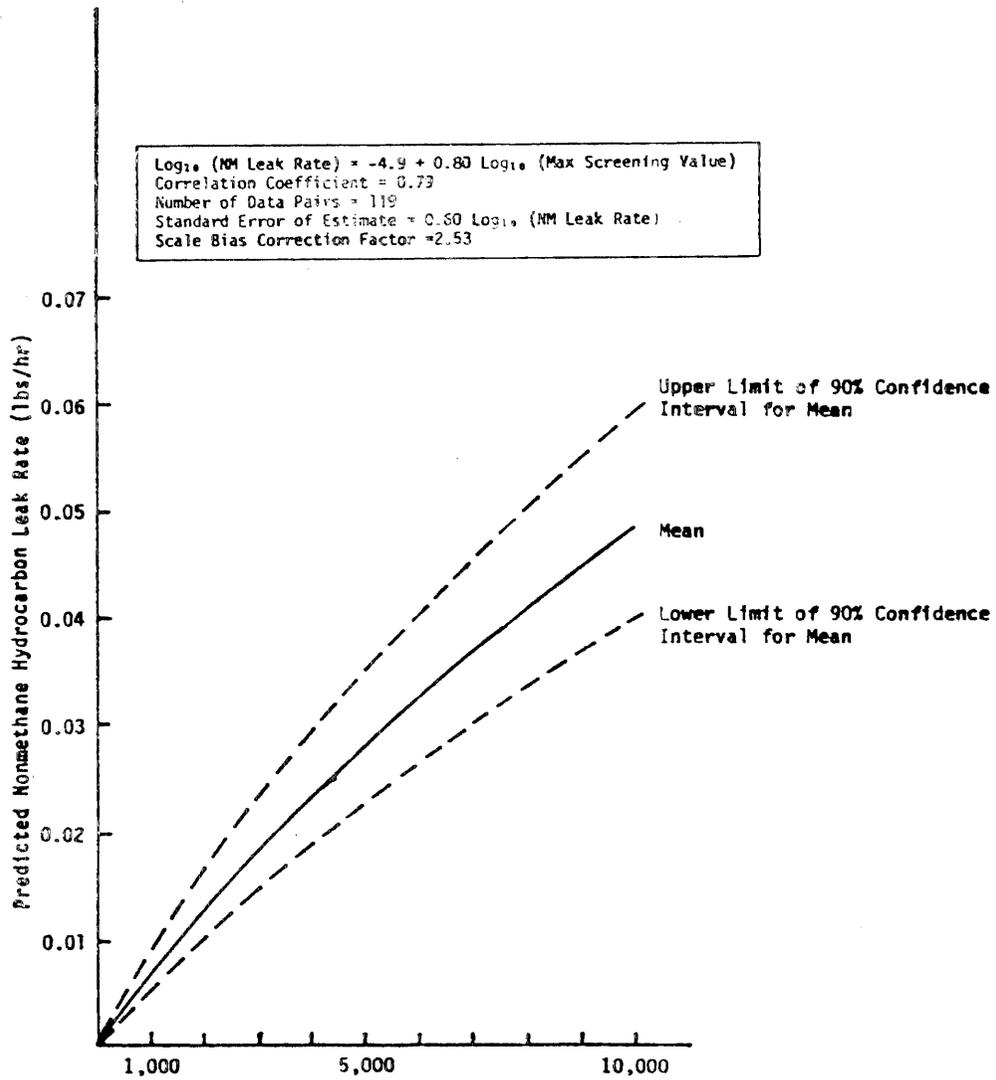
TABLE 7.2-3
COMPONENT MIXTURES

<u>Compound</u>	<u>Concentration (ppm)</u>	<u>Response Factors</u>	<u>Expected Meter Response</u>
Hexane	48	1.0	48
Benzene	70	2.7	190
EDC	78	11	86
CHCl ₃	78	0.77	60
PERC	61	0.99	60
	335 ppm v/v		444
			actual = 495,475
Benzene	250	2.7	685
Hexane	100	1.0	100
			785
			actual = 755,760
PERC	200	0.95	190
CCl ₄	1000	0.093	93
Hexane	100	1.0	100
			383
			actual = 350

*calibrated to 100ppm hexane

Figure 7.2-2

NOMOGRAPH FOR PREDICTING TOTAL NONMETHANE HYDROCARBON LEAK RATES FROM MAXIMUM SCREENING VALUES - VALVES, LIGHT LIQUID/TWO-PHASE STREAMS



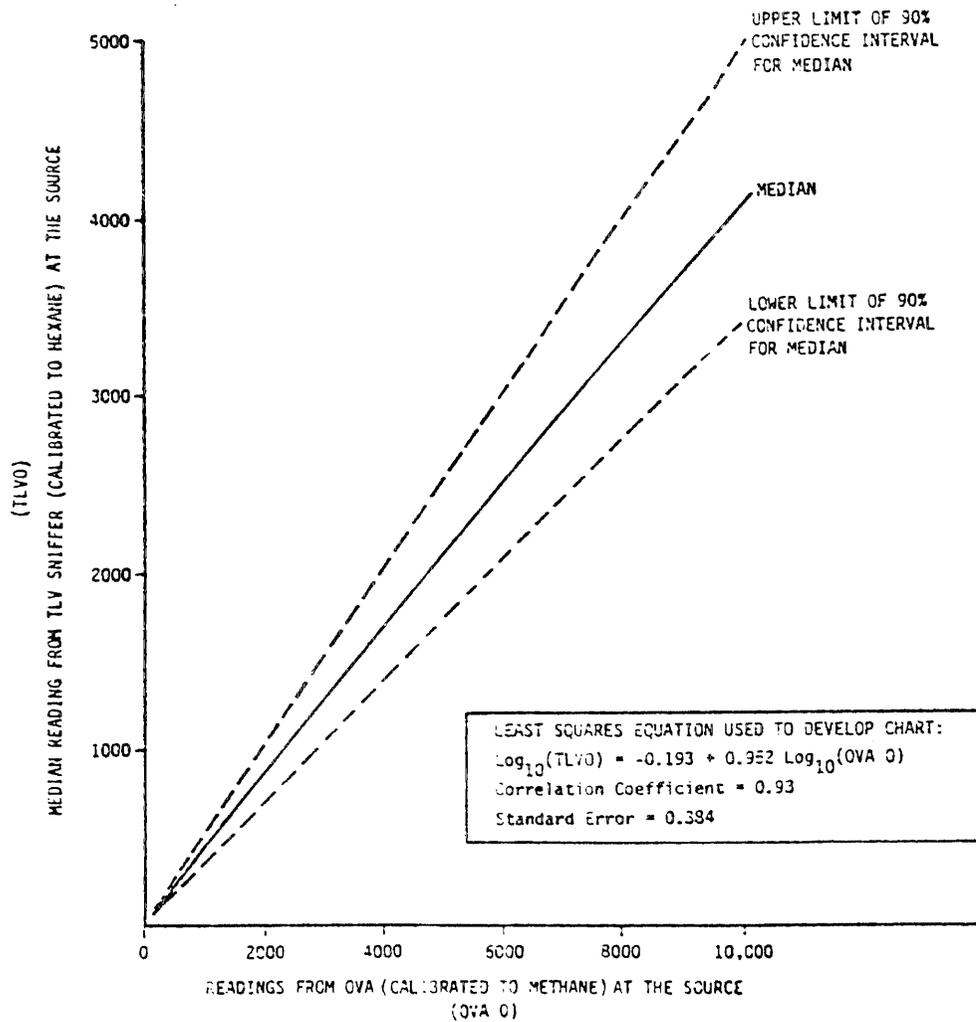
actual leak rates is imperfect. However, it was determined in the Radian studies that prediction of leak rates based upon directly measured data on individual devices would be inappropriate. Clearly at any time an individual device may or may not be found to leak and exhibit a particular relationship between its leak rate and screening value. It is necessary, therefore, to place the sampling emphasis on obtaining screening values for the greatest percentage of process devices and utilize statistically derived mean emission factors and confidence limits. Note that data published by Radian, of the type shown in Figure 7.2-2 corresponds to the Bacharach TLV device. Figure 7.2-3 is included to illustrate the Radian derived correlation between the OVA and TLV devices.

Data to be collected for each device will be:

- source identification number
- source type
- screening value (and liquid droplet leak rate, if applicable)
- type of service (gas, light liquid, heavy liquid)
- composition of the line
- physical properties of the line and the ambient environment.

Properties cited in the final data category will be collected but no attempt will be made at this time to examine interrelationships.

Two procedures were used to obtain a range of mass emissions rates from OVA screening values. For a stream with pure (100%) substance content the relationships derived from SAI's Table 7.2-1 were used to obtain the "true" concentration from the observed OVA response. This "true" concentration was inserted into the Radian derived substance specific relationships to obtain a Bacharach TLV response (Brown, 1980). Using device type nomographs such as Figure 7.2-2 the leak rate is derived. Note that Figure 7.2-2 is not substance specific but rather only device dependent. The nomographs were derived by averaging all the various substances tested in the Radian program. Therefore, for a substance such as carbon tetrachloride to which the OVA is very insensitive the nomograph will significantly underpredict mass emissions. The nomographs were then adjusted by the substance's Bacharach TLV response function to account for this possible underestimate. Comparison of results



02-4245-1

Figure 7.2-3 Nomograph for Relating OVA Readings and TLV Sniffer Readings at the Source - Part I

from these two calculations i.e. device specific-compound averaged and device specific compound-specific, allows the estimation of the range in predicted mass emission rates.

Quality Control

Several quality control procedures were utilized in this program. These include the following:

- equipment calibration
- independent instrument replication
- repeat measurements
- spot confirmation of composition

Specifically the OVA was calibrated immediately prior to and after each set of measurements were made. Arrangements were made in most cases to utilize a second OVA unit for replication of measurements. All screening values above 200 ppmv (hexane equivalent) or less were termed significant for the immediate purposes of the study and were repeated by both instruments. The screening values for each substance and expected known mixtures which define a significant leak (based on laboratory derived response functions) were determined prior to sampling. The instrument was calibrated in the field using hexane both prior to and after sampling and with and without the dilution probe.

7.3 DOW CHEMICAL U.S.A. - DETERMINATION OF EMISSIONS

Approximately 1100 devices were surveyed for fugitive leaks at the facility. This constituted nearly all accessible and active streams containing greater than 1% perc or CT. In order to be certain not to miss any potentially important mass emissions all OVA screening values greater than 100 and 20 ppm were recorded for perc and CT lines respectively. Background values were found to be less than 3 ppm in all areas of the plant surveyed and therefore did not interfere with screening.

All accessible components were surveyed with the exception of flanges of which on the order of 75% were screened. There were relatively few inaccessible components of interest and no attempt was made to account for their potential mass emissions. It was not possible to directly measure

emissions from the product check tanks since maintenance was underway and the area was unavailable for testing. Since these tanks are utilized to store product and are directly vented to the atmosphere with each filled and off-loaded approximately 120 times per year, it was appropriate to calculate working emissions from the tanks since they would be expected to contribute significantly to total tank emissions. Two additional product storage tanks were expected to contribute to emissions by normal tank breathing. Their emissions were determined by calculation.

Thirty one (31) devices were found to leak with screening valves greater than the cutoff thresholds. Twenty eight (28) were valves, one an outer seal on a gas compressor, one a pump seal and the final, a flange. Dow staff independantly performed screening readings of all leaking devices with their own OVA. In addition all readings were repeated by SAI and, as often occurred, values fluctuated with time and maxima were averaged. In all cases Dow staff were able to identify the approximate stream composition, physical state and parameters of temperature and pressure. Table 7.3-1 presents the OVA screening value data and the parameters utilized to determine the range of mass emissions rates for the most significant leakers among the 28 devices. The SAI response factors were derived from data presented in Table 7.2-1. Radian constants relating actual concentration to observed Bacharach TLV response are from Brown, 1980, and take the form

$$IR_C = \exp (a + b \ln C + Se^2/2)$$

where IR_C is the TLV response and C the actual concentration. Device source functions of Table 7.3-1 are given by the codes -

- A. Pump Seals (Light Liquid/Two-Phase Streams) Compressors and Relief Valves
(Gas/Vapor Streams)
 $\log_{10} (\text{leak rate}) = -4.4 + 0.83 \log_{10} (IR_C)$
- B. Valves + Compressor Seals, Hydrogen Streams
 $\log_{10} (\text{leak rate}) = -7.0 + 1.06 \log_{10} (IR_C)$
- C. Valves, Gas/Vapor Streams
 $\log_{10} (\text{leak rate}) = -7.0 + 1.23 \log_{10} (IR_C)$
- D. Valves, Light Liquids/Two Phase
 $\log_{10} (\text{leak rate}) = -4.9 + 0.80 \log_{10} (IR_C)$

Table 7.3-1
 DOW CHEMICAL U.S.A.
 MASS EMISSION PREDICTION FROM OVA SCREENING VALUES

Compound	OVA Response*	SAI Response Factor	Actual Conc.*	a	b	Se	IRc*	Source Function	Leak Rate lb/yr	Upper Bound Leak Rate lb/yr
PERC	10,000	0.95	10,526	0.32	0.69	0.47	904	D	23.3	161
	3,500		3,684				439		13.1	74
	7,000		7,368				707		19.2	119
	4,000		4,210				401		14.1	78
	4,000		4,210				401	A	53.6	304
CT	900	.085	10,588	4.66	0.093	0.739	329	D	10.4	168
CT	700	.085	8,235	"	"	"	322	D	10.2	133
60% CT	5,000		6,961(CT)	"	"	"	317	D	10.1	116
40% PERC			4,640(PERC)	0.32	0.69	0.47	514	D	14.9	86

* ppm

E. Drains

$$\text{Log}_{10} (\text{leak rate}) = -4.9 + 1.10 \text{Log}_{10} (IR_c)$$

F. Flanges

$$\text{Log}_{10} (\text{leak rate}) = -5.2 + 0.88 \text{Log}_{10} (IR_c)$$

G. Pump Seals, Heavy Liquid Streams

$$\text{Log}_{10} (\text{leak rate}) = -5.1 + 1.04 \text{Log}_{10} (IR_c)$$

Finally the upper bound leak rate was determined by utilizing the true concentration rather than the Bacharach TLV response in the relationship between screening value and leak rate e.g. in A above $\text{Log}_{10} (\text{leak rate}) = -4.4 + 0.83 \text{Log}_{10} (C)$. This was done because relationships such as Figure 7.2-2 are based upon screening data on a range of substances which may significantly underpredict the leak rate, for a substance less responsive to detection by OVA or TLV than methane or hexane.

Incorporating the remaining 20 leaking devices yields approximately an equal contribution to the mass emission rate found for the 8 heaviest leakers. Thus, for the entire plant the emissions are estimated to range between 338 and 2478 lb/yr or between 0.033 and 0.242 lb/day/leaking valve. Approximately 2% of all valves inspected were found to leak above the detection threshold. Thus, factoring in the nonleakers one has between 9.3×10^{-4} to 6.8×10^{-3} lb/day/plant valve of CT or perc emissions. By way of comparison in 1978 the Dow plant was among several sampled by the CARB to determine plant fugitive emissions. Almost 2400 valves and flanges were surveyed and four (4) valves among 1080 were found to leak with a combined averaged (assumed) mass emission rate of 3942 lb/year. Leaks were found in the butadiene storage and service areas (not considered in the present study) and not in the CT or perc areas.

Calculation of Working Emissions from Dow Check Tanks

Four check tanks are on-site with two each for CT and PERC. Ordinarily three days are required to fill one tank while the second is being off-loaded. Dimensions of each tank are 12 ft diameter and 21 ft height for a volume of 2375 ft³. Filled is typically 70% volume or 1662 ft³. Assuming an average temperature of 20°C the vapor pressures of CT and perc are approximately 92 and 20 mm respectively. therefore head space vapor composition at equilibrium is $92/760 = 12\%$ for CT and $20/760 = 2.6\%$ for perc. During one

complete fill cycle the volumes of CT and perc emitted are $0.12 \times 1662 = 200$ and $0.026 \times 1662 = 43 \text{ ft}^3$ respectively. The vapor density of CT and perc at 20°C are

$$\rho_{\text{CT}} = \frac{PM}{RT} = (1)(154)/(.082)(293) = 6.4 \text{ g/L} = 0.4 \text{ lb/ft}^3$$

$$\rho_{\text{perc}} = (1)(165.8)/(.082)(293) = 6.9 \text{ g/L} = 0.43 \text{ lb/ft}^3$$

Therefore the displacement weight of CT per tank fill for CT is $200 \text{ ft}^3 \times 0.4 \text{ lb/ft}^3 = 80 \text{ lb}$ and for perc = $43 \text{ ft}^3 \times 0.43 \text{ lb/ft}^3 = 18.5 \text{ lb}$. Since the number of fills per year are approximately 120^+ the total emissions become

$$\text{CT: } 80 \times 120 = 9600 \text{ lb}$$

$$\text{perc: } 18.5 \times 120 = 2220 \text{ lb}$$

Alternatively using the working loss emissions relationship of Section 7.2 for CT one has for each of the two check tanks:

$$L_w = 2.4 \times 10^{-2} M P K_n K_c$$

$$= (2.4 \times 10^{-2})(154) (92/760) \times 14.7 (0.6) (1) = 3.946 \text{ lb/} 10^3 \text{ gal}$$

Where the turnover fraction K_n is taken as 0.6 corresponding to 60 throughputs per year by AP-42.

Since each fill volume is $1662 \text{ ft}^3 = 12.4 \times 10^3 \text{ gal}$ and there are 60 fills per year, then the annual emission for each CT tank is 2936 or 5872 lb. total for both tanks. For perc

$$L_w = (2.4 \times 10^{-2})(165.8) (20/760) \times 14.7 (0.6) (1) = 0.923 \text{ lb/} 10^3 \text{ gal}$$

This corresponds to 1374 lb/year from both per tanks.

Normal tank breathing emissions were computed using the AP-42 emission formula for fixed roof tanks (as described in Section 9.1). The two check tanks for each substance are used in a coordinated fashion, i.e., one being filled while the other emptied. Therefore, the normal breathing emissions for both tank were equivalently modeled as a complete year's emission from one tank assumed

⁺ Tank emission calculations are based upon the displacement volume and number of fills cited by Dow (Anderson) during plant visits. It is recognized that year to year changes occur.

half full. Then L_B , the breathing loss in pounds per day for CT becomes:

$$\begin{aligned}
 L_B &= 6.19 \times 10^{-5} M \left(P / (14.7 - P) \right)^{0.68} D^{1.73} H^{0.51} T^{0.5} F_p C K_C \\
 &= (6.19 \times 10^{-5}) (154) \left(1.78 / (14.7 - 1.78) \right)^{0.68} (12)^{1.73} (10)^{0.51} (26)^{0.5} (1)(0.6) \\
 &= 1.78 \text{ lb/day} = 652 \text{ lb/year}
 \end{aligned}$$

For perc $P = .386$ $M = 165.8$ and $L_B = 231$ lb/year. The diurnal temperature variation, T , was obtained from Dow site average annual meteorological data (Anderson, Personal Communication) and the small tank adjustment factor from an AP-42 (EPA, 1981) plot.

The check tank emissions are not based upon actual measured values of head space product concentrations. Measurements taken at DuPont for CT showed that saturation vapor pressure concentration values were not attained in the relatively quick fill (5 hours) monitored. However in the absence of direct measurements and the longer fill time the saturation vapor pressure derived quantities are appropriate for use in determining the upper bound of plant emission factors. The AP-42 derived numbers will be used to determine the lower bound.

Calculation of Emissions from Dow Storage Tanks

In addition to the check tanks there is a large permitted CT storage tank and evidently also a perc storage tank (W. Anderson, Personal Communication). Tank dimension for CT are $D = 48$ ft and $H = 50$ ft while for perc $D = 42$ ft and $H = 30$ ft. Utilizing the AP-42 (EPA, 1981) emission formula for fixed roof tank breathing (see Section 9.1 for definition of terms) one has in lb/day:

$$L_B = 6.19 \times 10^{-5} M \left(P / (14.7 - P) \right)^{0.68} D^{1.73} H^{0.51} T^{0.5} F_p C K_C$$

For CT, taking the vapor pressure at 20°C , the average diurnal temperature variation as 26°F , and the average vapor space height based upon a 50% liquid fill, one has

$$\begin{aligned}
 L_B &= (6.19 \times 10^{-5}) (154) \left(1.78 / (14.7 - 1.78) \right)^{0.68} (48)^{1.73} (25)^{0.51} (26)^{0.5} \\
 &= 52.8 \text{ lb/day} = 19,285 \text{ lb/year}
 \end{aligned}$$

For perc

$$\begin{aligned}
 L_B &= (6.19 \times 10^{-5}) (165.8) \left(.386 / (14.7 - .386) \right)^{0.68} (42)^{1.73} (15)^{0.51} (26)^{0.5} \\
 L_B &= 11.5 \text{ lb/day} = 4,186 \text{ lb/year}
 \end{aligned}$$

The working emissions are calculated using AP-42's fixed roof working loss equations and the same parameter values and throughput assumed for the check tanks. Then for CT

$$L_w = 2.4 \times 10^{-2} MP K_n K_t$$

$$= (2.4 \times 10^{-2})(154)((92/760) \times 14.7)(1.0)(1) = 6.58 \text{ lb}/10^3 \text{ gal}$$

where the turnover fraction $K_n \approx 1$. Since the total assumed throughput is $12.4 \times 10^3 \text{ gal} \times 120$ (check tank fills), the total emission are 9802 lb. Similarly for perc total emissions become 2293 lb.

Summary of Dow Emission Source Strength

Emission from the plant sources surveyed are tested below. All quantities are in lb/year.

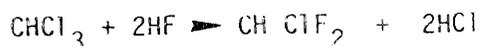
	<u>perc</u>	CT
1. Fugitives	225 lower estimate 1600 upper estimate	113 lower estimate 800 upper estimate
2. Check Tanks- working Emissions	1374 lower estimate 2220 upper estimate	5872 lower estimate 9600 upper estimate
3. Check Tanks- Breathing Emission	231	652
4. Storage Tanks - Breathing	4,186	19,285
Working	2,293	9,802
	8,309 lower estimate 10,530 upper estimate	35,724 lower estimate 51,883 upper estimate
<hr/>		
Total CT and perc	44,033 lower estimate	62,413 upper estimate

8.0

SOURCE TESTS - ALLIED CHEMICAL

8.1 SITE OVERVIEW

Allied Chemical, El Segundo, has a fluorocarbon synthesis plant. It either uses carbon tetrachloride or chloroform as feed and produces Genetron 11, 12, or 22. The plant was projected to be operating with chloroform during the measurement period and producing G-22 according to:



Chloroform is offloaded from tank cars to a storage tank for feed to the reactor. Chloroform enriched streams (>0.5%) occur prior to the reactor and just beyond. Based upon venting and process configuration it is concluded that fugitive emissions from valves, flanges and pump seals constitute the potential emission sources. The number of components of interest is less than 100 and therefore 100% can be leak tested. When the plant feed is switched to carbon tetrachloride a storage tank vented to the atmosphere is incorporated into the process and emissions must be accounted for.

Basic Process Equipment

The plant produces fluorocarbons from either carbon tetrachloride or chloroform feedstock. Emissions of carbon tetrachloride will be estimated indirectly in this study since the site was operating on chloroform feed throughout the testing period.

Chloroform is offloaded from tank cars and stored in closed unvented tanks. As the storage tank is filled the air space displaced is fed back to the tank car. The storage tank is not vented in its breathing mode and is part of a closed feed system to the reactor. Material is fed to a reactor and reacted with hydrogen fluoride in the presence of an antimony pentachloride catalyst. Unreacted product is recycled in a closed system. Process steps beyond the reactor and recycled loop do not contain appreciable concentrations of chloroform nor do reconcentration mechanisms or controls exist.

It is expected that fugitive emissions from the valves, flanges and pump seals will constitute the bulk of chloroform emissions. Less than 100 components are involved.

Emission sources associated with carbon tetrachloride feed include the storage tank since it is equipped with a breather and vented to the atmosphere. Offloading as well as breathing modes of operation would be emission processes.

8.2 MEASUREMENT PROGRAM

The basic approach toward the measurement of fugitive emissions is by use of the Foxboro OVA Model 128 portable hydrocarbon analyzer as was described in Section 7.2.

Plant management was cooperative and advised us 72 hours prior to beginning chloroform off-loading activity. Measurements were conducted of fugitive emissions from components involved in off-loading and reactor feed/recycle. It was possible to sample 100% of the pump seals, valves and flanges associated with components handling chloroform. Based upon our laboratory characterization of chloroform response we identified an instrument reading of 100 ppmv as a threshold concentration which was recorded to determine the mass emission rate. Above this threshold concentration all survey readings were recorded and line compositions determined. Based upon our laboratory derived response factors, stream composition and the Radian nomographs, resulting leak rates were determined.

Comparisons were made with Allied Chemical Company data taken by the CARB in a previous study of fugitive emission from the plant. These data will provide a useful data base with which to examine the historical rate of device leakage found.

Carbon tetrachloride emissions cannot be measured directly because plant operations were switched to chloroform feed. However, based upon the rate of device leakage found and the frequency of operation with CT feed, a fugitive emissions factor will be derived.

Emissions of CT associated with the storage tank vented breather will be determined based upon the emission factor relationships specific in AP-42*. We will consider both modes of emission from storage tanks: (a) loss due to tank breathing and (b) working loss due to tank filling. According to AP-42, the relationship between working loss and vapor pressure is given by:

* AP-42-ED-3-PT-B Compilation of Air Pollution Emission Factors - Environmental Protection Agency, Research Triangle Park, NC.

Where: $L = 2.4 \times 10^{-2} M P K_n K_c$
 M^W = molecular weight
 P = true vapor pressure at bulk liquid conditions (psia)
 K_n = turnover fraction $\left| \frac{\text{annual throughput}}{\text{tank capacity}} \right|$
 K_c = crude oil fraction
 L_w = working loss (lb/10³ gal)

For normal tank breathing the AP-42 emission formula is:

$$L_B = 6.19 \times 10^{-5} M \left(\frac{P}{14.7-P} \right)^{0.68} D^{1.73} H^{0.51} T^{0.5} F_p C K_c$$

Where: L_B = breathing loss lb/day
 M = molecular weight
 P = true vapor pressure at bulk liquid condition (psia)
 D = tank diameter (ft)
 H = average vapor space height (ft)
 T = average ambient temperature change, diurnal (°F)
 F_p = paint factor
 C = small tank adjustment factor
 K_c = crude oil factor

The formula is estimated to be within $\pm 10\%$ of actual measured values.

8.3 DETERMINATION OF EMISSIONS

8.3.1 Fugitive Releases

Ninety (90) devices were surveyed with the OVA. This constituted 100% of the chloroform service. Six leaks above 100 ppm were detected. Background response was less than 3 ppm and therefore did not interfere with leak detection measurements. Table 8.3-1 summarizes the fugitive emissions testing. Chloroform has a response factor of about 0.25 i.e. IR_c divided by the actual concentration and the upper bound on mass emission worked out to between 2 and 13 times the Radian derived baseline estimate. Leaks in two (2) valves, two (2) couplings and two (2) flanges were found. One liquid leak dominated the mass emission. It was important that the off-loading procedure was functioning since four leaks were associated with this operation. If the plant was assumed to operate the entire year on chloroform feedstock, Allied estimates 412 hours of off-loading activity. Therefore the first four leaks are scaled to 412 hours/year and the final two are at 8760/year.

Table 8.3-1

ALLIED CHEMICAL MASS EMISSION PREDICTION FROM OVA SCREENING VALVES

Device/ Location	OVA Response (ppm)	SAI Response Factor	Actual Conc. (ppm)	a	b	Se	IRc	Source Function	Leak Rate lb/yr	Upper Bound Leak Rate lb/yr
Off-loading coupling	700	0.72	972.	1.13	0.64	0.27	258.	D	0.4*	1.3*
Off-loading coupling	200	0.75	267.				113.	D	0.2*	0.4*
Flange-off- loading	100	0.77	130.				72.	F	0.1*	0.2*
End Fitting- Valve Drain Hose	liquid leak 2.1 m ³ /min	---	---	---	---	---	---	---	155. *	155. *
Relief Valve Plug-Storage Tank Area	2000	0.72	2778.	1.13	0.64	0.27	504.	D	14.6	63
Flange-Heat Exchanger at Reactor	1000	0.72	1389.	"	"	"	323.	F	8.2	105

All emissions 100% chloroform

* Based upon an estimated yearly off-loading time of 412 hours

Valve leakage rate was approximately 7% (2/28), while for flanges it was nearly 4% (2/52). The couplings were of the quick disconnect type and 40% (2/5) of those tested were found to be leaking. Excluding the liquid leak the remaining five devices were determined to emit between 23 and 170 lb/year of chloroform. Note that the liquid leak was repaired during the test day and should have been easily spotted as part of a routine inspection procedure.

Total fugitive leaks range between 178 lb and 325 lb with the liquid leak included.

8.3.2 Storage Tank Emissions

Calculations rather than a direct experimental determination were made because the plant was currently operating on chloroform feedstock. It is known that the chloroform off-loading and storage system is fully closed and recycled back through the railcar. The carbon tetrachloride tank is vented to the atmosphere. Allied is permitted to operate the tank at a maximum temperature of 61.9⁰F. The displacement volume of carbon tetrachloride is 13,000 gal. For the purposes of bounding the calculation it will be assumed that between 4 and 9 million pounds per year of CT are consumed.

The vapor pressure of 76 mm H_g at 60⁰F is applied. The saturation vapor pressure at equilibrium is 72/760 = 9.5% by volume or approximately 1.4 psi.

Displacement volume during fill is:

$$13,000 \text{ gal} = 1738 \text{ ft}^3$$

The volume of CT emitted is;

$$0.095 \times 1738 = 165 \text{ ft}^3$$

The density of CT vapor is given by,

$$\rho_{CT} = (1) (154) / (0.082) (793) = 6.4 \text{ g/L} = 0.41 \text{ lb/ft}^3$$

Therefore, the displacement weight of CT per off-load is equal to $165 \text{ ft}^3 \times 0.4 \text{ lb/ft}^3 = 65.9 \text{ lb}$

Maximum number of loads per year is

$$\frac{9 \times 10^6 \text{ lb/yr}}{1.72 \times 10^5 \text{ lb/load}} = 52 \text{ loads/year}$$

$$1.72 \times 10^5 \text{ lb/load}$$

where the product of the displacement volume (1738 ft^3) and the specific gravity (99.3 lb/ft^3) is $1.72 \times 10^5 \text{ lb/load}$.

Therefore the maximum quantity of emissions per year are:

$$65.9 \text{ lb/load} \times 52 \text{ loads/yr} = 3427 \text{ lb.}$$

Assuming 4 million pounds feed this becomes 1523 lb.

Alternatively AP-42 (EPA, 1981) can be utilized to calculate working emissions. For 9×10^6 pounds feed and 52 turnovers per year one has

$$L_w = \text{lb}/10^3 \text{ gal} = 2.4 \times 10^{-2} M P K_n K_c$$

$$= 2.4 \times 10^{-2} (154) 72/760 \times 14.7 (0.7)(1)$$

$$= 3.83 \text{ lb}/10^3 \text{ gal.}$$

For 9×10^6 lb of carbon tetrachloride one has 678×10^3 gal. Therefore, total working emissions become 2596 lb/year. For 4×10^6 pound feed the turnover factor K_n for 23 loads per year is nearly 1.0 and $L_w = 5.47 \text{ lb}/10^3 \text{ gal}$. Therefore, annual total working emissions become 1648 lb.

For the normal tank breathing emissions utilizing the AP-42 formula given in Section 8.2 and approximate tank dimensions of 24 feet diameter, an average vapor level of 5 feet, CT vapor pressure at 20°C and a diurnal

temperature variation of 26⁰F, one has:

$$\begin{aligned}
 L_B &= (6.19 \times 10^{-5}) M (P/(14.7-P))^{0.68} D^{1.73} H^{0.51} T^{0.5} F_P^{0.51} C K_C \\
 &= (6.19 \times 10^{-5})(154) (1.4/(14.7-1.4))^{0.68} (24)^{1.73} (5)^{0.51} (1)(1)(1) \\
 &= 5.81 \text{ lb/day} \\
 &= 2123 \text{ lb/year}
 \end{aligned}$$

Summary

Therefore total emission for chloroform feed are fugitive and range between 23.5 (no liquid leak assumed) lb. and 325 lb. For year long operation on carbon tetrachloride, total emissions are fugitive plus storage tank releases and range between 3669 lb/yr (no liquid leak; 4 million pounds CT consumption; and computation of tank working emissions by saturation vapor displacement) and 5875 lb/yr (liquid leak; 9 million pounds CT consumption level; computation of tank working emissions by assuming saturation vapor displacement). If it is assumed that plant activity is divided into 50% chloroform and 50% carbon tetrachloride operation, then predicted emissions are between 1847 and 3099 pounds.