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16. Abstract (Limit 200 words)

Occupational exposure to methylene-chloride (75092) was studied. An industrial hygiene survey was conducted at Robins Air Force Base, Warner Robins, Georgia, to determine methylene-chloride concentrations. Breathing zone samples were collected from 12 of 22 aircraft stripping workers using charcoal tubes attached to sampling pumps for 6.5 to 7 hours. Ammonia (7664417) area samples were also collected. The range of methylene-chloride exposure concentrations was 15.7 to 268 parts per million (ppm), with an average concentration of 64ppm. The highest exposure concentrations was for the paint stripper personnel working on the aircraft wheel well (a single sample exceeded 200ppm). Ammonia concentrations ranged from less than 1ppm to 5.6ppm, with an average concentration of 3.2ppm. The authors conclude that although measurable amounts of methylene-chloride exist in the paint stripping facility, the time weighted average exposure of workers was below the OSHA standard of 500ppm. The sample exceeding 200ppm was due to inadequate ventilation in the wheel well of the aircraft.

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ROBINS AIR FORCE BASE

Survey Conducted on May 1979

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INTRODUCTION

SRI recommended to NIOSH in its Task II walk-through survey report that a more detailed industrial hygiene survey, including personal sampling, should be conducted at Robins Air Force Base, Warner Robins, Georgia. This recommendation, which was approved by NIOSH, was based essentially on airborne methylene chloride levels in the working environment; possible changes to personal exposures when a new paint stripping facility was to be used; the number of workers potentially exposed to methylene chloride; and on the basis that the process was representative of aircraft paint stripping operations.

The objectives of this report are to:

1. Summarize the current literature relating to the toxicological effects of methylene chloride
2. Document and describe the workplace and industry information on the production and use of methylene chloride.
3. Identify job types and develop specific job descriptions.
4. Describe current industrial hygiene and safety practices.
5. Document worker exposures to methylene chloride as a function of job type and document relevant process and production changes that occurred during the survey which may affect the evaluation of job function exposure.
6. Describe analytical procedures for the collection and analysis of methylene chloride.

Robins Air Force Base is located in Warner Robins, Georgia, and was initially visited on June 15, 1978 to conduct a preliminary industrial hygiene survey and epidemiological feasibility study. It was determined from SRI

sampling data obtained during that visit that airborne methylene chloride levels in the working environment around the stripping operation ranged from 9 to greater than 200 parts per million. Work practice procedures and other process information were also reported.

Robins Air Force Base was again visited during the week of May 14, 1979 to conduct a more detailed industrial hygiene survey to quantify worker exposures to methylene chloride. The focus of this report is on the findings and conclusions from the detailed survey.

BACKGROUND

Methylene chloride, also known as methylene dichloride and dichloromethane, is a colorless, heavy, mobile, and volatile liquid with a pleasant odor.[1] It is considered the least toxic of all the chloromethanes with a current Occupational Safety and Health Administration (OSHA) standard of 500 ppm, based on an eight-hour time weighted average (TWA) exposure.[2] A Threshold Limit Value (TLV) of 200 ppm has been adopted by the American Conference of Governmental Industrial Hygienists (ACGIH). There is a faction within the ACGIH, however, who propose that the TLV be lowered to 100 ppm.[3,4] The basis for the recommended lowering of the standard is to ensure complete protection of workers for carboxyhemoglobin (COHb) hazard. In March 1976, a National Institute for Occupational Safety and Health (NIOSH) criteria document on methylene chloride was released which recommends a still lower TWA of 75 ppm.[5] The basis for these standards will be discussed later on in this section.

It has been estimated that one-half billion pounds of methylene chloride are produced in the U.S. annually.[6] Methylene chloride is widely used for a variety of purposes, including paint stripper, manufacture of photographic film, aerosol propellants, manufacture of triacetate fibers, metal degreasing, extraction in the food products industry, fumigation, and fire extinguishing. Paint removing accounts for this chemical's greatest use.[5,7]

The current OSHA standard of 500 ppm is based on original work by Heppel in 1944. He demonstrated through animal experimentation that methylene chloride is a narcotic and irritant at high airborne concentrations (5,500 - 10,000 ppm).[8] Several reports and studies indicate that methylene chloride can produce stupor, headache, irritability, giddiness, and other central

nervous system effects among exposed workers.[5] At levels well above those normally found in the occupational environment, methylene chloride can cause damage to lungs, liver and kidneys.[5]

Studies in 1970 demonstrate that methylene chloride is metabolized in the body to carbon monoxide, ultimately causing an elevation in COHb.[5,9,10,11] The effect is well documented in the NIOSH criteria document and will not be discussed here. Based on these studies, NIOSH has recommended a TWA of 75 ppm.[5] As part of this recommendation, as well as to account for the concomitant effects of methylene chloride and carbon monoxide, NIOSH recommends that the exposure to methylene chloride be limited so that the combined exposure of methylene chloride and carbon monoxide (when levels of carbon monoxide exceed 9 ppm) follow this equation:[5]

$$\frac{C(CO)}{L(CO)} + \frac{C(CH_2Cl_2)}{L(CH_2Cl_2)} \leq 1$$

where:

$C(CO)$	=	TWA carbon monoxide, ppm
$L(CO$	=	recommended TWA carbon monoxide, ppm
$C(CH_2Cl_2)$	=	TWA methylene chloride, ppm
$L(CH_2Cl_2)$	=	recommended TWA methylene chloride, ppm

Several other effects have been attributed to methylene chloride exposure. A Russian study reported that methylene chloride was found to cross the placenta in pregnant workers.[12] Some teratogenic effects were observed in experimental animals which include incidences of cleft palate and rotated kidneys.[5] Methylene chloride has also been found to be mutagenic in salmonella typhimurium (strains TA100 and TA1535) and E. Coli (WP2) when exposed for 6-8 hours in a desiccator to concentrations as low as 11 ppm.[13]

The Eastman Kodak Company recently reported on the results of an epidemiology study of a large working population exposed continuously to relatively low levels of methylene chloride for up to thirty years. The

purpose of the study was to determine whether employees exposed to methylene chloride exhibited an increased risk for specific causes of mortality, specifically ischemic heart disease that could be attributed to the work environment. Air sampling results based on each sample obtained in the work area revealed a methylene chloride concentration range of 0-350 ppm with a mean value of less than 100 ppm. Continuous personal monitoring showed a time-weighted average concentration of 33 ppm.

While the results are not reported in complete detail, those that are published indicate no excess mortality for ischemic heart disease in the production workers exposed to methylene chloride. It would be helpful to have a detailed presentation of standardized mortality ratios for ischemic heart disesase, to know more about the selection procedure for hiring production workers; to see if the results change when the 7% of employees who have terminated are also included; and to learn whether the results are supported by another mortality study currently being performed by Dow Chemical Company and Celanese Corporation.[14,15]

DESCRIPTION OF THE PROCESS SURVEYED

Description of Base

Robins Air Force Base located in Warner Robins, Georgia (18 miles south of Macon) began operation in 1941 during the defense build-up preceding World War II. The site occupies 7,625 acres of land. The primary mission of the base is to function as one of the several Air Force Logistics Command installations. A map of the base is provided (see Figure 1).

The Warner Robins Air Logistics Center has a three-fold mission:

- It is the worldwide logistics manager for assigned aircraft and commodities.
- It is the repair center for aircraft and five district technologies.
- It serves as a storage center for Air Force spare parts and systems.

Approximately 21,500 personnel (15,000 civilian and 6,500 military) are employed at the base. Approximately 6,500 are involved in the maintenance of Air Force aircraft and equipment.

Personnel

Approximately 106 persons work in the aircraft stripping operation. They work on a three shift, five day per week schedule. The personnel are all designated as Paint Strippers and have a job grade of WG-5. Approximately 22 Paint Strippers work on an aircraft with each worker responsible for the stripping of an assigned area of the plane. General area assignments are:

Location	Number of Workers
nose	4
fuselage, front	2
fuselage, center	2
fuselage, top	2
wing, engine	2
wing	3
wheel well	3
tail section	4
Total:	22

Both men and women are involved in the paint stripping operation and each worker masks off, applies the needed stripper, and washes down the assigned area. In addition to the personnel identified above, there are supervisory personnel, drivers, maintenance personnel, and other "depainter" personnel who may be exposed intermittently to methylene chloride. The exposure duration for these workers is quite variable; however, for most of the paint stripping crew, the exposure to methylene chloride may be up to eight hours per day.

Process and Control Operations

Methylene chloride is used at Robins Air Force Base as the major constituent in stripping compounds for removing paint from the aircraft outer skin. During the Task II survey, the paint stripping operation was conducted in Building 110 close to the flight operations area (see map, Figure 1). Since then, Building 54 (Figure 2), a newly constructed depainting facility, has been completed and occupied, and the bulk of the paint stripping operations now are being conducted in this building.

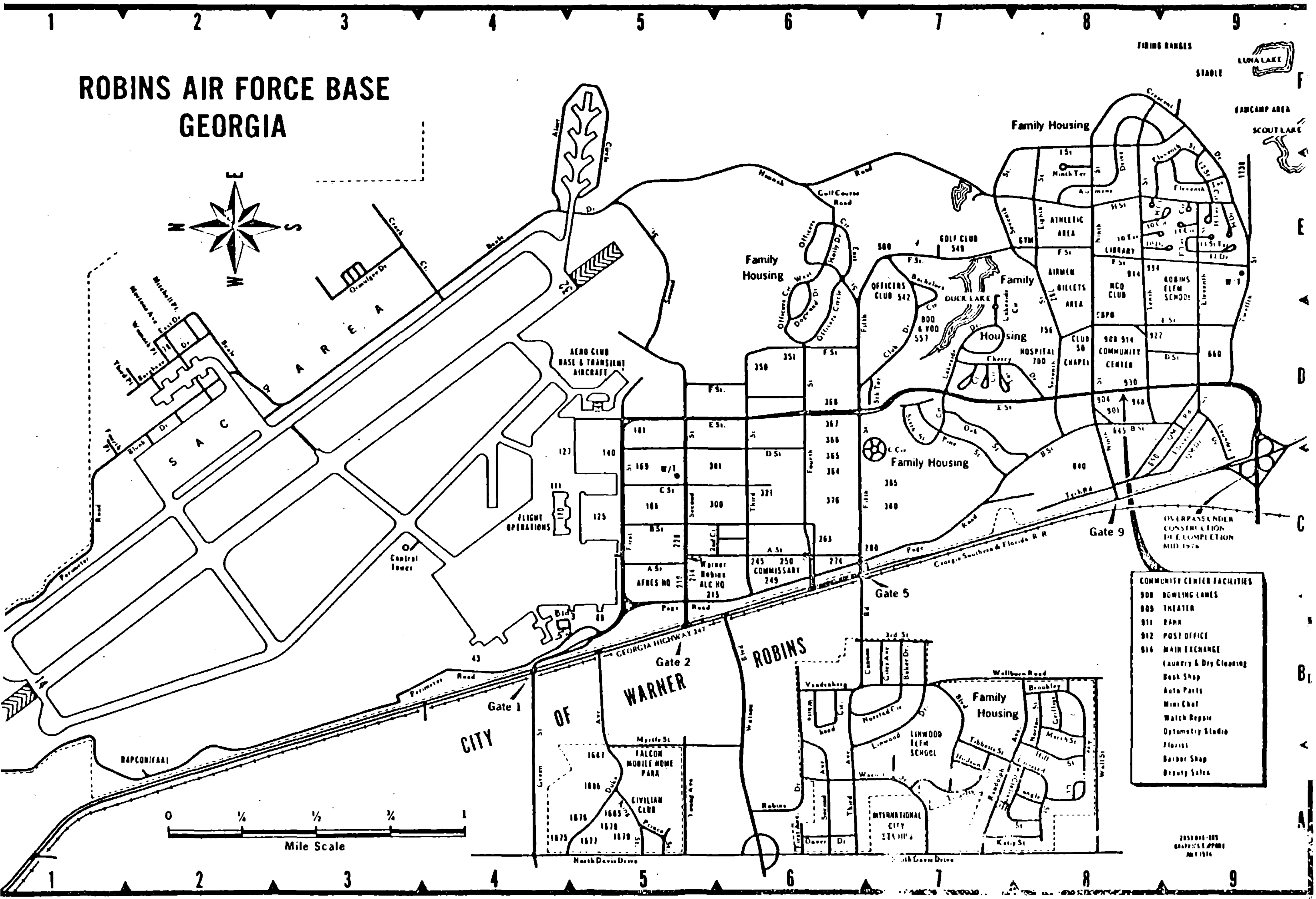
ROBINS AIR FORCE BASE
GEORGIA
Mile Scale
0
¼
½
¾
1
Family Housing
OFFICERS CLUB 542
GOLF CLUB 549
DUCK LAKE
HOSPITAL 700
COMMUNITY CENTER
ROBINS ELEM SCHOOL
LIBRARY
NCO CLUB
ATHLETIC AREA
AIRMEN BILLETS AREA
AERO CLUB BASE & TRANSIENT AIRCRAFT
FLIGHT OPERATIONS
Control Tower
AFRES HQ
Warner Robins ALC HQ
COMMISSARY
GEORGIA HIGHWAY 247
Gate 1
Gate 2
Gate 5
Gate 9
CITY OF WARNER ROBINS
SAC AREA
FALCON MOBILE HOME PARK
CIVILIAN CLUB
LINWOOD ELEM SCHOOL
INTERNATIONAL CITY
RAPCON (FAA)
FIRING RANGES
LUNA LAKE
STABLE
FANCAMP AREA
SCOUT LAKE
OVERPASS UNDER CONSTRUCTION DUE COMPLETION MID 1976
COMMUNITY CENTER FACILITIES
908 BOWLING LANES
909 THEATER
911 BANK
912 POST OFFICE
914 MAIN EXCHANGE
Laundry & Dry Cleaning
Book Shop
Auto Parts
Mini Chef
Watch Repair
Optometry Studio
Florist
Barber Shop
Beauty Salon

FIGURE 1

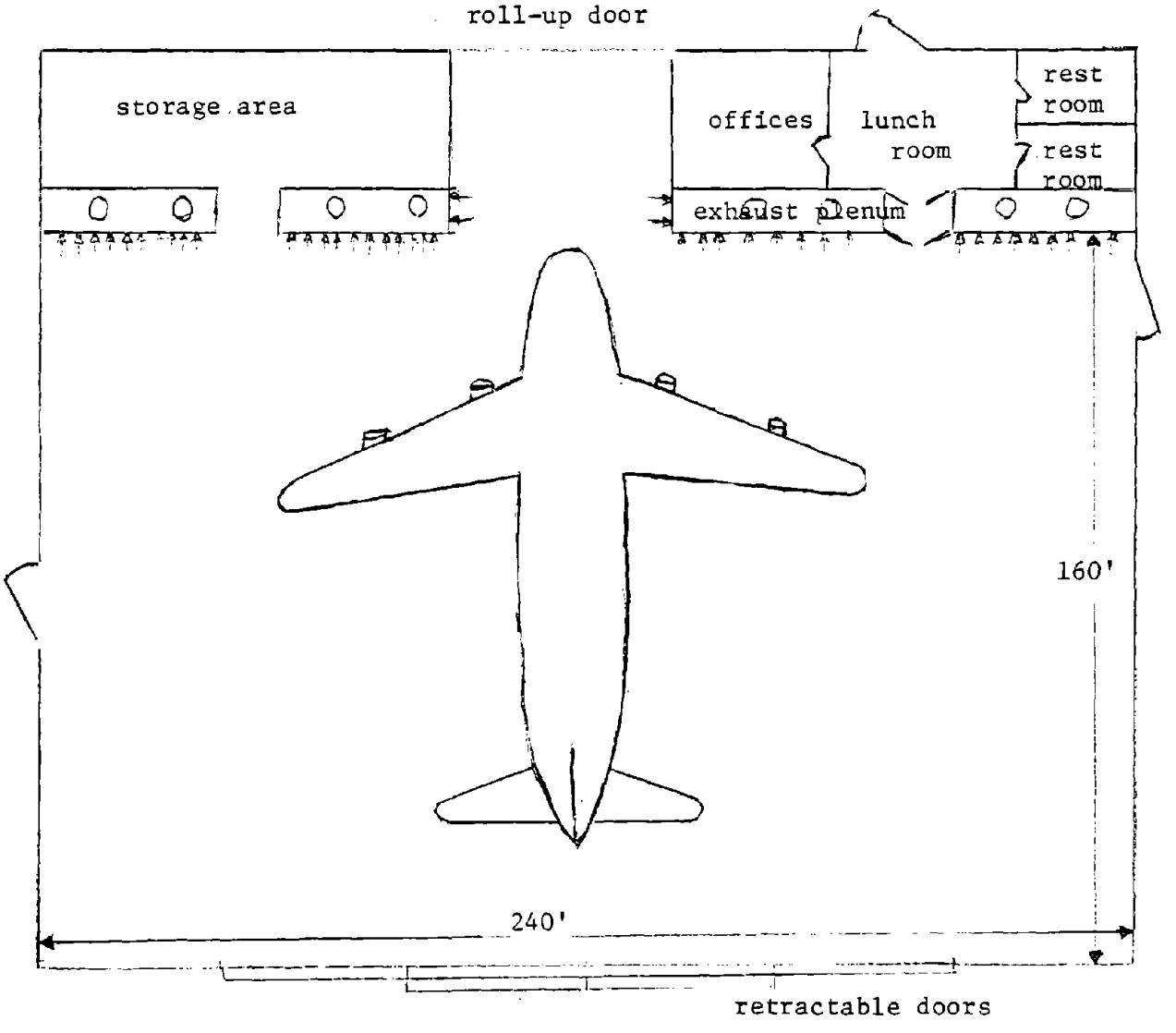

Figure 2

Building 54, Robins AFB

Preparatory to stripping, the parts and equipment which are not to be stripped or which could be affected by the stripping compound are masked and covered with aluminum sheeting and aluminum tape. This operation consumes considerable time but must be performed to protect vital parts from damage.

Once the aircraft is masked, the building doors are closed and the exhaust ventilation fans are turned on. Air enters the building from louver openings in the door and in the side walls. The personnel apply the paint stripping compound to the various sections of the plane. The tail section, approximately 50' high, is sprayed by the depainters working from large, elevated, hydraulically operated lifts. The top and sides of the fuselage are sprayed by personnel working from two cages suspended from overhead cranes. Controls on this equipment enable the operator to raise or lower the lift or cage as well as to move them from side to side in order to attain the desired location. In addition to the personnel in the overhead cages and on the lift, there are persons applying the stripper from the ground, from elevated platforms, and hydraulically operated stairs.

The stripping compound initially used is Intex 857 "mild" stripper which contains approximately 50% methylene chloride, 25% aliphatic and aromatic hydrocarbons, 10% non-volatile hydrocarbons and 14% water and ammonia. This compound is supplied in large 300 gallon containers which are positioned at appropriate locations near the aircraft. Two containers are placed on either side of the tail section while two others are positioned on each side of the fuselage in front of the wings.

Pneumatically operated pumps placed in the containers force the stripping compound through hoses to the spray handle. The stripper is sprayed onto the painted surfaces in the form of a fine mist, in most instances working from above and directing the spray downward. For certain areas, such as the under-

side, the spray was directed upwards but by proper positioning of the lift and cages this was kept to a minimum. Several coats of the "mild" stripper are applied with scraping and brushing of the surfaces being performed in between to assist in loosening and removing the paint. Spot applications of a phenolic based "hot" stripper are made to stubborn areas to complete the job. Table 4 lists several of the stripper solutions which could be used for this operation.

Tools used for the stripping and removal of the paint include a polypropylene scrubbing brush, a rubber squeegee, aluminum wool on a mop handle, wire brush, and a scraping tool. These aid in loosening the paint and in polishing the aircraft surface.

For applying the stripping compound to small areas such as around the windows in the cockpit, a bristle brush dipped in an open plastic pail of stripper is generally used.

Approximately 1000 gallons of the non-phenolic "mild" stripper is used for an aircraft. Another four to fifteen drums (average six drums) of "hot" phenolic stripper is used for the final coat application.

The new depainting facility, Building 54, is approximately 240 feet long and 160 feet wide with a ceiling 70 feet high. Its orientation is with the length of the building in the North-South direction. The East wall of the building consists of overlapping sliding doors which are electrically operated and are opened to permit the aircraft to enter the bay. When depainting, the doors are kept closed and the exhaust ventilation fans on the opposite west wall of the facility are activated, creating an air flow east to west of approximately 25-50 linear feet per minute. At the entrance to the exhaust plenum, directly in front of the filters, the air velocity ranged from 100 fpm to as high as 625 fpm. These values were attained with three of the four

fans in an operating mode. Additional air removal is provided by a system pulling vapors through gratings into a trough located in the floor.

The aircraft being stripped during the survey was a C-130 Hercules cargo plane. The work on the plane would continue for approximately nine full shifts before the entire stripping job is completed.

Health and Safety Programs

As described in the Task II report, the safety, medical, and industrial hygiene programs at the Base are the responsibility of the Safety Officer, Occupational Medical Services, and Bioenvironmental Engineering Services, respectively. The Safety Officer is responsible to the Air Logistics Center (ALC) commander for flying, ground, explosive ordinance, and missile safety programs. ALC safety function consists of 19 persons. This group is responsible for safety in the paint stripping and other ground maintenance activities.

The Bioenvironmental Engineering Services Division consists of four military officers, one civilian industrial hygienist, two civilian industrial hygiene technicians, and five military industrial hygiene technicians. This group is under the direction of Lt. Colonel A.H. Perry.

The Occupational Medical Services consists of three physicians, four nurses, and several technicians and other ancillary staff. These people operate a dispensary which is open from 0730 to 1600 hours. A hospital located on the Base supplements the services of the dispensary during the off hours.

Pre-employment physical examinations are required of all Air Force personnel (except those in clerical positions). These physicals include medical history, audiograms, chest X-ray, EKG (if over 40), tests for vision, serology, and urinalysis. Annual examinations are required for certain jobs (paint stripping is a required job group) and are tailored to the exposure.

Annual physicals are similar to the pre-employment examination. Those workers who perform paint stripping receive, in addition to the tests already mentioned, SGOT, audiometric examination, total blood count, and urinalysis annually. Exit physicals are required in certain jobs such as those that expose workers to high noise levels.

Personnel working in the depainting areas are required to wear protective clothing which includes coveralls, monogoggles, rubber gloves, safety shoes or rubberized boots. Organic vapor cartridge half mask respirators were required while the stripping operation was conducted in Building 110; however, with the exhaust ventilation system in the new facility, respirators are no longer required.

Every area on the Base has established requirements for protective clothing and equipment specific to the operation. Workers are able to change from their work clothing in the locker room of Building 54 and the clothing may be left to be laundered by a private contractor.

METHODOLOGY

Walk-Through Survey

On June 15, 1978, a walk-through survey was conducted at Robins Air Force Base to determine if the aircraft paint stripping operation was suitable for a more detailed industrial hygiene survey to quantify worker exposure to methylene chloride and to conduct a retrospective mortality study on persons exposed to this chemical. Based on the findings from this survey, NIOSH determined that a suitable population could not be identified at this plant. However, preliminary air sampling in the depainting facility, using a Century Systems Organic Vapor Analyzer and charcoal tube personal and area sampling indicated the presence of the solvent in concentrations varying from 9 to 57 ppm for area samples and 113 to 206 ppm for personal samples. Charcoal tube area and personal samples for toluene ranged from below detectable limits to 2.2 ppm as a personal sample. Table 1 presents the results of the charcoal tube sampling performed during the walk-through survey.

In-Depth Survey

The survey team sampled for methylene chloride on 12 of the 22 plant stripping crew members in Building 54. Breathing zone samples were collected on these personnel during the period they were involved in the stripping operation, using charcoal tubes attached to sampling pumps. Total sampling time for the personal samples ranged from approximately 6.5 to 7 hours. Due to the very low toluene levels found during the walk-through survey, it was decided not to sample for toluene during the in-depth survey.

Several area samples were collected for the presence of ammonia in the stripping compound. These samplers were attached to the railing of the elevated platform and collected for a period of approximately 1 hour at several intervals during the day.

Ammonia concentrations were also measured with a Draeger indicator tube and a Draeger hand-held bellows pump. The ammonia-containing air is drawn through the indicating packing in the glass tube and, in the presence of ammonia, the packing turns from a yellow color to black. The length of stain or discoloration corresponds to the concentration of ammonia present. In several locations, the detector tube indicated the short term concentration to be approximately 1 ppm and in one instance the level detected was approximately 5 ppm.

SAMPLING AND ANALYTICAL

Personal and area environmental samples of methylene chloride vapors and ammonia were collected from the air within the aircraft stripping facility, Building 54, at Robins Air Force Base. Personal sampling employed MDA Accuhaler® sampling pumps which were attached to belts worn by the workers. Tubing connected the pump to the sampling media, two charcoal tubes (one large tube in front, a standard tube as the back-up) manufactured by SKC. The two charcoal tubes were connected by tygon tubing and were used to detect overloading or pulling through of the methylene chloride. Also the use of the two tubes eliminates the possibility of sample migration after the sample is collected. The large tube contains a total of 600 milligrams (mg) of charcoal and the standard charcoal tube contains 150 mg. Each tube is separated into two sections, two-thirds of the charcoal in front with a porous urethane foam plug separating the second section containing the remaining one-third of the charcoal. Silylated glass wool is installed in front of the first section to hold the charcoal in place and a second urethane foam plug is inserted in the tube behind the second section. The charcoal tubes are intended to be used individually, however, with the problem of migration and possible overloading or pull-through, the sampling method required the two tubes in series.

The entire charcoal content of the front tube was combined and formed the primary section while the standard tube was used as the backup tube and analyzed separately.

The sampling pumps were used to draw air through the sampling train at a nominal rate of 20 milliliters per minute (ml/min). Calibration of the

pumps was performed prior to use of the pumps and rechecked following the survey using a bubblemeter (an inverted buret) and measuring the flow over a set period of time.

While the sampling for methylene chloride was performed for a 6.5 to 7 hour period and not the entire 8 hours, the exposure for the individuals is not expected to vary for the 1-1.5 hours not sampled. Therefore, a time-weighted average (TWA) exposure has been calculated for each person as an eight-hour TWA. The calculation was:

$$\text{TWA (ppm)} = \frac{24{,}450 \times \text{mg per liter}}{\text{MW}}$$

TWA is expressed as parts of methylene chloride vapor per million parts of air.

MW = molecular weight (methylene chloride = 84.93)

mg per liter = milligrams of methylene chloride in one liter of air sample collected

The analysis of the methylene chloride samples was accomplished using the NIOSH-approved analytical method S329 (see Appendix B) with minor adjustments in technique. Once the samples had been collected, the NIOSH method required desorption of the charcoal using 1 ml of carbon disulfide. However, since 600 mg of charcoal were used in the primary adsorbing tube, it was decided to desorb with 2 ml of carbon disulfide. Desorption time of at least 30 minutes was used. Following desorption, a portion of the sample was injected into a Gas-liquid chromatograph equipped with a flame ionization detector. The area under the sample peak was measured and integrated and the results were read directly from a standard curve that was prepared earlier from injections of known quantities of methylene chloride. Each tube (front and backup combined) was analyzed separately.

Desorption efficiency (DE) tests were performed for the analytical method described above. The results of these tests indicated good precision and

accuracy with the NIOSH-approved method. The average DE was .97 $\pm$ .02 (from 18 samples) and recovery was also very good, with an average recovery of .95 $\pm$ .03 for 17 samples (approximately six in each of three test levels).

The sampling for ammonia was performed using Draeger indicator tubes as well as a dilute sulfuric acid solution (10 ml) in a midget impinger and using a Bendix Model BDX-44 sampling pump to draw air through the absorbing solution at the rate of one liter per minute. The flow rate on the pumps were determined by calibration with the bubblemeter. The flow indicator on the pump was checked periodically during the sampling period and adjusted as necessary.

Following collection, the absorbing solution was transferred into glass vials and capped. Analysis was performed using NIOSH Method No. P&CAM 205. Nessler reagent is added to the collected sample to produce a yellow-brown complex. The absorbance of the yellow-brown solution at 440 nanometer is read on a spectrophotometer and is compared with a standard curve to determine the ammonia concentration.

RESULTS AND DISCUSSIONS

The in-depth survey of the depainting operation at Robins Air Force Base was limited to a single shift due to aircraft scheduling difficulties. During the day shift on May 15, 1979 paint stripping personnel were requested to wear portable sampling pumps with charcoal adsorbing tubes attached. Methylene chloride concentrations were calculated following analysis of the collected samples and are presented in Table II. Area samples collected for the presence of ammonia were analyzed and are shown in Table III.

Time-weighted average (TWA) exposures for depainting personnel working in Building 54 were well below the permissible exposure limit (OSHA) of 500 ppm and with one exception (Sample R-10) below the American Conference of Governmental Industrial Hygienist (ACGIH) recommended Threshold Limit Value (TLV) of 200 ppm. The range of methylene chloride exposure concentrations was 15.7 to 268 ppm with an average concentration of 64 ppm.

The highest exposure concentration was to the paint stripper personnel working on the wheel well of the aircraft. This may indicate possible disruption of the airflow and the creation of stagnant pockets of air which result in higher vapor concentrations being present. Other locations were less than 100 ppm, indicating that the exhaust removal system in the building was functioning well.

In comparison, during the walk-through survey the previous year, the stripping operation was conducted in Building 110 which had no exhaust ventilation system and relied upon natural ventilation through open doors to dilute and disperse the vapors. The wind movement was sufficient at the time of the initial survey and the results of the area and personal sampling

indicated methylene chloride concentrations similar to those detected during the recent survey. However, the new facility is definitely an improvement over the previous building since it can be used regardless of outdoor weather and meteorologic conditions.

Ammonia concentrations were determined by area samples using impinger with absorbing reagent and ranged from less than 1 ppm to 5.6 ppm. Average concentration for the workday was 3.2 ppm. Present permissible exposure levels (OSHA) for ammonia is 50 ppm with the ACGIH TLV currently at 25 ppm. The levels present in the depainting facility were well below these standards and should not be considered as an exposure problem.

CONCLUSIONS

From the data collected during this survey and from the previous walk-through survey, the following conclusions are made:

- Measurable amounts of methylene chloride exist in the work area atmosphere and time-weighted average concentrations ranged from 15.7 to 268 ppm.
- The TWA exposure of workers to methylene chloride during the depainting operation was found to be below the current OSHA standard of 500 ppm and with one exception, below the ACGIH TLV of 200 ppm.
- The single sample exceeding 200 ppm was for a worker in the wheel well of the aircraft. Possible airflow problems or inadequate ventilation to this location may exist.
- The new facility for depainting of aircraft appears to be well designed and equipped to maintain potential worker exposure within acceptable levels.

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A P P E N D I X A

RESULTS

TABLE I

CHARCOAL TUBE - AREA/PERSONAL MONITORING RESULTS

Robins Air Force Base, Warner Robins, Georgia

Walk-Through Survey Conducted June 14, 1978

Sample Location	Time (min)	Volume (liters)	Concentration (ppm) Methylene Chloride	Toluene
right side cage (back)	314	13.55	53.3	0.6
left side cage (front)	316	0.48*	BD	BD
right side cage (front)	313	10.96	57.3	0.5
left side cage (back)	319	14.86	19.8	0.2
left tail cage	296	1.23	9.4	BD
right tail cage	294	5.34	36.1	0.5
Personal Samples				
H.	112	5.22	113.0	0.8
J.J.	112	1.07	139.0	1.2
J.B.	110	5.43**	206.2	2.2
Blank			BD	

* Sampling pump stopped -- results are questionable

** Two injections of this sample did not closely agree - results are questionable.

BD means below detectable limits.

The front and back charcoal tubes were analyzed separately. Methylene chloride and toluene recovery was based on the total value from both the front and back tubes. All back-up tubes contained less than detectable limits for methylene chloride and toluene.

TABLE II

PERSONAL SAMPLING RESULTS

Methylene Chloride

Robins Air Force Base, May 15, 1979

Sample Number and Location*		Sampling Time (min)	Volume (liter)	Methylene Chloride	
				Amount Detected (mg)	Concentration (ppm)
R-1	Tail section, right side, J.R.	432	6.7	692	28.7
R-2	Fuselage, right side, R.R.	428	9.3	718	21.4
R-3	Fuselage, right front side, L.B.	423	5.9	851	40.1
R-4	Wing, I.H.	417	10.5	1250	33.1
R-5	Fuselage and top, M.G.	414	9.4	532	15.7
R-6	Wing, E.B.	411	2.9	958	91.7
R-7	Wing, engine, D.W.	412	11.2	1197	29.7
R-8	Fuselage, Center, T.F.	414	2.0	638	88.6
R-9	Tail section, left side, J.J.	409	3.5	426	33.6
R-10	Wheel well, J.H.	407	4.4	4260	268.0
R-11	Wheel well, tail, J.H.	404	5.0	1516	84.2
R-12	Tail section, right side, R.T.	408	5.8	585	28.0
R-13	Blank	---	---	ND**	

* Location refers to area of aircraft worked primarily

** ND - none detected - detection limit: 10 micrograms

The front and back tubes were analyzed separately. All backup tubes contained less than detectable limits of methylene chloride.

TABLE III

AMMONIA AREA SAMPLING RESULTS

Robins Air Force Base

May 15, 1979

Sample Number, Location	Sampling Time (min)	Volume (liter)	Ammonia Detected (µg)	Concentration (ppm)
1 - Left side, front fuselage	63	63	42	0.9
2 - Right side, front fuselage	69	69	96	1.9
3 - Right side, front fuselage	56	56	72	1.8
4 - Left side, front fuselage	50	50	184	5.1
5 - Left side, front fuselage	60	60	58	1.3
6 - Right side, front fuselage	59	59	60	1.4
7 - Left side, front fuselage	37	37	150	5.6
8 - Blank	--	--	7.3	

TABLE IV

GENERAL CHEMICAL COMPOSITION - CLEANING COMPOUNDS

TURCO 5351 THIN:	Phenols	24%
	Methylene Chloride	48%
	Caustic Soda	1%
	Water, Soaps, & Corrosion Inhibitors	
TURCO 5873:	Methylene Chloride	58%
	Water	18%
	Ammonia	2%
	Xylene	3%
	Pine Oil	6%
	Chromate as total Cr.	2000 ppm
PENNWALT 739-A: (Hot Strip)	Methylene Chloride	55%
	Sodium Chromate	1%
	Phenols	15%
ELDORADO PR-3400:	Methylene Chloride	72%
	Tetrahydrofuran	2%
	Ethanol	4%
	Ammonium Hydroxide	6%
	Potassium Hydroxide	3.5%
INLAND CHEM. CO. AP-599:	Methylene Chloride	75%
	Perchloroethylene	2%
	Petronate HL	6.7%
	Ammonium Hydroxide	3.7%
	Methanol	8.8%
	Sodium Chromate	0.5%
INTEX 857	Methylene Chloride	50%
	Aliphatic and Aromatic Hydrocarbons	25%
	Nonvolatile Aliphatic and Aromatics	11%
	Water and Ammonia	13%
	Chromates	0.16%
PENWALT 768-A:	Data not readily availabe	
	Phenolic-type paint remover	
ALODINE:	Chromate Salts	1/2-3 oz/gal
	Nitric Acid (PH - 1.5-2.0)	8-12 mg/gal
	Inert Ingredients	

A P P E N D I X B

NIOSH ANALYTICAL METHOD FOR THE DETERMINATION OF METHYLENE CHLORIDE IN AIR

Methylene Chloride

Analyte:	Methylene Chloride	Method No.:	S329
Matrix:	Air	Range:	1700-7100 mg/cu m
OSHA Standard:	1000 ppm (3475 mg/cu m)-Ceiling 500 ppm (1740 mg/cu m)-T.W.A.	Precision (CV_T):	0.073
		Validation Date:	6/6/75
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC		

1. Principle of the Method

   1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

   1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

   1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

   1.4 The area of the resulting peak is determined and compared with areas obtained from injection of standards.

2. Range and Sensitivity

   2.1 This method was validated over the range of 1700-7100 mg/cu m at an atmospheric temperature and pressure of 25°C and 763 mm Hg, using a 1-liter sample. Under the conditions of sample size (1-liter) the probable useful range of this method is 350-10,400 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 10.4 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

   2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 23.3 mg of analyte when a test atmosphere containing 6726 mg/cu m of analyte in air was sampled at 0.187 liters per minute for 18.5 minutes; breakthrough was observed at this time, i.e., the concentration of analyte in the effluent was 5% of that in the influent. The breakthrough data are based on a prior experiment.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 1700-7097 mg/cu m was 0.073. This value corresponds to a 254 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 2.8% lower than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3).

6.2 Charcoal tubes: Separate front and backup glass tubes with both ends of each tube flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D. Each tube contains the appropriate amount of 20/40 mesh activated charcoal. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The front adsorbing tube contains 100 mg of charcoal, the backup tube contains 50 mg. A plug of silylated glass wool is placed at each end of the charcoal tubes. The pressure drop across the tubes must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (20-ft x 1/8-in stainless steel) packed with 10% FFAP stationary phase on 100/120 mesh Supelcoport.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 1.0 ml, graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 Methylene Chloride, reagent grade

7.3 Decane, or other suitable internal standard

7.4 Purified nitrogen

7.5 Prepurified hydrogen

7.6 Filtered compressed air

8. Procedure

8.1 Cleaning of equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tubes to provide an opening at least one-half the internal diameter of the tube (2 mm).

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

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 For determining the ceiling and peak concentrations, a maximum sample size of 1.0 liter is recommended; sample for 5 minutes at a flow of 0.2 liters per minute. For determining the TWA concentration, a sample size of 2.2 liters is recommended; sample at a flow of 0.05 liters per minute or less. The flow rates should be known with an accuracy of at least $\pm 5\%$.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) Nitrogen carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 60°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

Six tubes at each of three concentration levels (0.5X, 1X and 2X of the OSHA ceiling) are prepared by adding an amount of analyte equivalent to that present in a 1.0-liter sample at the selected level. The tubes are allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$\text{D.E.} = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube
mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$ppm = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.