STANFORD RESEARCH INSTITUTE

AN INDUSTRIAL HYGIENE STUDY OF ETHYLENE DIBROMIDE AT DU PONT

Plant Location:
Deepwater, New Jersey

Survey Dates:
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ABSTRACT

The E. I. du Pont de Nemours and Company Chambers Works plant in Deepwater, N.J. which is a producer of antiknock products containing ethylene dibromide, was surveyed on 6, 7, and 8 July 1977 as a part of an industrywide study of worker exposure to ethylene dibromide. For purposes of these studies E. I. du Pont is considered a user of EDB and is not involved in the manufacture of EDB. The 8-hour TWA concentrations of ethylene dibromide were determined by sampling in the breathing zone of workers in job classifications associated with the processing of ethylene dibromide. The median values were: Blend Operator, 0.006 ppm (6 samples, range 0.001-0.009 ppm); Reactor Operator, 0.002 ppm (2 samples, range 0.001-0.003 ppm); Compound Bulk Operator, 0.004 ppm (2 samples, range 0.001-0.008 ppm); Laboratory Technician, 0.0004 ppm (4 samples, range 0.0001-0.0005 ppm); Drum Loader, 0.014 ppm (4 samples, range 0.008-0.018 ppm); Raw Material Handler, 0.054 ppm (2 samples, range 0.027-0.082 ppm); Relief Operator, 0.004 ppm (2 samples, range 0.0005-0.007 ppm); and Drum Processing, 0.026 ppm (4 samples, range 0.012-0.036 ppm).

Worker exposure to EDB was found to be within the limits of the current federal standard of 20 ppm as an 8-hour TWA concentration. The performance of specific tasks including the taking of quality control samples of EDB from tank cars, the manual dipping of storage tanks to determine the level of EDB, and the unloading of EDB tank cars was shown to result in exposure to EDB that may exceed the NIOSH recommended ceiling of 1 mg/cu m (0.13 ppm). However, the use of respirators should provide the necessary protection to control worker exposure below the ceiling limit.

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I INTRODUCTION

The Williams-Steiger "Occupational Safety and Health Act of 1970" was passed into law "to assure safe and healthful working conditions for working men and women..." This act established the National Institute for Occupational Safety and Health (NIOSH) in the Department of Health, Education, and Welfare and the Occupational Safety and Health Administration (OSHA) in the Department of Labor. The Act provides for research, informational programs, education, and training in the field of occupational safety and health and authorizes the enforcement of standards.

NIOSH has been given the authority and responsibility under the Act to conduct field research studies in industry, evaluate findings and report on these findings. Section 20(a)7 states that NIOSH shall conduct and publish industrywide studies of the effects of chronic or low-level exposure to industrial materials, processes, and stresses on the potential for illness, disease or loss of functional capacity in aging adults. Section 20(c) provides the authority to enter into contracts, agreements, or other arrangements with appropriate public agencies or private organizations for the purpose of conducting studies relating to responsibilities under the Act. For this purpose NIOSH has established a contractual agreement with SRI International (formerly Stanford Research Institute) to study worker exposure to ethylene dibromide at the Deepwater, New Jersey facility of Du Pont as part of an industrywide study.

A. Description of Plant

The Du Pont Chambers Works plant in Deepwater, New Jersey is a producer of antiknock compounds, fluorocarbons, and organic dyes such as the aniline-based and azo-based dyes. The facilities for the production of antiknock blends using ethylene dibromide and either tetramethyl or tetraethyl lead occupy only a small portion of the 1 square mile of plant area and consist of three adjacent enclosed brick structures (drumming, blending, reactor). Storage tank facilities (18) for the antiknock blends are located approximately 1/4 mile from the process area. Facilities for the unloading of tank cars containing EDB and other raw materials used within the plant and facilities for the loading of tank cars and tank trucks with antiknock blends are located between the drumming and blending buildings. Of the more than 6,000 Du Pont employees, approximately 60 work in this production area.

Tetramethyl and tetraethyl lead are manufactured at the plant, but the processing area is removed (1/3 mile) from the antiknock blend processing area. Other compounds used in antiknock blend production include ethylene dichloride and toluene. These are unloaded at the same site as EDB.

B. Description of Process

Ethylene dibromide (EDB) is used by Du Pont in the closed-system batch production of antiknock blends having a final EDB composition of 18-35 percent and in the production of "Tetramix", a special antiknock blend that also contains ethylene dichloride, toluene, and five alkyl (methyl and ethyl) lead compounds. All EDB consumed in this process is shipped in by tank cars at an average rate of 4 cars per week. Each car is coupled to a hose through a valve outlet under the car and the EDB is transferred by pump to a steam-heated storage tank located outside of the blend building. The EDB is then pumped to a secondary storage tank located on the third floor of the blend building.

In the manufacture of the antiknock blends, any of eight blend tanks may be used. Each blend tank is equipped with a weighing device which is used in measuring the blend ingredients being added to the tank. EDB is transferred from the secondary storage tank to one of the eight blend tanks by gravity along with either tetramethyl or tetraethyl lead, and ethylene dichloride. All compounds are added into a piping system at the top of the blend tank which terminates near the bottom of the tank. A homogeneous blend is assured by a recirculation system which removes the mixture from the bottom of the tank and reintroduces it under pressure at a point one-third of the way up the tank. Semiblends are also manufactured and consist of a homogeneous mixture of EDB, alkyl lead, and other compounds. To each batch of blend is added an oil-based dye for easy leak detection because of the colorless nature of the blends. The blending process is performed under a nitrogen plug to control vapor release into the work environment.

The homogeneous blends are then pumped to one of 18 storage tanks, to tank cars or under special circumstances tank trucks, or to two storage tanks on the third floor of the blend building for drum loading. From the storage tanks, the blends can be transferred back to the blending tank for tank car or tank truck loading or to the reactor room for the production of "Tetramix". The semiblends can be pumped from the blend tank to storage tanks or into tank cars or drums for shipping. From the storage tanks, the semiblends may be transferred back to the blend tanks for the completion of the blending operation or be transferred to the reactor room.

The loading of tank cars is controlled at the blend room by the Blend Operators. Preweighed amounts of blend are pumped from the blend tank to the tank car using a 2-inch feeder hose coupled to a valve located at the top of the tank car. A 1-inch vent line is also coupled to another valve on the top of the car to remove the displaced air. The displaced air is passed through a separating tank which removes any liquid present in the vented gas and then through a stack.

Drum loading is conducted in the drum building using two enclosed locally exhausted hoods. Each 55-gallon drum is equipped with a double bung to minimize leakage. Drums are placed in either of two hoods and coupled to the feeder line. The valve control is located outside the hood and is operated only after the hood is closed. A scale located in the hood is used to determine when the drums are filled. Filled drums are sealed with the bungs and stored for 24 hours on their sides with the bung side facing the floor to test for leakage.

Leaking drums and drums containing water or other impurities are set aside for later reclamation at the end of the shift. An enclosed, locally exhausted hood is used in the reworking of the blends in these drums. A drum is placed within the hood; the bung is removed and a suction hose is placed in the drum. With the hood closed, the blend is pumped through a vacuum line to the heels tank for reclamation.

Drums used in drum loading are reusable and must undergo a cleaning operation prior to reuse. Users of this product flush the drums with gasoline prior to shipping the drums back to Du Pont. As they are received at Du Pont, the bungs are removed from each drum by an employee wearing a half-mask respirator with organic vapor cartridge. The drum is then placed in an enclosed, locally exhausted hood and a water hose is placed in the drum. The drum is flushed in the closed hood and aspirated manually to remove excess water. Chains are then added to the drum and the drums are mechanically rotated to loosen any scale formation. Drums are steam cleaned to remove the scale and are then dried. The outer surface of the drums is grit blasted in an enclosure to remove old paint and rust and is repainted. The cleaned and painted drums are then inspected for damage prior to drum loading.

In the reactor rooms, blends of tetraethyl lead and EDB are mixed with other blends consisting of tetramethyl lead, toluene, and ethylene dichloride in a continuous flow process. Mixing occurs at the beginning of the system, which consists of a network of piping (pipe reactor) on the third floor of the reactor building. A catalyst is then added to the system to produce a redistribution of the methyl and ethyl groups to form an alkyl lead mixture of tetramethyl, trimethylethyl, dimethyldiethyl, triethylmethyl, and tetraethyl lead. Toluene, ethylene dichloride, and EDB are not involved in the redistribution reaction. When the desired mixture is obtained, the catalyst is poisoned by adding dilute caustic to the pipe system. The solution then passes through a decanter tank where water is removed and the final product (Tetramix) passes by gravity to one of four tanks. From there the product is transferred to a storage tank for tank car loading.

The production of antiknock products takes place in a closed system reducing the hazard of exposure to EDB and other blend constituents. The primary means of exposure would be through leaks within the system or through the performance of tasks that by-pass the closed system. These tasks include sampling of the EDB tank cars prior to unloading, sampling of the blend and reactor tank products, the unloading of EDB tank cars and the loading of drums and tank cars with the antiknock blend. The sampling of the EDB tank car is performed by personnel wearing rubber gloves, chemical goggles, and a half-mask respirator with organic vapor cartridge. Sampling is performed using a glass sample bottle attached to a long metal rod which is lowered into the tank car.

For the following tasks, engineering controls have been instituted to reduce worker exposure. A blend sample is taken once per batch and uses an enclosed, locally exhausted hood. The Blend Operator places the glass sample bottle under a spigot in the hood and closes the hood prior to filling the sample bottle by means of a control valve located outside the hood. The reactor sample is taken once every hour in the same manner as described for the blend sample. Drum loading and unloading has been described earlier and utilizes an enclosed locally exhausted hood. Tank car loading uses a venting system to direct gases away from the work area while the unloading process for EDB was designed to minimize EDB loss into the working environment. The accidental release of EDB into the atmosphere during the blending process is also controlled by the use of a nitrogen atmosphere within the system.

C. Medical, Industrial Hygiene, and Safety Programs

The safety and health of the employees at the Du Pont Chambers Works plant is the responsibility of the Central Safety Committee.

The committee is headed by the Plant Manager and is made up of 20 ranking members of supervision throughout the plant. The committee sets plant policies, reviews questions, and conducts investigations. Line organization is charged with implementing these policies. The committee is assisted in the implementation of these tasks by a safety office with five safety engineers, an Industrial Hygiene Committee of 12 members, and a medical staff of 39 members.

All employees are given a preplacement comprehensive medical examination and a comprehensive medical examination every 2 years up to the age of 40 years and annually thereafter. None of the examination is directed towards health effects attributable to EDB exposure because the organo lead compounds were considered by plant management to be more toxic and the principal health concern to employees within the EDB processing area. For this reason, all employees within the EDB area participate in a medical surveillance program for lead exposure in which they are monitored at least once every 2 months. Urinalysis, blood pressure, pulse, and body weight are checked and any discrepancies or trends are monitored by the medical staff and the necessary action is taken to safeguard the employee.

The control of EDB exposure is conducted on a number of different scales. Air concentrations are controlled by the use of limited access hoods at key points within the operation where potential exposure through the handling of EDB or organolead products may occur. These hoods are maintained by the engineering department at their prescribed face velocities (range 85-150 fpm) through annual checks with more frequent checks if performance questions arise.

The committee with the assistance of the appropriate staff issues safe operating procedures for those tasks that are considered to involve potential hazards. These instruction sheets are listed in Appendix 1 and include general operating instructions for the handling of EDB, safety requirements for the handling of undiluted EDB, and laboratory procedural instructions for the handling of solutions containing EDB in excess of 1 percent by weight. This information is available to all personnel and supplements training programs on hazard information, new employee training, and emergency procedures.

The industrial hygiene staff conducts periodic sampling for EDB, ethylene dichloride, and alkyl leads. Sampling for EDB is by charcoal tube and analysis is by gas chromatography. Appendix II lists the analytical procedure used by Du Pont for EDB analysis and Appendix III provides current data obtained by Du Pont for EDB, ethylene dichloride, and alkyl leads. With regard to EDB, 8-hour TWA concentration determinations and short-term sampling of specific tasks are provided.

As a part of the safety program, all employees are required to wear side-shield safety glasses, hard hats, fire retardant "Nomex" shirts and trousers, and safety shoes; all of which are supplied by Du Pont. In addition, impervious gloves are worn when exposure to liquid EDB is likely and respirators with organic vapor cartridges are used during the unloading of EDB from tank cars, the taking of quality control samples from EDB tank cars, and in the dipping of EDB storage tanks. All employees are required to change into work clothes prior to entry into the production area and into street clothes prior to leaving the plant. Clothes are laundered twice a week by Du Pont and any contaminated clothing (with EDB or lead) is discarded immediately.

D. Recordkeeping

The Du Pont Chambers Works has been in operation for 60 years and has used EDB in its processing since 1923. The plant currently employs about 6,700 workers with 5,800 being involved in production. The total number with potential exposure to EDB is 88 with 14 supervisors and 74 operators. Personnel records are available and contain general information on date of birth, Social Security number, dates of employment, department or operations code, and home address. The available records may be useful in obtaining an estimate of length of service within the EDB area and in determining the types of chemicals to which an employee was exposed. Recordkeeping information provided by Du Pont is presented in Appendix I.

E. Union

The production employees at Du Pont's Chambers Works are members of an independent union, Chemical Workers Association, Inc.

II PLANT SURVEY

A. Job Classification

The Du Pont Chambers Works plant operates 24 hours per day, seven days per week, using a three-shift-per-day schedule and four shift crews. For each production area the shift crews rotate among the three shifts but there is no rotation of personnel between the different production areas outside of job transfers. For the blending operation the shift crews are composed of two Blend Operators, one Relief Operator, and one Reactor Operator. In the drum loading operation, a day activity, there are 17 personnel involved in various stages of the processing of drums. There are 10 different tasks involved in the processing operation and there is a rotation of workers on a weekly basis. Duties which have been identified as involving the potential for worker exposure to EDB include those performed by the two drum loaders, the raw material handler, and the person assigned to wash out the drums. The other duties involve the handling of empty, clean drums or the sealed, filled drums. A job description for these job classifications follows.

- Blend Operator (two)

  The primary duties of the Blend Operators consist of mixing blends, loading the finished blend products into tank cars and occasionally tank trucks and making rounds of the blend building to check for leaks. Blend mixing occurs on all three shifts, and tank car loading is performed as needed and may involve any of the shifts. The blend operation is performed by use of a control panel located next to the blend tank and does not involve any handling of the blend ingredients by workers. Ingredients are transferred to the blend tank through a control valve until the desired amount has been added as determined by a weight sensing device located in the blend tank. The blend is allowed to mix by recirculating the mixture and this process is overseen by the operator. With the completion of blending, a sample is taken using an enclosed, locally exhausted hood and taken to the laboratory for analysis. If the blend is deemed of unacceptable quality, the Blend Operator will adjust the blend to make it acceptable. The adjustment takes place using the control panel and does not involve any increase in exposure to EDB. If acceptable, the blend is transferred to tank cars, the main storage tank, or to storage tanks on the third floor for drum loading. All transfer operations are performed by the adjustment of the necessary control valves to divert the blend to its proper destination and do not involve, under normal conditions, any additional exposure to EDB.

Tank car loading as described earlier involves the coupling of a 2-inch feeder line and 1-inch vent line to the appropriate valves on the top of the empty tank car. The tank car is grounded to prevent the buildup of static electricity. The operator must enter the blend building to start the pumping operation. Du Pont currently averages six tank cars per 24-hour period, so the maximum that any one operator would handle would be six cars.

- Relief Operator

The Relief Operator has a number of odd jobs such as the testing of all emergency showers within the blend area. Duties which result in potential exposure to EDB include assisting the Blend Operator in the loading of tank cars, overseeing the mixing of the blends, and relieving the Blend Operators and Reactor Operator during their lunch and break periods (two 15-minute breaks per shift).

- Reactor Operator

The Reactor Operator spends all of his time in the vicinity of the reactor building overseeing the reactor control panel. The reaction is a continuous flow process controlled from the control area on the first floor and does not involve any direct exposure to EDB except during the taking of quality-control samples once every 2 hours. Sampling is conducted in an enclosed, locally exhausted hood by the operator with rubber gloves. This task generally takes less than 2 minutes to complete. The operator makes a 5-minute round of the building once each hour to check for leaks. Duties outside the building involve checking the supply of caustic and catalyst in their respective storage tanks every hour.

- Raw Material Handler

The Raw Material Handler is on day work and has been assigned a number of duties such as the shipping of small packages and supply inventory which do not involve handling of EDB or other chemicals. Of special relevance to this survey were his duties involving the unloading of raw materials and keeping an inventory of these raw materials. The Raw Material Handler is responsible for unloading raw materials coming into the plant in tank cars; these include EDB, ethylene dichloride, and toluene. The unloading operation consists of coupling a hose to a valve located on the bottom of the tank car and opening a valve on the top of the car to prevent the creation of a vacuum while unloading. The raw material is then pumped to the proper storage tank. The handler does use rubber gloves, chemical goggles, and a half-mask respirator with organic vapor cartridge during this task.

Prior to unloading EDB, a quality-control sample is taken using a glass sample bottle attached to a long metal rod. A sample is dipped out of the tank at the top and sent to the laboratory for analysis. The same personal protective equipment is used in this task as in the unloading operation.

A raw material inventory is made of all storage tanks by checking their levels on a periodic basis. Most tanks are equipped with a metering device which allows checking of tank levels without physically opening the tanks. In the case of ethylene dichloride, the level has to be measured with a dipstick twice a week. This task consists of lowering into the tank a ruler to measure the distance between the surface of the liquid and the top of the tank. Half-mask respirators with organic vapor cartridge, chemical goggles, and rubber gloves are used.

- Processing of Drums

  As described earlier, this process involves the performance of 10 different tasks. Of these tasks, however, only two are considered to present a potential problem with regard to EDB exposure. These are drum washing and drum loading and are described in detail under Description of Process. On a normal operation, an average of 100 drums are loaded per day by the two drum loaders.

Peripheral people who may through the course of their duties become exposed to EDB include the maintenance crew, Compound Bulk Operator, and Laboratory Technician. The maintenance crew works on an as needed basis within the EDB use area and is therefore only sporadically exposed to EDB. At the time of the survey no maintenance work was scheduled for the blending and drumming operations.

The Compound Bulk Operator is one of about 20 workers who work in the bulk storage area. However, he is the only one with assigned duties which provide him with possible exposure to EDB. His primary duty is to patrol the bulk storage area once every hour for leaks and to oversee from his control room the loading of storage tanks or the transfer of material from the storage tanks to the blend or reactor room. He is also responsible for checking the level of blends in the bulk storage tanks by physically measuring with a tape rule the distance between surface of blend and tank top.

The Laboratory Technician spends all of his time within the laboratory and normally does not venture into the production area. About 1/4-1/3 of his time is spent in the analysis of blend and EDB samples. All samples are analyzed in hoods having face velocities of 100 fpm.

B. Existing Controls

Safety requirements for the plant require all employees to wear safety glasses with side shields, safety shoes, and hard hat while in the production area. Chemical goggles are required in jobs where eye contact may occur. These include loading and unloading of tank cars, drum washing, and drum loading. Rubber gloves and respirators with organic vapor cartridges are worn in the loading and unloading of tank cars, drum washing, and drum loading.

Respirator usage is limited only to those duties, generally short-term, where additional protection is believed to be necessary. Within the blend operation, the primary protection against EDB exposure rests in the maintenance of the integrity of the closed-system operation. For this reason, periodic checks are being made for leaks by the Blend, Reactor, and Compound Bulk Operators. To facilitate this visual inspection for leaks, an oil-based dye is added to the blend product in the blend tank. Additional controls in the form of enclosed, locally exhausted hoods and a venting system have been installed at points of operation where exposure to EDB and alkyl lead is most likely to pose a problem. These systems have been described earlier in the Description of Process and coincide with those tasks where respiratory protection is required by Du Pont. A form of administrative control is also in operation in the drum building and on certain shifts in the blend and reactor buildings. This control takes the form of rotating workers among the different tasks within the operating unit on a weekly basis thereby limiting exposure relative to the other tasks. The rotation of duties has been instigated at the preference of the shift foreman and is not a management mandate. Its use has been to maximize worker interest within the department, and the limited exposure is a byproduct of this policy.

Eyewash fountains and emergency showers are located throughout the production area and are tested daily by the Relief Operator. Rest areas and lunch rooms are located away from the production area. Personal hygiene is stressed throughout the plant and clean uniforms ("Nomex" flame retardant uniforms) are provided twice a week. Change rooms and showers are also provided.

C. Survey Procedures

Area sampling and personnel monitoring were conducted on 6-8 July 1977. About 60 employees over three shifts were identified as having potential exposure to EDB in the production area. It was further determined that the Blend, Reactor, and Compound Bulk Operators and the Laboratory Technicians had similar duties over the three shifts. Personnel in the three shifts were therefore pooled by job classification and sampled accordingly. The nonshift (day only) workers were sampled on 7 and 8 July. The schedule followed for the shift workers was:

		6 July	7 July
Day (8 am-4 pm)	Blend Operator A		X
	Blend Operator B		X
	Reactor Operator		X
	Relief Operator		X
	Compound Bulk Operator		X
Afternoon (4 pm-12 pm)	Blend Operator C	X	
	Blend Operator D	X	
	Reactor Operator	X	
	Relief Operator	X	
	Compound Bulk Operator	X	
Midnight (12 pm-8 am)	Blend Operator A		X[a]
	Blend Operator B		X
	Reactor Operator		
	Relief Operator		
	Compound Bulk Operator		

[a] 6-7 July.

The two Laboratory Technicians involved in the analyses of the blend and EDB quality control samples were sampled at shift 2 on 6 July 1977 and shift 1 on 8 July 1977. The drum processing workers are nonshift (day only) workers. The two Drum Loaders were sampled on 7-8 July 1977; the drum washing and drum inspection tasks were monitored on 7 July. Drum inspection consists of visual inspection of the cleaned drum for damage and cleanliness of the inside walls. Two peripheral people were sampled on 8 July 1977. Their duties involved the manual moving of cleaned empty drums to the drum loading area and the manual moving of filled drums to the shipping area.

A preliminary surveillance of the EDB use area with the Century OVA Model 128 revealed no total organic readings significantly above the instrument noise level. However, area monitors were placed at the EDB unloading site, on the outside of the drum loading hood, near the control panel for one of the blend tanks, and at the third floor EDB storage tank in the blend building. In all, a total of 36 samples were taken: 26 personal samples, 6 short-term peak exposure samples, and 4 area samples.

During the sampling period, the plant was not operating at its normal capacity. The reactor room operation was shut down on 7-8 July 1977 because of an excess of "Tetramix" product and drumming operations were below normal on the same two days (32 and 85 percent less than normal, respectively) due primarily to problems with the blend mix of the day before. Results of these samples would therefore reflect a lower than normal exposure to EDB.

D. Sampling and Analytical Method

NIOSH Method No. P&CAM 260 (Draft)[1] formed the basis for all sampling and analyses. Sampling was done by drawing a known volume of air at an accurately determined nominal rate of 200 ml per minute through a charcoal tube to trap the EDB (1,2-dibromoethane) vapor present. Generally, Bendix Super Sampler Permissible Air Pumps adapted for low flow sampling at 200 ml per minute were used for personal monitoring for TWA concentration determinations and SKC Model 222-3P Air Check Personal Pumps operating at a nominal flow rate of 200 ml per minute were used for obtaining the short-term and area samples.

The charcoal tubes consist of glass tubes with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal and the backup section contains 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than 25 torr at a flow rate of 200 ml per minute.

Personal samples were collected in the breathing zone of individual employees. These were obtained by attaching the sampling tube to the shirt collar or lapel of the employee to collect the sample in the employee's breathing zone, without interfering with the employee's freedom of movement. Plastic tubing was used to connect the sampling tube to the personal sampling pump on the employee's belt. The flow rate through this sampling train was determined both before and after sampling by use of a buret (soapbubble meter).

Immediately after sampling, the charcoal tubes were placed in dry ice. At the end of the survey, all samples were shipped by air to SRI's laboratories in Menlo Park, California. The samples, still packed in dry ice, were received the same day that they were shipped.

All analyses were performed by SRI's laboratory which is accredited under the Laboratory Accreditation Program of the American Industrial Hygiene Association. In accordance with NIOSH Method No. P&CAM 260 (Draft), the analyte was desorbed from the charcoal with 10.0 ml of 99:1 benzene-methanol (v/v). An aliquot of each desorbed sample was later subjected to gas chromatographic analysis using an electron-capture detector.

Two tubes containing charcoal from the same batch as the sample tubes were treated in the same way as the samples, except that no air was drawn through them. Both ends of each of these tubes were broken off, the tubes were resealed with the caps supplied by the manufacturer, and then they were packed in the dry ice with the samples. These tubes served as blanks. Analysis showed no blank correction to be necessary; no EDB was detected in either of the blanks (less than 40 nanograms).

The front and backup sections of each tube were desorbed separately, and all front sections were analyzed. The backup sections from the nine tubes with the greatest amount of EDB in the front sections were then analyzed. Since EDB was not detected (less than 40 nanograms) in these sections, the remaining backup sections from the tubes which had collected less EDB were not analyzed.

E. Evaluation Criteria

The American Conference of Governmental Indus rial Hygienists (ACGIH) adopte n 1953 a threshold limit value (TLV) of 25 ppm as an 8-hour time-weighted average (TWA) exposure concentration for 1,2-dibromoethane.[2] In 1954, the ACGIH[3] changed the name to ethylene dibromide in the official TLV list, and in 1973[4] the name was again listed as 1,2-dibromoethane. In 1965, the ACGIH[5] recommended that special emphasis be given to the skin absorption potential of ethylene dibromide by adding the designation "skin" after the name in the TLV list. This notation refers to the potential contribution to overall exposure by the dermal route, particularly by direct contact with ethylene dibromide. This designation was intended to suggest that appropriate measures for the prevention of dermal absorption are necessary in addition to measures to control potential airborne exposure.

In 1966, the ACGIH[6] recommended that the TLV of 25 ppm as a TWA concentration for EDB be changed to a ceiling limit of 25 ppm. In 1971, the ACGIH[7] recommended changing the ceiling limit of 25 ppm to a TLV of 20 ppm as an 8-hour TWA concentration, as it is currently listed.

The present federal standard (29 CFR 1910.1000) for occupational exposure to EDB is 20 ppm as an 8-hour TWA concentration limit, with an acceptable ceiling concentration of 30 ppm and an acceptable maximum peak above the acceptable ceiling concentration for an 8-hour work shift of 50 ppm for 5 minutes.[8] This standard was adopted from the American National Standards Institute's (ANSI) recommendation Z37.31-1970.[9]

Based on highly suggestive evidence that EDB can be mutagenic, teratogenic, or carcinogenic, on the potential of EDB to cause irreversible damage in experimental anaimals, and on the total lack of quantitative data which clearly delineate no-effect concentrations from those at which adverse effects occur, NIOSH recommends that employee exposure to EDB not exceed 1 mg/m^3 (0.13 ppm) as a ceiling limit for any 15-minute sampling period.[10]

III RESULTS AND DISCUSSION

Results of duplicate personnel monitoring for 8-hour TWA concentration determinations conducted by SRI and Du Pont are given in Table 1 by job classification. Samples were collected over nearly the entire shift and include the routine tasks performed by workers in each of these job classifications. The time periods not covered by the samples involved tasks such as discussions and activities associated with shift changeover which have a negligible effect on total EDB exposure. Results are therefore representative of the full-shift exposure to EDB and may be considered to be essentially 8-hour TWA concentration determinations.

There are no discernible differences in the magnitude of the results to indicate the existence of shift-to-shift variation within a job classification. This is supported by a description of these job classifications which shows no differences in the duties of the three shifts.

Duplicate short-term personal sampling was conducted by SRI and Du Pont at six specific tasks to determine their contribution to the overall EDB exposure of workers in the job classification. The results are given in Table 2. These duties have been identified as being major sources of EDB exposure. From Table 2, it can be seen that the four tasks with the highest exposure are conducted by the Raw Material Handler. It is not unexpected then to find that, of the people sampled, the Raw Material Handler has the highest exposure.

The reactor building was not in operation on 7-8 July 1977 because of an excess of product. A comparison of this data with that of 6 July 1977, a normal operating day, shows no difference in the average exposure of the Reactor Operator suggesting that exposure is not dependent upon the reactor operation. Because the Reactor Operator does spend his shift within the reactor building, his average exposure can be considered to be representative of background levels.

Table 1

E. I. du Pont de Nemours & Company
TIME-WEIGHTED AVERAGE EXPOSURES TO ETHYLENE DIBROMIDE BY
JOB CLASSIFICATION AND SHIFT AT THE CHAMBERS WORKS PLANT, DEEPWATER, N.J.

Sample	Job Classification	Date	Shift	Concentration (ppm) SRI[a]	Concentration (ppm) Du Pont
1	Blend Operator	7/6/77	Afternoon	0.002	(lost)
2		7/6/77	Afternoon	0.001	<0.0051
3		7/6/77	Midnight	0.006	0.0086
4		7/6/77	Midnight	0.007	0.0057
5		7/7/77	Day	0.009 (0.007)	0.0039
6		7/7/77	Day	0.009	0.0072
7	Reactor Operation	7/6/77	Afternoon	0.001	<0.0047
8		7/7/77	Day	0.003	0.0014
9	Compound Bulk Operator	7/6/77	Afternoon	0.001	<0.0054
10		7/7/77	Day	0.008	0.026
11	Laboratory Technician	7/6/77	Afternoon	0.0001	<0.0062
12		7/6/77	Afternoon	0.0003	<0.0063
13		7/8/77	Day	0.0004	<0.0062
14		7/8/77	Day	0.0005	<0.022
15	Drum Loader	7/7/77	Day (nonshift)	0.018	<0.0028
16		7/7/77	Day (nonshift)	0.014	<0.0029
17		7/8/77	Day (nonshift)	0.008	<0.028
18		7/8/77	Day (nonshift)	0.015	(lost)
19	Raw Material Handler	7/7/77	Day	0.082 (0.01)	0.16 (0.049)
20				0.027 (0.004)	(0.012)
21	Relief Operator	7/6/77	Afternoon	0.007	<0.0032
22		7/7/77	Day	0.0005	0.0029
23	Drum Washer	7/7/77	Day ~~(nonshift)~~	~~0.016~~[b]	~~0.016~~
24	Drum Inspector	7/7/77	Day (nonshift)	0.012	<0.021
25	Operator[c]	7/8/77	Day (nonshift)	0.036	0.035
26	Operator[c]	7/8/77	Day (nonshift)	0.036[d]	0.0083

---

a Values in parentheses are the results of long-term sampling. The TWAs are calculated on the basis of these values and short-term samples given in Table 2. In those cases where there are no values given in parentheses, the long-term values are equivalent to the TWA.

b Wore respirator entire shift.

c These are odd-job people in drum processing area. On day of sampling they moved empty and filled drums to different sites as needed by rolling drums.

d Left work early--total sampling time 2 hours 19 minutes.

Table 2

E. I. du Pont de Nemours & Company
EDB CONCENTRATIONS FOR SHORT-TERM PERSONAL MONITORING
OF SPECIFIC TASKS AT THE CHAMBERS WORKS PLANT, DEEPWATER, N.J.

ple			Duration	EDB Concentration (ppm)	
.	Worker Title	Task Description	of Task	SRI	Du Pont
	Raw Material Handler	Attaching hose to Tank Car for unloading EDB[a]	13 min.	2.39	3.75
	Blend Operator	Disconnecting vent and filler lines after filling tank car with blend[a]	7 min.	0.14	<0.28
	Blend Operator	Taking quality-control sample of blend in locally exhausted hood	3 min. 33 sec.	0.037	<1.25
	Raw Material Handler	Disconnect hose from EDB tank car after unloading[a]	7 min. 23 sec.	0.085	<0.30
	Raw Material Handler	Determining level of EDB in storage tank[a]	2 min.	0.299	<0.59
	Raw Material Handler	Taking quality-control sample of EDB from tank car prior to unloading[a]	13 min. 10 sec.	0.699	<0.32

Respirators are worn during the performance of these tasks.

Results for the Drum Loader must be considered to be below the normal exposure because drum loading activities were well below the average of 100 drums per day on 7 July 1977 (68 drums) and 8 July 1977 (15 drums). On 8 July 1977, blends in rejected drums were pumped out in locally exhausted hoods, and this task may account for the similarity in exposure between the two days even though less drums were loaded on one day. Other drum processing tasks which by their nature would be expected to have a lower exposure potential are similar to drum loading with regard to exposure levels.

Results of area monitoring to determine average EDB concentrations in areas routinely entered or occupied are given in Table 3.

The Du Pont Chambers Works plant uses a rotating shift schedule to operate on a 24-hour-per-day, 7-day-per-week basis with each individual working on each of the three shifts at various times over successive scheduling periods. The duties to be performed within a job classification are the same for all three shifts so shift-to-shift exposure to EDB should be the same. Therefore, a worker's 8-hour TWA concentration can be determined on a long-term basis by pooling the results of all shifts. Median shift values and ranges for each job classification are given in Table 4.

E. I. du Pont de Nemours & Company
AREA SAMPLING FOR ETHYLENE DIBROMIDE AT BREATHING ZONE
HEIGHT IN ANTIKNOCK BLENDING AREA AT CHAMBERS WORKS PLANT, DEEPWATER, N.J.

Sample	Date	Description	EDB Concentration (ppm)	
			SRI	Du Pont
1	7/8/77	EDB tank car unloading area; no unloading in process during sampling	0.050	0.034
2	7/8/77	At the drum loading site with sampler attached to exhaust hood	0.008	< 0.015
3	7/8/77	Adjacent to blend tank controls in blending building	0.002	< 0.0074
4	7/8/77	Adjacent to EDB storage tank on third floor of blending building	0.008	< 0.0033

Table 4

SUMMARY DATA

E. I. du Pont de Nemours & Company
8-HOUR TWA CONCENTRATIONS AT SPECIFIED JOB
CLASSIFICATIONS AT DEEPWATER, N.J., 6-8 JULY 1977

Job Classification	Number of Samples	EDB Concentration (ppm)	
		Range	Median
Blend Operator	6	0.001-0.009	0.006
Reactor Operator	2	0.001-0.003	0.002
Compound Bulk Operator	2	0.001-0.008	0.004
Laboratory Technician	4	0.0001-0.0005	0.0004
Drum Loader[a]	4	0.008-0.018	0.014
Raw Material Handler[a]	2	0.027-0.082	0.054
Relief Operator	2	0.0005-0.007	0.004
Drum Processing[a,b]	4	0.012-0.036	0.026

[a] Day worker only.

[b] Values are for the different tasks which comprise the drum processing activity.

IV CONCLUSIONS AND RECOMMENDATIONS

Existing controls (local exhaust hoods and personal protective equipment) are adequate to maintain ethylene dibromide concentrations well within the limits set by the present federal standard and the ACGIH TLV. These controls include the use of local exhaust hoods at points in the operation (drum loading, drum washing, taking of quality control blend and reactor samples) where exposure to lead may be significant and in the use of full facepiece respirators with organic vapor cartridges and rubber gloves in the taking of quality-control samples of EDB, the unloading of EDB tank cars, the loading of blend tank cars, and the dipping of EDB storage tanks. The use of local exhaust hoods is aimed at controlling airborne concentrations of lead, a compound that has been considered to be more toxic than EDB. Respirators are used in the above tasks because these tasks result in the major part of the total potential exposure for the jobs surveyed.

NIOSH recommends that personnel exposure to EDB not exceed a ceiling limit of 1 mg/cu m (0.13 ppm) as determined by a 15-minute sampling period. Activities such as taking EDB quality-control samples from EDB tank cars and unloading or loading tank cars have the potential to result in worker exposure exceeding this limit during the performance of these activities. However, the practice of using respirators during the performance of these tasks is considered to be adequate to control these potential exposures below the ceiling limit, especially when used in conjunction with a comprehensive respiratory protective program which meets the requirements of 29 CFR 1910.134. Other quality-control sampling activities performed under local exhaust ventilation are below the ceiling limit, indicating the effectiveness of engineering controls in controlling worker exposure to EDB.

REFERENCES

1 P&CAM Method No. 260 (Draft), 1,2-Dibromoethane, NIOSH Manual of Analytical Methods, Volume 2, 1977, National Institute for Occupational Safety and Health, Cincinnati, Ohio. In preparation.

2 American Conference of Governmental Industrial Hygienists: Threshold Limit Values for 1953. Cincinnati, ACGIH, 1953.

3 American Conference of Governmental Industrial Hygienists: Threshold Limit Values for 1954. Cincinnati, ACGIH, 1954.

4 American Conference of Governmental Industrial Hygienists: Threshold Limit Values for 1973. Cincinnati, ACGIH, 1973.

5 American Conference of Governmental Industrial Hygienists: Threshold Limit Values for 1965. Cincinnati, ACGIH, 1975.

6 American Conference of Governmental Industrial Hygienists: Threshold Limit Values for 1966. Cincinnati, ACGIH, 1966.

7 American Conference of Governmental Industrial Hygienists: Threshold Limit Values for 1971. Cincinnati, ACGIH, 1971.

8 US Dept. of Labor (OSHA): Recodification of air contaminant standards. Federal Register 40:23072-073, 1975.

9 American National Standard: Acceptable Concentrations of Ethylene Dibromide (1,2-Dibromoethane), Z37.31-1970. New York, American National Standards Institute, Inc., 1970.

10 NIOSH Criteria for a Recommended Standard ... Occupational Exposure to Ethylene Dibromide, US Dept. of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health. August 1977.

APPENDIX I

OPERATING INSTRUCTIONS FOR HANDLING EDB

OPERATING INSTRUCTIONS

A. Bakker
Chambers Works

NO. TEL-4A-01.1

DATE 2-04-77

SUBJECT: Thawing, Sampling and Unloading Ethylene Dibromide Tank Cars

OPERATION: Drumming Building No. 568

Important steps in the operation	"Key points"-- knacks, hazards, "feel," timing, special information

Ethylene dibromide is poisonous. It is injurious if spilled on the skin or if vapors are inhaled. In case of a spill on clothing or body, wash immediately with kerosene and then with soap and water. Report to the hospital. Use impervious gloves and an air mask or respirator when handling ethylene dibromide.

In cold weather, it is necessary to melt the contents of ethylene dibromide tank cars by circulating steam through the heating coils in the car. (Freezing point of ethylene dibromide is 10°C. or 50°F.)

Important steps in the operation	Key points
1. Check the record book of the Clerical Department to determine if car was overloaded.	1. Maximum load for GATX tank cars is 200,000 pounds and for DOWX cars 210,000 pounds.
2. If record indicates net weight of car approaches maximum weight, special	2. The high temperature coefficient of EDB can cause a maximum loaded car to over-

ETHYLENE DIBROMIDE (EDB) OPERATING PROCEDURES

The following procedures shall apply and be complied with whenever solutions of EDB in excess of 1% (wt.) are handled and stored. This also applies to lead alkyl blends as follows:

All "Tetramix" blends
TEL-MMI (but not TEL Crude)
TEL-MM
Aviation Mix
TML-MM (but not TML Crude)

1. All samples, regardless of quantity, shall be confined to and handled only in designated "Limited Access" hoods.

2. Transport of samples shall be permitted only in sealed, unbreakable containers. Transport from one area to another shall be direct with no stops in an uncontrolled area.

3. Impervious gloves similar to those used to handle lead alkyls, shall be worn at all times when handling samples.

4. "Nomex" protective clothing, similar to that currently issued in the Petchem Area, shall be worn when handling samples.

5. Sample storage shall be in a locked, ventilated location.

6. Sample disposal shall be into the laboratory TEL waste disposal system.

7. Disposable contaminated materials (sample bottles, rags, papers, etc.) shall be placed in a lined fiberpak container in a limited access hood. When full it shall be incinerated similar to TEL contaminated waste.

8. Reusable contaminated materials (e.g. glass) shall be drained of residual EDB into the TEL disposal system, rinsed with a solvent ("Freon" 113, acetone, etc.) and washed thoroughly with detergent and water. All cleanup of this type is to be performed in limited access hoods while wearing gloves.

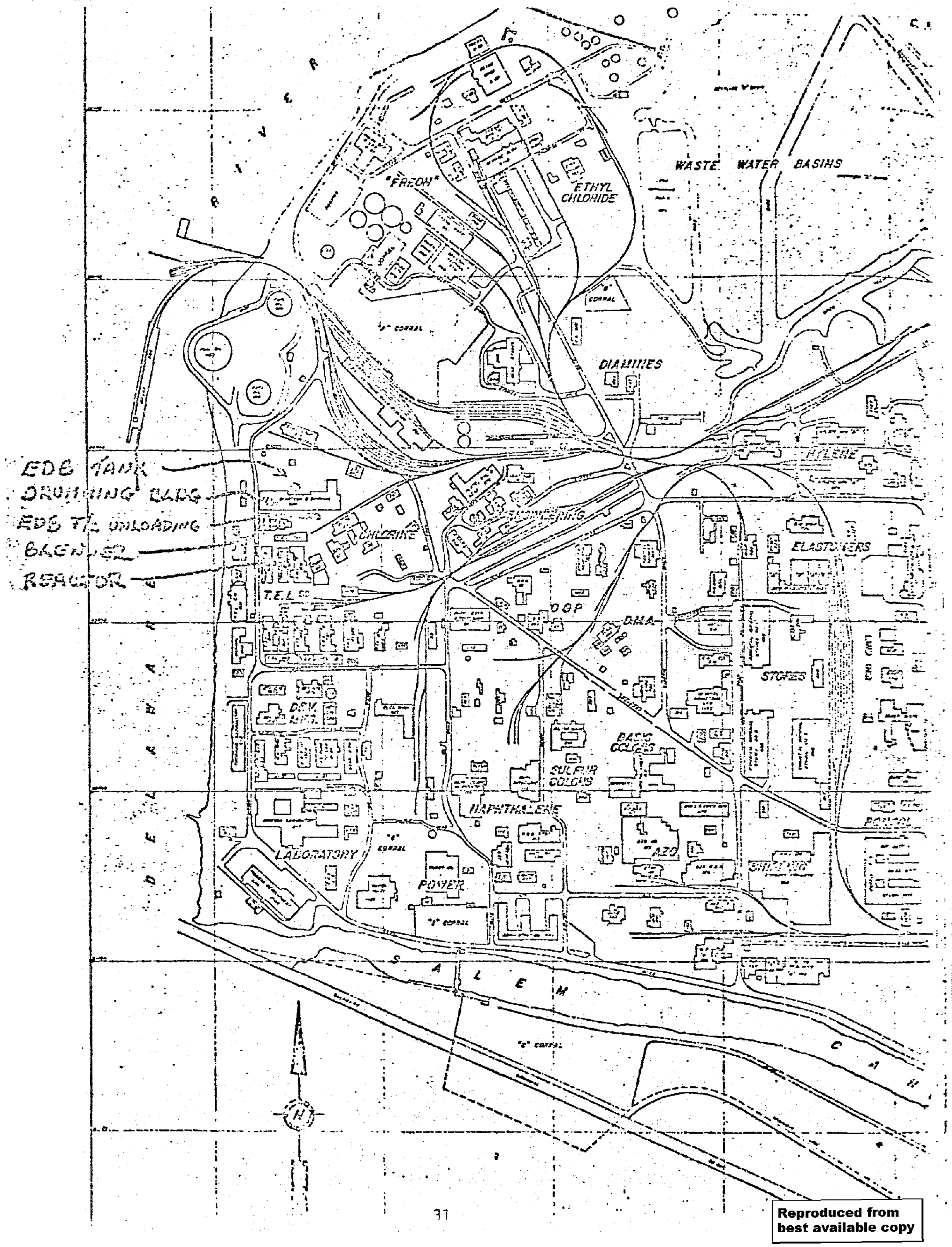
9. Any spill of EDB shall be immediately wiped up with an absorbent material. If the spill involves a lead alkyl blend then normal lead decontamination procedures shall apply. If the spill does not contain lead alkyls, the area shall be thoroughly washed with detergent and water.

10. Contact of EDB with the skin (not eyes) requires immediate flushing with kerosene followed by a thorough washing with soap and water. Report immediately to supervision and then to Medical

11. Contact of EDB with the eyes necessitates immediate flushing with water for at least fifteen (15) minutes. Report to supervision and then to Medical.

12. High vapor concentrations of EDB should be avoided at all times. Nausea and vomiting are normal reactions to high vapor exposure. If exposed, get to fresh air immediately or call for help if unable to do so. Report to supervision and then to Medical.

emo
1/28/77


EDB TANK
DRUMMING BLDG
EDB T/C UNLOADING
BLENDER
REACTOR
"FREON"
ETHYL CHLORIDE
WASTE WATER BASINS
DIAMINES
CHLORINE
T.E.L.
OOP
D.M.A.
ELASTOMERS
XYLENE
STORES
BASIC COLORS
SULFUR COLORS
NAPHTHALENE
AZO
LABORATORY
POWER
D E L A W A R E
R I V E R
S A L E M
C A N
N

APPENDIX II

DU PONT ANALYTICAL METHOD FOR EDB DETERMINATION

E. I. DU PONT DE NEMOURS AND COMPANY

ORGANIC CHEMICALS DEPARTMENT

ANALYTICAL PROCEDURE

ORCHEM METHOD 70-9-30-5

AIR

Determination of Ethylene Dibromide by Gas Chromatography

I-A. Principle

This method is based on the charcoal adsorption of ethylene dibromide (ethylene bromide; 1,2-dibromoethane) from a known volume of air, desorption with carbon disulfide, and quantitative analysis by vapor phase chromatography (VPC) with a flame ionization detector (f.i.d.).

I-B. Scope

1. Application

Although the range investigated was 1 to 9 mg of ethylene dibromide (EDB), it is felt that this method may be satisfactorily used in the arbitrary range of 0.013 to 13 mg of EDB per sample, representing 0.01 to 10 times the threshold limit value (TLV) of 145 mg per cubic meter. This is equivalent to 0.04 to 40 mg of EDB per cubic foot of air sampled or 1.45 mg to 1.45 g per cubic meter. These values are based on a 10-minute air sample taken at a flow rate of 2 SCFH, and desorbed in 0.5 ml of carbon disulfide (CS_2).

2. Limitations

A sampling flow rate of 2 SCFH (ca one liter per minute) or less is required for maximum adsorption efficiency. At this flow, a one-minute air sample would be sufficient to measure EDB in air at a concentration of 0.1 TLV. However, a minimum 10-minute sample is recommended for sample volume accuracy. The lower limit of sensitivity may be extended by taking a correspondingly larger air sample. Maximum concentration of EDB *per sample is that concentration at which the amount of EDB found on the back-up section of the charcoal adsorption tube is 25% of that found adsorbed on the front section. Beyond this limit, the possibility of sample loss exists. For each new lot of charcoal adsorption tubes, the percentage of EDB removed in the desorption process with carbon disulfide must be determined (desorption efficiency). The presence of other organics in the air can adversely affect the adsorption capacity and efficiency of the charcoal.

*For Sipin charcoal tubes, Lot No. 100, this maximum was found to be 110 of EDB.

C. Precision and Accuracy

1. Precision

The development precision of this procedure was determined from the analyses of four samples at different concentration levels, in duplicate, over a two-day period. Weighed amounts of [illegible] were swept with air from a micro-impinger into Sipin charcoal absorption tubes, using a Unico C-110 air sample pump at a flow [illegible] 2 SCFH. These samples were then desorbed and chromatographed [illegible] each of two consecutive days. The range selected was such as [illegible] maintain weighing accuracy at the low end of the range. The [illegible] confidence limits were calculated on the basis of the average [illegible] duplicate analyses.

Component	Range Investigated	No. of Determinations	F	Dev. of F (2σ)
EDB	1-9 mg	8	0.00245	$\pm$ 0.00014

F = response of compound relative to concentration (slope of curve)

In determining the desorption efficiency of CS_2 and EDB for Lot No. 100 of the charcoal scrubbers, the following peak areas and standard deviation were obtained:

Standards	Samples
921106	897069
931284	882507
900268	863119
	875075
	899033
$\sigma = \pm$ 15810	$\sigma = \pm$ 15105

These deviation are indicative of the reproducibility of measuring [illegible] µl of EDB, 0.5 ml of CS_2, and sampling and injection of the sample into the chromatograph. In fact, they are representative of all phases of this method, except the actual taking of the air sample.

2. Accuracy

The work involved in developing this method indicated overall accuracy of $\pm$ 15% or better, with the greatest source error being the volumetric measurement as determined from a tameter.

D. Special Apparatus (Equivalent apparatus may be substituted)

1. Gas chromatograph, Aerograph Hy-Fi Model 600-D, equipped with a flame ionization detector.

2. Digital Readout System, Infatronics Model CRS-11 HSB.

3. Recorder, Leeds and Northrup Speedomax H, 1 mv full scale, chart speed 1 inch per minute.

4. Gas chromatograph column, stainless steel type 316 seamless, 6 meters long x 1/8-inch o.d. x 3/32-inch i.d.

5. Syringe, Hamilton No. 701-N, 10-µl capacity.

6. Developing vials, Cat. No. 226-02-100 (100 per package), S.K.C. Inc., P.O. Box 8538, Pittsburgh, Penna. 15220.

7. Charcoal adsorption tubes, consisting of a flame-sealed glass tube, 7 cm. long x 6-mm o.d. x 4-mm i.d., containing a 100-mg adsorbing section and a 50-mg back-up section of 20/40 mesh activated charcoal, separated by a 2-mm portion of urethane foam, a 3-mm portion of urethane foam at the outlet end, and a plug of silylated glass wool at the inlet end, with a pressure drop across the tube not exceeding one inch of mercury at a flow rate of 1 liter per minute. These prepared tubes, in packages of 12, are available from A. J. Sipin Co., 386 Park Avenue South, New York, N.Y. 10016.

8. Weighing paper, Glassine, No. 3.

The following equipment is recommended for the type of sampling required, as indicated:

9. Sipin Personal Sampler Pump, Model SP-1, A. J. Sipin Co. (address above) (For personal monitoring).

10. Air sample pump, Unico C-110, Unico Environmental Instruments, Inc. P.O. Box 590, Fall River, Mass. 02720 (for spot sampling).

11. Air meter, LPG 1 cubic foot ST. RDG. Air, Cat. No. AL-110, American Meter Co., 60 East 42nd Street, New York, N.Y., fitted with glass orifice to limit air flow rate to 2 SCFH maximum (for area sampling using house vacuum).

I-E. Reagents (Reagent grade except as noted)

1. Column packing: 12% neopentyl glycol sebacate on Chromosorb W, 60/80-mesh, NAW, NP, Analabs, Inc. North Haven, Conn.

DC 200 Silicone packing may be substituted, or any other packing that will give clean separation of the EDB peak.

2. Ethylene dibromide.

3. Carbon disulfide.

4. Helium Liquid Carbonic Corp., Specs. L-114.

5. Hydrogen, Matheson, Extra dry.

6. Air, breathing, Liquid Carbonic Corp., Specs. L-117.

I-F. Notes

The developing vials referred to above are glass vials, having a capacity of ca 4.5 ml, with a plastic cap having a 1-1/2 mm hole drilled through its center and lined with a "Teflon"-coated rubber septum.

I-G. References

1. NIOSH, Physical and Chemical Analysis Branch, Method No. P & CAM 127, Rev. 6/22/73.

2. Mueller, F. X., and Miller, J. A., American Laboratory, p. 49, May, 1974.

I-H. Appendix

A. Determination of Desorption Efficiency*

The amount of EDB removed from the charcoal in the desorption process for every new lot of charcoal tubes should be determined.

1. From each of six charcoal tubes from the same lot, remove the front or larger section of charcoal, and deposit on a No. 3 Glassine weighing paper.

2. Remove and discard the glass wool, urethane foam, and back-up sections of charcoal.

3. Replace the charcoal previously removed from each tube and cap each tube with a plastic cap.

4. To each of five of the prepared tubes, inject exactly 1 microliter EDB through the plastic cap into the charcoal layer, and immediately seal the punctured cap with "Teflon" tape.

*Desorption efficiency is essentially checked on each sample since both layers of charcoal are analyzed.

One microliter of EDB is equivalent to 1.5 TLV for a 10-minute sample taken at a flow rate of 2 SCFH. Since the TLV is the level of greatest concern, the determination of the desorption efficiency at approximately this level permits the greatest analytical accuracy at the most critical level.

5. The sixth tube is retained as a blank.

6. Allow the tubes to set overnight for complete adsorption of the EDB.

7. After the adsorption period, transfer the charcoal from each tube to six developing vials, and analyze as described in Section II-B of Part II.

8. Prepare three standards by injecting exactly 1 microliter of EDB into each of 3 developing vials, each containing 0.501 ml of carbon disulfide (CS_2), and mix.

9. Analyze the standards along with the above samples.

Calculation

$$\frac{\text{Average Area Sample - Area Blank}}{\text{Average Area Standard}} = \text{Desorption Efficiency}$$

The desorption efficiency for charcoal tubes of Lot 100 was 0.96.

H. V. Pfaff
Petroleum Chemicals Division
December 5, 1974

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II-A Unusual Safety Considerations

1. Product Hazards

Ethylene dibromide is toxic. Wear an air mask if sampling an atmosphere of high EDB concentration.

2. Procedure Hazards

Carbon disulfide is a very toxic and highly flammable (flash point -30°C) whose vapors are heavier than air. Its autoignition temperature is 125°C. Perform all work in a hood, away from any source of heat, and avoid prolonged or repeated contact with skin. Use caution in handling the hypodermic syringe. Keep needle protected when not in use.

II-B Procedure

1. Instrument Settings

Instrument		
Mfg. Wilkens Inst. & Res. Co.		
Model Hy-Fi 600-D		
Detector		
Thermal Cond. [ ]		
Flame Ioniz. [x] Hyd. 7 psig Air 14 psig		
Electron capture [ ] Other		
Carrier gas		
He [x]	N_2 [ ]	Other [ ]
Flow**** 20 psig		

Column	
Mat'l of Const. S.S. 316	
Length* 6 M	Diam** 1/8" o.d.
Packing Substrate 12% Neopentyl Glycol Sebacate	
Packing*** Support Chromosorb W 60/80 mesh, NAW, NP	
Column Temp. °C. 150	Inject Temp. °C. 190
Detec. Temp. °C.	Max. Safe Temp. °C. 225
Programming	
Initial Column Temp., °C.	
Temp. Rise/min., °C.	
Temp. Limit, °C.	
Pre-program Hold, min.	

* Specify units (in., ft., meters, etc.)
** Specify o.d. or i.d. and units
*** Specify mesh size
**** Specify as ml./min. or psig

2. Order of Elution

COMPONENT	RETENTION TIME (SECONDS)	RANGE INVESTIGATED mg/0.5 ml
Unknown	230	-
CS_2	540	-
EDB	740	0.1-2.7

3. Sample Collection

1. Immediately before sampling, break the ends of the charcoal tube to provide an opening at least one-half the internal diameter of the tube or 2 mm.

2. The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

3. The charcoal tube should be placed in the holder in a vertical position during sampling.

4. Air being sampled should enter the charcoal tube directly without passing through any hose or tubing.

5. The sample should be taken at a flow rate of 1 LPM or less for a minimum sample volume of 10 liters (10 minute sample at 2 SCFH).

6. Immediately after sampling, cap the charcoal tube with the plastic caps supplied. Under no circumstances should rubber caps be used.

7. One tube should be handled in the same manner as the sample tube (break ends and seal with plastic caps). This tube should be labelled as a blank.

4. Sample Preparation

1. Remove and discard the glass wool from the inlet end of the charcoal tube.

2. Transfer the front or larger section of charcoal to a developing vial.

3. Similarly, transfer the back-up or smaller section of charcoal to another developing vial.

4. Pipet 0.50 ml of carbon disulfide (CS_2) into each developing vial and immediately cap tightly.

5. Allow to set for 30 minutes with occasional mixing.

6. Prepare two standards by weighing 3 ul and 5 ul of EDB, injected thru the cap into each of 2 developing vials, each containing 4.00 ml (pipet) of CS_2 and tared. Determine the weight of EDB added by difference.

5. Sample

1. Analyze each sample and standard, in duplicate, by VPC, using a 5-ul sample followed by a 2.8 ul CS_2 flush.

   Using the solvent flush technique, the 10-ul syringe is first flushed with CS_2 to wet the barrel and eliminate all bubbles. Then 2.8 ul of CS_2 are drawn into the syringe. With the needle removed from the solvent, the plunger is pulled back 0.2 ul to the 3.0 ul mark. The needle is then immersed in the sample and a 5-ul aliquot is withdrawn, making a total of 8 ul. The needle is then removed from the sample and the plunger immediately pulled back a short distance (0.4 or 0.6 ul) to minimize sample loss from the needle tip by evaporation. Inject immediately into the chromatograph. Duplicate areas should be within $\pm$ 3%.

Calculations

$$\frac{S \times 125}{A_S} = F$$

Where: S = weight of EDB in standard, mg

A_S = area of EDB peak in standard (average of duplicate chromatograms)

$125 = \frac{1000}{8}$ = conversion to 0.5 ml CS_2 and area/1000

F = mg EDB per area/1000

The F value for the 2 standards should agree within 10% of the larger value. Average the 2 values for F.

$$\frac{F \times A_P}{1000} = \text{mg EDB}$$

Where: A_P = area of EDB peak in sample (average of duplicate runs)

1000 = conversion to area/1000

$$\frac{(S_f - B_f) + (S_b - B_b)}{V \times E} = \text{mg EDB/meter}^3$$

Where: S_f = mg EDB found in front section of sample tube

B_f = mg EDB found in front section of blank tube

S_b = mg EDB found in back-up section of sample tube

B_b = mg EDB found in back-up section of blank tube

V = volume of air sampled in cubic meters

E = desorption efficiency (see Section I-H)

If the volume of air sampled is determined on a time basis with a rotameter at 2 SCFH,

$$V = \frac{2 \times .02831 \times T}{60}$$

Where: T = sampling period in minutes

If a Sipin Personal Sampler Pump is used,

$$V = \frac{N_s \times K_v}{10^6}$$

Where: N_s = number of strokes = final counter reading - initial counter reading

K_v = volume factor for pump used (ccs/stroke)

10^6 = conversion ccs to cubic meters

If the volume of air sampled is metered in cubic feet,

V = 0.02831 x cubic feet

H. V. Pfaff
Petroleum Chemicals Division
December 5, 1974

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APPENDIX III

DU PONT INDUSTRIAL HYGIENE DATA

PERSONNEL MONITORING FOR ATMOSPHERIC LEAD*

Sample Date	Location	Sampling Hours	Organic ug. Pb/ Cu.Ft.
6/14/76	536 Bldg.	7.7	1.0
6/22/76	Drum Bldg.	7.2	0.2
6/21/76	Compound Bulk	6.4	0.3
11/3/76	Compound Bulk	7.5	2.6
6/16/76	Blender (856 Bldg.)	7.1	0.4

PERSONNEL MONITORING FOR ETHYLENE DICHLORIDE*

Sample Date	Location	Sampling Hours	mg. EDC/ cu.m.
1/29/75	Shipping & Receiving	8	5.9
1/31/75	Shipping & Receiving	8	1.8
7/14/75	Shipping & Receiving	8	8.7
3/31/76	Blender (856 Bldg.)	6	0.1
4/2/76	Blender (856 Bldg.)	5.8	0.2

FIXED POSITION ETHYLENE DICHLORIDE MONITORING

Sample Date	Position	Sampling Hours	mg. EDC/ cu.m.
3/31/76	EDC Stg. Bldg. #680	6.3	0.2
4/1/76	EDC Stg. Bldg. #680	6.7	0.2

*These breathing zone concentrations do not necessarily reflect what the man actually breathed, since respirator use is specified for certain operations in most buildings.

24-HOUR AIR SAMPLING DATA*

(ug. Pb/cu.ft.)

uilding	Location	Thurs. 6/2	Fri. 6/3	Sat. 6/4	Sun. 6/5	Mon. 6/6	Tues. 6/7	Wed 6/8
6	E. Wall	0.7	0.6	0.7	1.0	1.2	0.6	1.3
	Center	1.9	1.4	1.4	4.2	4.3	1.1	1.3
	N. Door	1.0	0.8	1.0	0.6	0.8	0.9	1.1
L Blender	V.P.	6.6	0.5	0.8	0.6	0.7	0.8	1.0
	S.Bl.	2.3	0.7	0.7	1.0	0.6	0.7	0.6
	W. Wall	–	0.7	1.1	0.8	0.9	0.7	1.7
um Bldg.	D.B.	1.1	1.0	1.0	1.0	1.1	1.1	1.1
	Ch.Wash	2.1	1.4	1.3	1.1	1.6	1.9	1.7
	W.H.	0.9	0.7	0.6	0.6	0.7	0.7	0.8

Above values are for process monitoring so leaks can be identified and corrected; the samples are not necessarily in locations of high personnel occupancy.

8-HOUR PERSONAL MONITORING
FOR EDB AND EDC IN AIR

Date	Major Activities	EDB (mg/cu m Air)	Max. EDC (mg/cu m Air)
1-27-75	Sampled 2 EDB cars; filled 5 gal. can with EDB for lab.	<0.03	(insufficient sample)
1-28-75	Connected, pumped and disconnected 2 EDB cars	0.25	2.00
1-29-75	Sampled 2 EDB cars; took temperature of EDC in cup raised from work tank	<0.03	5.89
1-30-75	Connected, pumped and disconnected 2 EDB cars; trouble with icing required inspection inside top of car several times	4.45	2.23
1-31-75	Sampled 2 EDB cars	<0.03	1.81

EDB CONCENTRATION IN AIR AT SELECTED
SITES IN TETRAETHYL LEAD AREA

Date	Activity	Site	Sample Time	Concentration (mg/cu m)
2/24/75	Sample analyses by laboratory technician	Tetraetyl Lead Laboratory	8 hours	<0.05
11/21/74	Taking EDB quality control sample	Top of EDB tank car	2 min. 40 sec.	23.6
11/5/74	Hookup of EDB tank car for unloading	Ground level by EDB tank car	5 min.	0.47
11/5/74	Emptying of EDB from tank car	Ground level by EDB tank car	4 hours 7 min.	<0.58
11/5/74	Disconnecting hose from empty tank car	Ground level by EDB tank car	2 min.	<0.01
8/12/74	Area sample taken during blending process	Between blenders 3 and 4	—	<0.01

PERSONNEL MONITORING FOR EDB IN AIR

1975 Date	Time Start a.m.	Time Stop p.m.	Volume of Sample, l.	Conc. EDB Found mg./cu.m.*	Remarks
7/10	8	4	23.8	< 0.5	Checked EDB tank level.
7/11	8	4	23.9	1.0	Pumped 2 tankcars, checked tank level.
7/14	8	4	24.1	< 0.5	Sampled 2 tankcars, checked tank level.
7/15	8	?	7.9	< 1.5	Sample pump broken. Started unloading 2 tankcars early in shift.
7/16	8	2:30**	20.2	< 0.6	Sampled 2 tankcars, checked tank level.
7/17	8	4	24.8	1.97	Sampled 1 tankcar and pumped 2. Checked tank level.

* A "less than" (<) sign before number means that EDB was not detected in VPC scan.

**Samples removed early since operator had to work overtime on pier and would not be available at 4 p.m.

R. Moore:emb
7/23/75

Attachment
Table I

EDB-IN-AIR ANALYSES

No.	1975 Date	Time	Location	Sample Volume cu.m.	mg. EDB Found**	Conc. EDB, mg./cu.m.*
1	11/5	8 am-3 pm	Blender Oper. (Clements)	0.0141	< 0.012	< 0.88
2	11/5	8 am- 1:30 pm	EDB Pump House	0.0348	Trace†	< 0.35
3	11/5	9 am- 12 noon	Chainer Transfer	0.0132	< 0.012	< 0.91
4	11/6	8:40 am - 1:30 pm	Top EDB Tank	0.0102	0.087	8.53††
5	11/10	8:20 am - 4:25 pm	Top of TS-8	0.0470	< 0.012	< 0.26
6	11/10	8:15 am - 4:25 pm	Compound Bulk 5-ft. above ground	0.0333	< 0.012	< 0.37

* Compare with TLV of 145 mg./cu.m.

**Lower measurable limit was 0.012 mg. EDB/sample.

† Small amount seen but was below our measurable level. Samples 1, 3, 5 & 6 had no detectable EDB under conditions employed.

†† Two tank cars of EDB unloaded into tank during period. Sampler about 6 ft. from vent.