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IN-DEPTH INDUSTRIAL HYGIENE REPORT OF THE AMERICAN ENKA COMPANY

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DATES OF SURVEYS:
March 6-14, 1979
March 26-April 13, 1979

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PURPOSE OF STUDY:	The purpose of this study was to collect the industrial hygiene data as part of NIOSH's cross-sectional medical and industrial hygiene study to determine the health effects of an occupational exposure of at least one working year to a documented carbon disulfide level approximating the current OSHA exposure limit of 20 ppm.
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STANDARD INDUSTRIAL CLASSIFICATION:	2823

ABSTRACT

Under the Occupational Safety and Health Act of 1970, the National Institute for Occupational Safety and Health (NIOSH) was given the mandate to conduct research and health studies for the development of health standards for a broad range of occupational environments. In compliance with this mandate the Industrywide Studies Branch of the Division of Surveillance, Hazard Evaluations and Field Studies has conducted a study entitled "A Cross Sectional Medical and Industrial Hygiene Survey of Workers Exposed to Carbon Disulfide". The study was divided into three categories, behavorial/psychological, medical and industrial hygiene.

Industrial hygiene surveys were conducted at the American Enka Company in Lowland, Tennessee on March 6-14, 1979 and March 26-April 13, 1979. The purpose of the survey was to determine workers exposure to carbon disulfide (CS_2) as part of NIOSH's cross-sectional medical and industrial hygiene study to determine the health effects of an occupational exposure of at least one working year to a documented CS_2 level approximating the current OSHA exposure limit of 20 ppm.

The American Enka Company located in Lowland, Tennessee was selected because it had detailed historical environmental sampling data on CS_2 which documented a work environment less than the 20 ppm standard for CS_2. The purpose of this industrial hygiene report is to document the work performed by NIOSH in developing an exposure profile which was used to support the medical study.

The results of the surveys confirmed the hypothesis that the environmental exposure to CS_2 was less than 20 ppm. A total of 262 personal samples were taken for CS_2 for a determination of time-weighted average (TWA) exposure. The TWA mean concentration for the 262 samples taken by NIOSH was 4.8 ppm. The job categories with the highest mean exposure were the staple spinner with a mean of 12.6 ppm and the washer operator with 11.0 ppm.

Since caprolactam, methanol, dimethylterephthalate, ethylene glycol and Dowtherm were used in the manufacture of nylon and polyester, some exposure to these materials by the control group was conceivable. Air analyses of the workers' environment had one detectable sample of 3.9 ppm caprolactam and a mean concentration of 2.6 ppm ethylene glycol. Air analyses for all other compounds were below the level of detection.

INTRODUCTION

Under the Occupational Safety and Health Act of 1970, the National Institute for Occupational Safety and Health (NIOSH) was given the authority and responsibility to conduct research and health studies for the development of health standards applicable to a broad range of occupational environments. In compliance with this mandate, the Industrywide Studies Branch of the Division of Surveillance, Hazard Evaluations and Field Studies has conducted a research study entitled "A Gross Sectional Medical and Industrial Hygiene Survey of Workers Exposed to Carbon Disulfide."

The study was designed in May 1977 after NIOSH released a criteria document with a recommended standard for occupational exposure to carbon disulfide (CS_2). NIOSH recommended "that carbon disulfide concentrations in workplace air not exceed 3 mg/cu m (1 ppm) as a 10 hour TWA (time weighted average) concentration during a 40-hour week" [29]. This represented a considerable change from the present standard of 20 ppm.

The NIOSH recommended standard was based on numerous human studies (see Table I) suggestive that carbon disulfide affects the cardiovascular system, the nervous system, the retinal vessels, and the reproductive system. Some of these studies were adequate but dealt with CS_2 exposures much higher than is usually seen in American workplaces. Therefore, a comprehensive medical and industrial hygiene study involving an American worker population exposed to the current standard of 20 ppm or less was planned and conducted at the American Enka Company in Lowland, Tennessee on March 6 - 14 and March 26 - April 13, 1979. The company manufactures rayon staple, synthetic filament and polyester staple. The viscose rayon industry was selected because all the human exposure information forming the basis for the recommended standard for occupational exposure to CS_2 has been taken from data derived from this industry. The American Enka Plant in Lowland, Tennessee was selected as the population to be studied because it had detailed work histories and a documented work environment less than the 20 ppm standard for CS_2. The industrial hygiene data collected by NIOSH during these surveys will be presented in this report. This industrial hygiene report is a compilation of the historical data obtained from the Company and the NIOSH personal sampling data. The NIOSH personal industrial hgyiene data was analyzed along with the historical CS_2 area samples taken by the Company between 1949 and 1978 to develop an exposure profile for each job category. The results of the industrial hygiene surveys will be used to support the medical study.

Data collected in the field study on March 6 - 14, 1979 was also used to support the graduate work of Dr. Marcel-Andre Boillat. The goal of Dr. Boillat's study was to present, discuss and hopefully answer two questions:

1. What can be expected from the iodine-azide test in the biological monitoring of workers exposed to levels of carbon disulfide at or below 20 ppm?

2. At the levels of exposure at or below 20 ppm, is there a progressive building up of CS_2 metabolites, manifested by a decreasing

E index (exposure coefficient to express the results of the iodine-azide test in the urine) in workers exposed over a seven day period?

The results of these survey objectives have been published in thesis form [1].

HEALTH EFFECTS OF CARBON DISULFIDE

Since it was synthesized by Lampadius in 1793, [2] carbon disulfide has found widespread use in many areas and in many cases has produced unwanted effects in humans that come in contact with it. Its use as an anesthetic gas caused hallucinations, headache, and nausea [3]. Its use in the India rubber industry, common in the mid 1850's, caused loss of "...will power... [and caused] self contempt" [4]. With the onset of large-scale rubber production in the early 20th century, symptoms of mania were reported. Steel bars were placed over the windows in the plants to prevent suicides. [5] As the viscose rayon industry developed, more varieties of carbon disulfide intoxication were reported. These included tingling and numbness of the extremities, weakness of limbs, loss of appetite, weight loss, severe and localized headache, sexual dysfunction, impaired vision, and gastrointentestinal disturbances [6,7]. Table 1 outlines the health effects of carbon disulfide exposure with references to some of the important papers detailing the investigational procedures and findings.

Table 1
Health Effects of Carbon Disulfide

A. Cardiovascular Effects
   1. Hypertension [8, 9]
   2. Coronary Heart Disease [8-11]
   3. Impaired Cardiac Contractility [12]
   4. Retinal Microaneurysms [13-18]

B. Psychiatric Effects [6]

C. Neuropsychological Effects
   1. Peripheral Neuropathies [19-21]
   2. Psychomotor Losses [22]
   3. Visual Function Alterations [23-24]

D. Endocrine and Metabolic Effects
   1. Diabetogenic [14, 17, 18]
   2. Hypercholesterolemia [9]
   3. Thyroid disorders [3, 25]
   4. Trace metal depletion [4, 7]

E. Reproductive Effects [26]

DESCRIPTION OF THE FACILITY

The American Enka Company started production of rayon filament in 1948 and rayon staple in 1956. The rayon filament production terminated in 1974. Other products, nylon and polyester, are also made at this facility. The nylon filament plant began operations in 1963, the polyester filament in 1966, and the nylon polyester staple plant in 1967.

The site had a total workforce of 3397 (April 23, 1977). There are 296 production workers in the viscose rayon staple area. Most employees are male. Some women are employed on the site, but not in the area of CS_2 exposures.

DESCRIPTION OF SAFETY, INDUSTRIAL HYGIENE AND MEDICAL PROGRAMS

The safety and health program at the site is under the direction of a qualified industrial hygienist. Each plant (rayon staple, nylon and polyester staple, nylon and polyester filament) has a safety and health coordinator who is responsible for the program at that plant. Carbon disulfide and hydrogen sulfide area samples are collected routinely at the rayon staple plant using a gas absorption bottle train and spectrophotometric analysis. Area samples have been collected since the rayon staple plant started production. Personal samples for CS_2, using charcoal tubes, began in early 1974 and continues on a regular basis. A continuous monitor for CS_2 has recently been purchased and is undergoing testing. A continuous monitor alarm system for hydrogen sulfide is in operation. Routine samples for lead and asbestos are collected when maintenance work involves handling these substances.

There is a full time physician at the site. A licensed nurse is on duty each shift with two nurses on the day shift. In addition, at least two other employees per shift have had informal first aid training. A required pre-employment medical examination includes a physical exam, chest x-ray, audiometric tests, blood profiles, visual tests and urinalysis. Periodic medical exams are given to employees with certain jobs depending on their work place exposures (lead). Since 1974, periodic iodine azide urine tests have been given to workers exposed to CS_2.

There is a formal safety program at the plant with five people devoted full time to it. Protective equipment required in various areas of the site include safety shoes, rubber gloves and aprons, goggles, and respirators. There are shower and clothes changing facilities in some areas of the site. The company supplies safety and health manuals detailing safety and health hazards and precautions to workers. Periodic safety meetings are held to emphasize existing precautions and introduce new safety topics.

DESCRIPTION OF THE PROCESSES

Rayon Staple Process:

The rayon staple plant consists of an enclosed multi-level building which accepts raw material for the process and converts these materials into a

marketable bale of rayon staple. A detailed discussion will be made of the rayon staple process. However, the synthetic filament and polyester staple plant which were used for comparison purposes in the medical study will be discussed using flow diagrams only (see Appendix 1 and 2).

A flow diagram for a typical viscose rayon staple process is given in Appendix 3. Cellulose, sodium hydroxide, carbon disulfide, modifiers (ethoxylated natural fatty acids) and water are the raw materials used in the manufacture of rayon staple. The first step is "mercerizing" in which the soaking press operator places sheets of pulp on edge in a tank approximately 20 feet long by 8 feet wide and 3 feet deep, divided into approximately 4 inch compartments by perforated plates mounted on a track. The mercerizing liquor is comprised of 18-20% sodium hydroxide and 0.5% to about 1.8% hemicellulose, at a temperature of about 25°C. The sheets are submerged in this solution and soaked for approximately 2 hours. The tanks are then drained and pressure is applied to the sheets until the weight of the alkali cellulose is approximately 2.8 times that of original cellulose.

The alkali cellulose is dumped from the soaking press into a shredder, where it is broken up and fluffed. This process provides uniform access of the alkali cellulose to air during aging and, subsequently, uniform access to CS_2. The cellulose is now referred to as "crumb". The shredded cellulose is removed and transported by the shredder operator in steel containers to a temperature controlled storage room where it will remain for 20-40 hours.

The "xanthation" process is carried out when the alkali cellulose crumbs are introduced into a churn, vacuum is applied and the CS_2 is drawn in to the churn. The churn is agitated for approximately 2 hours, resulting in orange colored crumbs. The reaction between the alkali cellulose and the CS_2 produces a soluble sodium xanthate derivative. The xanthated crumbs, are then dissolved in a sodium hydroxide solution to make an orange colored viscose slurry. This reaction takes approximately 3 hours and is controlled by the dissolver operator. This process introduces CS_2 to the reaction and creates the potential for CS_2 exposure. The potential for CS_2 exposure exists throughout the process until the drying operation is completed.

The viscose from the dissolver is transferred to a large blending tank to minimize possible variations in viscosity, composition, and degree of xanthation. From the blender, the spinning tank operator pumps the viscose through a series of filters. The filtration operation is handled by the receiving and filtration operator. The prime objective of this operation is to remove contaminants and undissolved cellulose particles. The filtered viscose is then pumped to a ripening and deaeration tank. The degree of ripening determines the physical properties of the final product.

The viscose is now ready to be spun. In spinning, several reactions take place simultaneously. First, exposure of the viscose to sulfuric acid permits coagulation which forms a skin around the filament which then regenerates to restore cellulose. Zinc sulfate, when added to the spinning bath, yields intermediate formation of a zinc xanthate. At this point modifiers such as poly (oxyethylene) glycol and derivatives of amines, are added to

further delay the regeneration reaction which results in the stretching of the fibers. The viscose has been pumped through spinnerets which are thimble shaped devices with 10-10,000 holes; this is the device that forms the fibers in the acid bath. The resulting fibers (tow), immediately after stretching, passes through the revolving blades of a cutter. This process is controlled by the cutter operator. The rayon fibers of uniform length are laid down on a conveyor belt and taken to the wash track. The wash track operator is responsible for the formation of a rayon blanket formed from the washing of the fibers and the subsequent squeezing of the fibers through rubber rollers. The fibers are desulfurized, neutralized, bleached or resin treated and a processing lubricant is applied prior to a final squeeze to remove excess liquid.

The damp fiber blanket is then fluffed by a mechanical beating action and the fibers are carried by conveyor belt to a drying oven. The rayon staple fibers are once again fluffed and then baled for shipment.

POTENTIAL EXPOSURES AND CONTROLS USED

In addition to CS_2, rayon staple workers have potential exposure to hydrogen sulfide, tin oxide, zinc oxide and sulfate, sodium hydroxide, sulfuric acid and noise. Hydrogen sulfide (H_2S) has been suggested as a possible confounding factor in previous studies on CS_2, especially in viscose rayon plants. Hydrogen sulfide's acute effects are well-known: cardio-respiratory failure (probably central) and possible convulsions. Subacute effects are related to the central nervous system (i.e., headaches, dizziness, staggered gait, tremors, weakness, and numbness of extremities). Chronic effects have not been fully substantiated but perhaps constitute progression of subacute effects. The Company monitors continuously for H_2S and the exposure records were reviewed and found to be below the OSHA standard of 10 ppm. Also, NIOSH took some area samples which indicated low environmental levels.

Engineering controls and personal protective equipment are used extensively in this plant. The historical environmental area air samples for CS_2 collected by the Company have been, on the average, below the OSHA Standard of 20 ppm (with the exception of the chip conveyor and 2nd stretch roller areas). Typical current levels of CS_2 in the spinning area are about 12 ppm and 5 ppm in the churn room. The spinning machines are completely enclosed in plexiglass and when maintenance is requried sections of the plexiglass can be opened and the worker will use a respirator while repairing the tow. The entire row of the spinning machines are ventilated. The cutter operators wear respirators when working around the cutters and staple, however, the majority of their time is spent in a sound proofed, air conditioned booth.

DESCRIPTION OF THE SURVEY METHODS

STUDY DESIGN

The medical study was designed to examine the effects of CS_2 on (a) central and peripheral nervous system; (b) the cardiovascular system, including the retinal vessels; (c) on carbohydrate, trace mineral, and lipid

metabolism; (d) testicular function; and (e) thyroid function. Psychological and behavorial studies were also conducted and are considered part of the total medical study. The industrial hygiene aspect of the study was designed to compliment the medical study and to develop an exposure index for each job category.

Individual work histories were obtained from the company before the study and were used in deciding eligibility for inclusion in the exposed and control groups of the medical study; the same information was used with the departmental exposure level data to calculate individual cumulative exposures. The exposed group was chosen from those members of the viscose rayon staple plant who had been employed in that plant for at least one year. Their employment prior to that time could have included the old rayon filament plant or one of the other synthetic fiber plants.

The control group was selected from either the polyester filament, nylon filament, or nylon polyester staple plant. Those included had to have been employed at least one year in any or all of these plants. Workers from these areas with previous experience in either the rayon staple or rayon filament plant were excluded from the control group.

A number of job types, including general maintenance, yard work, etc., were excluded from both exposed and control groups because their work would take them into both CS_2 exposure and non-exposure areas.

Of 273 workers who were potentially available and fit the study criteria for exposed workers, 189 (69.2 percent) signed informed consent forms. For the control population, 422 workers were originally asked to participate in the study; 245 (58.1 percent) signed consent forms.

The Company's CS_2 exposure levels, which were area samples, varied from less than 1 ppm to 20-25 ppm, depending on the area being considered. These area air samples were taken from 1957-1978 in the rayon staple plant. The areas sampled were the churn room, dissolving room, spinning room, at the cutter and chip conveyor, waste cutter area, basement receiving tank, second bath tanks and the correction operator's desk. The samples were analyzed by the Corporate analytical laboratory by the method in Appendix 4. Hydrogen sulfide samples were also taken during this period of time. Historical area air sampling data for CS_2 were available for the rayon filament plant from 1949 until it was closed in 1974 (Table 2). The average annual CS_2 concentrations for the rayon filament plant are shown in the graphs in Appendix 5 (data supplied by American Enka). The average area sampling data and the number of samples taken at each data point in the rayon staple plant are in Appendix 5. It cannot be assumed that the concentrations of CS_2 detected in area sampling is directly related to personal exposure. Most rayon staple workers are assigned to specific jobs which they perform each working day. They can be identified according to their job location (e.g., press operator, churn room, spinners). Some rayon staple workers, however, rotate to different jobs depending on the needs of the process (general relief operator). In order to determine the magnitude of carbon disulfide exposure, eight-hour personal sampling pumps were placed on the workers in the major job categories who signed consent forms.

There are historical Company data only for the previously mentioned job description areas. There are many job descriptions that were not monitored by the Company due to the limited potential for exposure to CS_2 i.e. lye room operator, soaking press operator. Personal sampling was conducted by NIOSH because it gives the best indication of the actual worker's exposure. To develop a correlation of exposure and work histories for each employee in the study an annual exposure index had to be developed for each job category from 1957-1979 (see Tables 2,3). The Company's area sampling data were extrapolated by NIOSH to personal sampling data by the use of a correction factor. The correction factor was developed by assuming that the personal air data obtained during the NIOSH survey in March and April of 1979 was the average exposure for that year. Using 1979 NIOSH personal data as the base and assuming no changes in 1978, a ratio was developed using 1979 personal exposure data. The concentrations for 1979 were divided into the average area concentration for each year from 1957-1977. The resulting correction factor ratio was then multiplied times the average 1979 CS_2 personal data to arrive at the exposure index for each year.

To calculate the individual cumulative exposure, the following formula was used:

Let CS_{ijk} be the exposure level in years i, department j and job code k; X_{ijk} be the number of months a worker worked in year i at department j and job code k then the exposure index of each job is equal to:

$$\text{Exposure Index} = X_{ijk} \times CS_{ijk}$$

The cumulative exposure index is the summation in months of each job by department and job code multiplied by the CS_2 exposure level. The following formula is for cumulative exposure index:

$$\text{Cumulative Exposure Index} = \sum_i \sum_j \sum_k X_{ijk} \times CS_{ijk}$$

If no job code was available then:

$$\text{Exposure Index} = \sum_i \sum_j X_{ij} \times CS_{ij}$$

An example of the cumulative exposure index is:

Employee: John Doe - Employed 18 months

Employment History	Dept.	Job Code	Job Description	Exposure	Exposure Index
Jan.-June 1972	12	73	Staple spinner	17.21 ppm	103.26 ppm
July-Dec. 1972	12	29	Correction operator	2.39 ppm	14.34 ppm
Jan.-June 1973	11	6	Churn operator	9.03 ppm	54.18 ppm
					171.78 ppm

John Doe's cumulative exposure index for his entire work history at American Enka is 171.78 ppm which is the summation of the exposure index of each job by department and job code Mr. Doe had while employed. If a job code did not have any historical environmental data then engineering controls, proximity to exposure area, personal air sampling by NIOSH, along with professional opinion, were used to develop the exposure index for each job description over the time period of 1957-1979.

For statistical purposes, each job was placed into categories of definitely low exposure (DL, less than 3 ppm), moderate exposure (M, 3 ppm through 7.1 ppm), and definitely high exposure (DH, greater than 7.1 ppm). A fourth category was necessary for a number of workers for whom no exposure data were available (e.g., waste handlers, laboratory workers). This group was designated, other (O). Exposure data were developed by NIOSH for the rayon staple and filament plants. Tables 2 and 3 are summary exposure data by job code of the rayon staple and filament plants. Table 4 is a summary of CS_2 area air concentrations for the rayon staple and filament plants by year which shows the potential for exposure for this population.

An exposure profile of the control population was also conducted. The synthetic filament (nylon polyester) and the nylon polyester staple plant were surveyed April 9-10, 1979. The compounds of interest were dimethylterephthalate (Appendix 7), caprolactam (Appendix 8), ethylene glycol (Appendix 9), methanol (Appendix 10) and Dowtherm (Appendix 11).

SAMPLING AND ANALYTICAL METHODS

Carbon Disulfide (CS_2):

Two hundred sixty two personal samples were taken for CS_2. The air samples were collected at a flow rate of 20 cc per minute using MDA Accuhaler Model 808 personal sampling pumps equipped with a 20 cc per minute limiting orifice. The pumps were calibrated before and after the survey (Appendix 14). The CS_2 samples were collected using 150 mg SKC charcoal tubes as the collecting media. The pumps were attached to the worker's belt, and the sampling tubes were clipped in a vertical position to his lapel or shirt collar. Full shift area samples were obtained in a similar manner using the same apparatus and sampling tubes, except that the sample tubes and pumps were placed at strategic locations in specific areas. Collected samples were kept in a freezer located in the plant's hospital to minimize sample loss or migration prior to analysis. The analysis of the charcoal tubes were completed using NIOSH P&CAM 248 (see Appendix 14).

The analytical method used by the Company for the analysis of the area and personal samples is in Appendix 4.

Hydrogen Sulfide (H_2S):

Sampling for hydrogen sulfide was performed using MDA Accuhaler Model 808 personal sampling pumps calibrated at 10 cc/minute with long term (8-hour), direct reading Draeger H_2S detector tubes as the collecting media. A total of 17 H_2S samples were taken.

SUMMARY OF AREA AIR SAMPLING FOR
CS_2 BY AMERICAN ENKA IN THE RAYON FILAMENT PLANT 1949-1974

JOB DESCRIPTION	DEPT.	JOB CODE	NUMBER OF YEARS	MEAN	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE
Dye Room Operator	21	1	0	0.7	0.00	0.7	0.7
Paper Assembler	21	2	0	1.3	0.00	1.3	1.3
Soaking Press Loader	21	3	0	1.3	0.00	1.3	1.3
Soaking Press Operator	21	4	0	1.3	0.00	1.3	1.3
Shredder Operator	21	5	0	6.03	2.68	3.0	12.1
Churn Operator	21	6	26	8.30	2.35	4.3	15.7
Dissolver Operator	21	7	26	8.52	2.60	4.1	17.1
Receiving & Filtration Operator	21	10	0	2.48	0.94	0.9	4.8
Spinning Tank Operator	21	11	0	17.75	4.08	10.5	27.5
Dialyzer Operator	21	12	0	1.00	0.0	1.0	1.0
Dialyzer Reclother	21	13	0	1.00	0.0	1.0	1.0
Chemical Tank Cleaner	21	14	0	9.00	0.0	8.0	8.0
General Cleaner & Miscellaneous Worker	21	15	0	1.00	0.0	1.0	1.0
General Relief Operator	21	16	0	5.86	2.08	2.1	11.0
Restricted Relief Operator	21	17	0	3.50	0.0	3.5	3.5
Press Packer Operator	21	69	4	4.08	0.70	3.3	5.5
Press Packer Operator	21	B6	1	2.50	0.0	2.5	2.5
Viscose Operator	21	B9	7	5.00	0.0	5.5	5.5
Unassigned (old)	21	C7	2	0.0	0.0	0.0	0.0
Unassigned	21	98	1	0.20	0.0	0.20	0.20
Trucker	22	A2	1	0.3	0.0	0.3	0.3
Rayon Filament Spinning	22	A3	1	14.4	0.0	14.4	14.4
Car Loader	22	A4	1	17.7	0.0	17.7	17.7
Sand Filter Relief Operator	22	B5	2	2.0	0.0	2.0	2.0
Draw Textering	22	C6	1	0.2	0.0	0.2	0.2

SUMMARY OF AREA AIR SAMPLING FOR
CS_2 BY AMERICAN ENKA IN THE RAYON FILAMENT PLANT 1949-1974
(Cont.)

JOB DESCRIPTION	DEPT.	JOB CODE	NUMBER OF YEARS	MEAN	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE
Spinnerette Changer & Inspector	22	C8	5	17.12	1.52	14.4	17.8
Waste Washer	22	D5	1	23.7	0.0	23.7	23.7
Cake Wrapper	22	18	26	7.17	3.63	3.3	18.5
Continuous Relief Operator	22	19	0	5.83	2.08	2.1	11.0
Continuous Spinning Operator	22	20	0	17.8	0.0	17.8	17.8
Continuous Winder	22	31	0	4.0	0.0	4.0	4.0
Flagman	22	33	0	4.0	0.0	4.0	4.0
Relief Operator	22	23	27	6.13	2.46	2.1	13.0
Relief Operator & Cake Operator	22	24	2	5.70	0.0	5.7	5.7
Socker	22	25	26	17.75	4.08	10.5	27.5
Spinner	22	26	27	17.75	4.00	10.5	27.5
Acid Bath Relief Operator	22	27	0	1.00	0.00	1.0	1.0
Acid Cleaner	22	28	0	4.00	0.00	4.0	4.0
Correction Operator	22	29	0	2.37	0.87	0.80	4.60
Crystallizer & Evaporator Operator	22	30	0	6.06	2.60	2.40	13.20
Salt Reclaiming	22	31	0	0.20	0.0	0.20	0.20
Sand Filter & Salt Loader Operator	22	32	0	1.95	0.78	0.70	3.80
Day Buggy Cleaner	22	23	0	17.74	4.09	10.5	27.50
Day Cleaner	22	34	0	8.30	0.0	8.30	8.30
Filter Crew Worker	22	35	26	17.75	4.08	10.50	27.50
Pot Handler	22	36	26	17.75	4.08	10.50	27.50
Pump Repairman	22	37	26	17.78	4.05	10.50	27.50
Pump Tester	22	38	26	17.75	4.08	10.50	27.50

SUMMARY OF AREA AIR SAMPLING FOR
CS_2 BY AMERICAN ENKA IN THE RAYON FILAMENT PLANT. 1949-1974
(CONT.)

JOB DESCRIPTION	DEPT.	JOB CODE	NUMBER OF YEARS	MEAN	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE
Restricted Relief Operator	24	17	0	0.30	0.00	0.30	0.30
Cake & Cone Sorting Operator	24	52	0	0.30	0.00	0.30	0.30
Creel & Duffing Operator Warper	24	53	0	0.30	0.00	0.30	0.30
Creel & Warping Operater	24	54	0	0.30	0.00	0.30	0.30
Emulsion Mix & Misscellaneous	24	55	0	0.30	0.00	0.30	0.30
Lift Truck Operator	24	56	0	0.30	0.00	0.30	0.30
Oil Coning Operator	24	57	0	0.30	0.00	0.30	0.30
Salvage Operator	24	58	0	0.30	0.00	0.30	0.30
Shift Cake Sorter	24	59	0	0.30	0.00	0.30	0.30
Slashing & Creel Operator	24	60	0	0.30	0.00	0.30	0.30
Sorting Trucker	24	61	0	0.30	0.00	0.30	0.30
Textile Monorail Trucker	24	62	0	0.30	0.00	0.30	0.30
Tube Inspector	24	63	0	0.30	0.00	0.30	0.40
Universal Winding Operator	24	64	0	0.30	0.00	0.30	0.30
Upwister Operator	24	65	0	0.30	0.00	0.30	0.30
Waste Baler	24	66	0	0.30	0.00	0.30	0.30
Cake Wash Textile	2F			7.1	0.00	7.1	7.1
Cake Wash Industrial Pot	2G			7.1	0.00	7.1	7.1
Inspection & Packing	2N			0.3	0.00	0.3	0.3
Wash Yarn & Handling	2P			1.0	0.00	1.0	1.0
Warehouse	2R			0.3	0.00	0.3	0.3
Shipping	2S			0.3	0.00	0.3	0.3

SUMMARY OF AREA AIR SAMPLING FOR
CS_2 BY AMERICAN ENKA IN THE RAYON FILAMENT PLANT 1949-1974
(CONT.)

JOB DESCRIPTION	DEPT.	JOB CODE	NUMBER OF YEARS	MEAN	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE
Rotometer Tester	22	39	26	17.75	4.08	10.50	27.50
Spinnerette Charges & Inspector	22	40	26	17.75	4.08	10.50	27.50
Unassigned	22	98	0	0.2	0.0	0.20	0.20
Car Loader	23	A4	0	17.7	0.0	17.7	17.7
Vacuum Dryer (old)	23	B7	0	0.4	0.0	0.4	0.4
General Relief Operator	23	16	0	5.86	2.08	2.10	11.00
Day Cleaner	23	34	0	1.00	0.0	1.00	1.00
Car Loader	23	41	0	17.75	4.00	10.50	27.50
Track Operator	23	42	0	7.10	1.63	4.20	11.00
Extractor Operator	23	43	0	1.00	0.00	1.00	1.00
Tunnel Dryer Operator	23	44	0	0.36	0.09	0.20	0.60
Vacuum Dryer Operator	23	45	0	0.37	0.09	0.20	0.60
Tube Winding	23	46	0	0.30	0.00	0.30	0.30
Cone Winding	23	47	0	0.00	0.31	0.30	0.30
Slashing	23	48	0	0.30	0.00	0.30	0.30
Chemical Mix Operator	23	49	0	0.60	0.00	0.60	0.60
Laundry Operator	23	50	0	17.75	4.08	10.50	28.50
Waste Wash & General Cleaner	23	51	26	23.71	8.73	9.50	43.10
Unassigned	23	98	5	0.20	0.00	0.20	0.20
Sorting Trucker	24	B8	1	0.30	0.00	0.30	0.30
Paper Assembler	24	C1	2	1.30	0.00	1.30	1.30
Shredder	24	C2	1	6.00	0.00	6.0	6.0
General Cleaner & Miscellaneous Worker	24	15	0	0.30	0.00	0.30	0.30
General Relief Operator	24	16	0	0.30	0.00	0.30	0.30

TABLE 2

SUMMARY OF AREA AIR SAMPLING FOR
CS_2 BY AMERICAN ENKA IN THE RAYON FILAMENT PLANT 1949-1974
(CONT.)

JOB DESCRIPTION	DEPT.	JOB CODE	NUMBER OF YEARS	MEAN	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE
All Maintenance	2X			1.0	0.00	1.0	1.0
Unknown	2Y			0.0	0.00	0.0	0.0
Laboratories	2Z			1.0	0.00	1.0	1.0

* Not every job description was sampled each year by the company. The years without data were extrapoleted by NIOSH based upon the best available information. The Plant was shut down in 1974.

TABLE 3
SUMMARY OF AREA AIR SAMPLING FOR
CS_2 BY AMERICAN ENKA IN THE RAYON Staple PLANT 1957-1979

JOB DESCRIPTION	DEPT.	JOB CODE	NUMBER OF YEARS	MEAN	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE
Lye Room Operator	11	1	1	0.7	0	0.7	0.7
Press Assembler Operator	11	2	1	1.3	0	1.3	1.3
Soaking Press Loader	11	3	1	1.3	0	1.3	1.3
Soaking Press Operator	11	4	1	1.3	0	1.3	1.3
Shredder Operator	11	5	1	6.65	2.49	3.0	12.1
Churn Operator	11	6	23	9.03	3.39	3.2	14.0
Dissolver Operator	11	7	26	9.02	3.35	3.2	14.0
TiO_2 Preparation	11	8	23	9.02	3.57	3.2	14.0
Continuous Viscose	11	9	23	3.97	0.12	3.6	4.0
Receiving & Filtration	11	10	23	2.53	1.01	0.8	4.8
Spinning Tank Operator	11	11	23	3,97	0.12	3.6	4.0
Chemical Tank Cleaner	11	14	23	7.92	0.26	7.1	8.0
General Cleaner	11	15	1	1.0	0.0	1.0	1.0
General Relief Operator	11	16	24	5.84	2.27	2.1	11.0
Restricted Relief Operator	11	17	1	3.50	0.0	3.50	3.50
Continuous Viscose Operator (old)	11	67	4	4.00	0.0	4.00	4.00
Dye Mix Operator	11	68	2	9.00	0.0	9.00	9.00
Receiving & Filtration (old)	11	69	27	2.54	0.930	0.80	4.80
Unassigned	11	98	3	0.20	0.0	0.20	0.20
Yard Laborer	11	A7	4	1.0	0.0	1.00	1.00
Press Packer	11	C9	6	2.5	0.0	2.50	2.50
Waste Handling	1F		0	10.0	0.0	10.00	10.00
Shipping & Stores	1G		0	0.5	0.0	0.50	0.50
All Maintenance	1X		0	1.0	0.0	1.00	1.00
Unknown	1Y		0	0.5	0.0	0.50	0.50
All Laboratories	1Z		0	0.5	0.0	0.50	0.50

SUMMARY OF AREA AIR SAMPLING FOR
CS_2 BY AMERICAN ENKA IN THE RAYON Staple Plant 1957-1979
(CONT.)

JOB DESCRIPTION	DEPT.	JOB CODE	NUMBER OF YEARS	MEAN	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE
Day Utility Washer	12	A1	5	13.26	1.21	11.8	14.5
Spinneratte Changer	12	B2	23	17.2	0.0	17.20	17.20
Salt Reclaimer	12	B3	1	0.20	0.0	0.20	0.20
Washer Operator	12	D2	6	23.87	21.17	8.30	60.00
Cleaner & Miscellaneous	12	D4	5	0.50	0.0	2.00	2.00
Salt Loader	12	D8	5	0-0	0.00	2.00	2.00
General Relief Operator	12	16	24	5.84	2.27	2.10	11.00
Cleaner & Salt Bagger (old)	12	20	2	0.20	0.0	0.20	0.20
Correction Operator	12	29	27	2.39	0.87	0.80	4.60
Crystallizer & Evaporator	12	30	23	6.45	2.59	1.30	13.20
Day Cleaner	12	34	24	0.50	0.0	0.50	0.50
Chemical Mix Operator	12	49	24	0.60	0.0	0.60	0.60
Cleaner and Salt Bagger	12	70	1	0.20	0.0	0.20	0.20
Salt Unit Operator	12	71	1	0.20	0.0	0.20	0.20
Sand Filter & Relief Operator	12	72	23	2.02	0.812	0.70	3.8
Staple Spinner	12	73	24	17.21	5.97	8.30	32.50
Utility Spinner	12	74	23	17.21	6.11	8.30	32.50
Tow Patrol	12	75	23	17.21	6.11	8.30	32.50
Cutter Operator	12	76	24	8.09	2.88	1.60	18.00
Shunt & Washer & Dryer Operator	12	77	23	2.00	0.0	2.00	2.00
Dryer Operator	12	78	1	8.3	0.0	8.30	8.30
Bale Operator	12	79	1	0.70	0.0	0.70	0.70
Washer Operator	12	80	23	37.35	24.41	6.50	83.40
Unassigned	12	98	6	0.20	0.0	0.20	0.20

TABLE 4

SUMMARY OF CS_2 AREA AIR CONCENTRATIONS FOR THE RAYON STAPLE AND RAYOM FILAMENT PLANTS BY YEAR FROM 1949-1979

YEAR	MEAN PPM	STANDARD DEVIATION	MAXIMUM VALUE	SUM
1948	4.04	6.30	17.8	56.50
1949	6.34	9.72	27.5	494.50
1950	6.74	9.73	27.30	532.70
1951	5.07	7.18	23.70	425.60
1952	4.88	6.51	23.70	414.90
1953	4.70	5.99	23.70	399.90
1954	5.45	7.24	23.70	441.60
1955	4.75	6.33	23.70	413.60
1956	5.10	7.83	43.10	474.40
1957	5.50	9.62	83.20	665.10
1958	4.69	8.90	83.40	553.10
1959	5.20	9.53	83.20	598.20
1960	4.56	5.74	22.60	524.00
1961	5.81	7.58	32.50	650.80
1962	4.73	6.83	28.00	539.90
1963	4.89	6.83	22.80	556.90
1964	5.19	6.89	22.80	597.20
1965	5.42	6.99	31.50	628.20
1966	5.43	7.10	37.00	651.60
1967	5.42	6.78	38.20	649.90
1968	5.39	7.02	34.60	657.60
1969	5.07	6.33	36.70	608.40
1970	4.50	5.83	36.50	553.50
1971	4.92	6.46	36.70	619.60
1972	4.99	6.27	40.80	603.90
1973	5.15	6.24	36.70	653.70
1974*	4.99	6.80	53.40	673.80
1975	5.19	10.42	73.4	295.60
1976	5.48	11.59	60.00	295.90
1977	4.80	7.95	37.90	239.80
1978	4.18	4.91	20.40	209.10
1979	4.46	5.16	20.40	187.50

*Year Rayon Filament Plant Closed

The analytical method used by the Company for the analysis of the area samples is in Appendix 4.

Caprolactam and Dimethylterephthalate:

The analytical method for these two compounds were developed specifically for this survey by NIOSH.

Full shift samples were collected at a flow rate of 2.0 L/minute using MSA Model G personal sampling pumps. The samples were collected on glass fiber filters using closed faced two staged polystyrene cassettes. Thirteen samples of caprolactam and 11 dimethylterephthalate samples were taken.

Prior to analysis, the cassette plugs were removed and the samples were kept in a dessicator for 7 days. The filters were removed from the cassettes and extracted in 2 dram vials with 5 ml of methylene chloride. To enhance the extraction process, the vials were held in an ultrasonic bath for 30 minutes.

The extracts were analyzed on an HP5731 gas chromatograph using a flame ionization detector (FID) and helium carrier gas. The limit of detection for caprolactam was 0.5 mg/sample and 0.1 mg/sample for dimethylterephthalate.

Methanol:

Methanol samples were collected on silica gel tubes. MDA Accuhaler Model 808 personal sampling pumps calibrated at 20 cc/minute were used to collect the samples. The limit of detection was 0.010 mg/sample and a total of 6 methanol samples were taken. The tubes were analyzed in accordance with Method S-59 (Appendix 15).

Dowtherm: (Phenyl Ether-Biphenyl Mixture)

Dowtherm samples were also collected on silica gel tubes. MDA Accuhaler Model 808 personal sampling pumps calibrated at 20 cc/minute were used to collect the Dowtherm samples. The limit of detection was 0.010 mg/sample and a total of 7 Dowtherm samples were taken. The tubes were analyzed in accordance with Method S-73 (Appendix 16).

Ethylene Glycol:

The ethylene glycol samples were collected using midget impingers containing 10% isopropanol in a water solution. A total of 7 area samples were collected using MSA Model G pumps at a flow rate of 1 liter per minute. The samples were analyzed in accordance with the method in Appendix 17.

RESULTS AND DISCUSSION

A total of 262 personal samples were taken for CS_2 during the two industrial hygiene surveys (see Appendix 13 for raw data and Table 5 for a summary

TABLE 5

SUMMARY STATISTICS OF THE NIOSH PERSONAL CS_2 EXPOSURE (PPM) BY JOB ASSIGNMENT IN THE RAYON STAPLE PLANT, MARCH-APRIL, 1979

JOB TITLE	DEPT.	JOB CODE	N	MAX	MIN	MEAN	STANDARD DEVIATION	STANDARD ERROR	GEOMETRIC MEAN	GEOMETRIC DEVIATION	UPPER LIMIT	LOWER LIMIT
Lye Room Operator	11	1	6	1.94	0.01	0.81	0.66	0.27	0.43	5.70	2.64	0.07
Soaking Press Operator	11	3	13	6.00	0.29	2.36	1.83	0.51	1.75	2.32	2.92	1.05
Shredder Operator	11	4	17	13.90	1.00	5.10	3.97	0.96	3.85	2.19	5.75	2.57
Churn Operator	11	6	30	21.24	1.15	6.70	4.08	0.74	5.73	1.79	7.12	4.61
Dissolver Operator	11	7	18	7.90	1.89	4.16	1.53	0.36	3.89	1.47	4.71	3.21
Receiving & Filtration Operator	11	10	2	3.38	3.32	3.35	0.04	0.03	3.35	1.01	3.75	2.99
Spinning Tank Operator	11	11	3	3.67	1.99	3.06	0.93	0.54	2.95	1.41	6.88	1.26
Chemical Tank Cleaner	11	14	4	15.07	0.96	7.13	6.33	3.16	4.58	3.38	31.81	0.66
Correction Operator	12	29	4	2.62	1.58	2.06	0.55	0.28	2.01	1.31	3.09	1.31
Crystallizer & Evaporator Operator	12	30	4	11.02	1.39	4.24	4.54	2.27	2.98	2.46	12.52	0.71
Chemical Mix Operator	12	49	3	0.98	0.34	0.58	0.35	0.20	0.52	1.74	2.08	0.13
Press Packer	12	69	13	6.90	3.33	4.69	1.14	0.32	4.57	1.26	5.26	3.97
Salt Unit Operator	12	71	4	0.37	0.02	0.16	0.16	0.08	0.09	3.89	0.80	0.01
Sand Filter & Relief Operator	12	72	5	2.84	0.92	1.74	0.70	0.31	1.63	1.50	2.71	0.98
Staple Spinner	12	73	55	217.6	1.28	12.64	29.09	3.92	6.74	2.65	8.77	5.17
Tow Patroller	12	75	3	17.06	6.11	11.86	5.50	3.17	10.89	1.69	28.60	4.15
Cutter Operator	12	76	21	30.70	0.02	9.42	6.40	1.40	6.21	4.32	12.11	3.18
Washer Operator	12	80	31	139.0	1.01	11.04	27.16	4.96	4.97	1.83	6.26	3.97
Dryer Operator	12	78	6	47.65	0.02	8.30	19.28	7.87	0.46	15.93	8.47	0.03
Baler Operator	12	79	17	2.21	0.02	0.87	0.65	0.16	0.48	4.65	1.05	0.22
Lift Truck Operator	12		4	0.45	0.03	0.23	0.23	0.12	0.11	4.68	1.33	0.01

of the results by job category). The average concentration for the personal CS_2 samples taken by NIOSH was 4.8 ppm. The yearly average (Table 4) for the area air samples taken by American Enka in 1978 at the rayon staple plant was 4.2 ppm.

On an intermittent basis the airborne concentrations of CS_2 in some areas was determined during the NIOSH study to be above the OSHA standard - i.e., churn operator - 21.2 ppm, staple spinner - 217.6 ppm, cutter operator - 30.7 ppm, washer operator - 159.0 ppm, and drying - 47.7 ppm. The more accurate personal sampling data have only been collected since 1974, making it impossible to ascertain before that time the extent of actual exposure levels incurred by individual employees. However, respirators have been available for personal protection since early in the plant's history and in the past several years management has increased emphasis until it is now mandatory to use an approved respirator during known or suspected periods of high exposure.

The nylon polyester filament plant was sampled for CS_2 on March 7-12, 1979 for the purpose of determining the potential of the control population being exposed. The average personal exposure for the control population was 0.2 ppm.

The rayon staple plant was also surveyed for hydrogen sulfide; the results can be found in Appendix 12.

One area of concern is the handling of waste rayon staple. This product is processed through a small department in the old rayon filament plant. The concern comes from the potential for CS_2 exposure. NIOSH did not take any samples of this process because the presence of this small operation was only discovered in the latter stages of the survey. However, from the visual observations at the time of the walk-through, it was not clear to the NIOSH industrial hygienists that appropriate engineering controls were being applied in the handling of the waste rayon staple.

Since the control group worked in the nylon or polyester plant, the exposure to caprolactam, dimethylterephthalate, ethylene glycol, methanol and Dowtherm were either nondetectable or well below the exposure standards (see Appendix 18 for exposure standards). The CS_2 level for the control population was approximately 0.2 ppm. Because there is no historical company data to document previous exposures to CS_2 for the control population it is assumed, for this study, that 0.2 ppm is also the average exposure level of the controls for the previous years.

RECOMMENDATIONS

The rayon staple plant's average exposure, 4.8 ppm, is below the present OSHA standard of 20 ppm. The engineering controls and work practices are adequate to maintain this level of exposure.

The area of concern is the handling of the waste rayon staple in the old rayon filament plant. The waste handling department employs only a few employees and is located at the end of the plant away from the cafeteria. From

a walk-through of this department at the end of the survey and without any industrial hygiene data to support the observations, it appeared that better work practices and engineering controls could be incorporated into this department. Systematic routine sampling of this department by the Company would be necessary to justify modification and improvement in the engineering control

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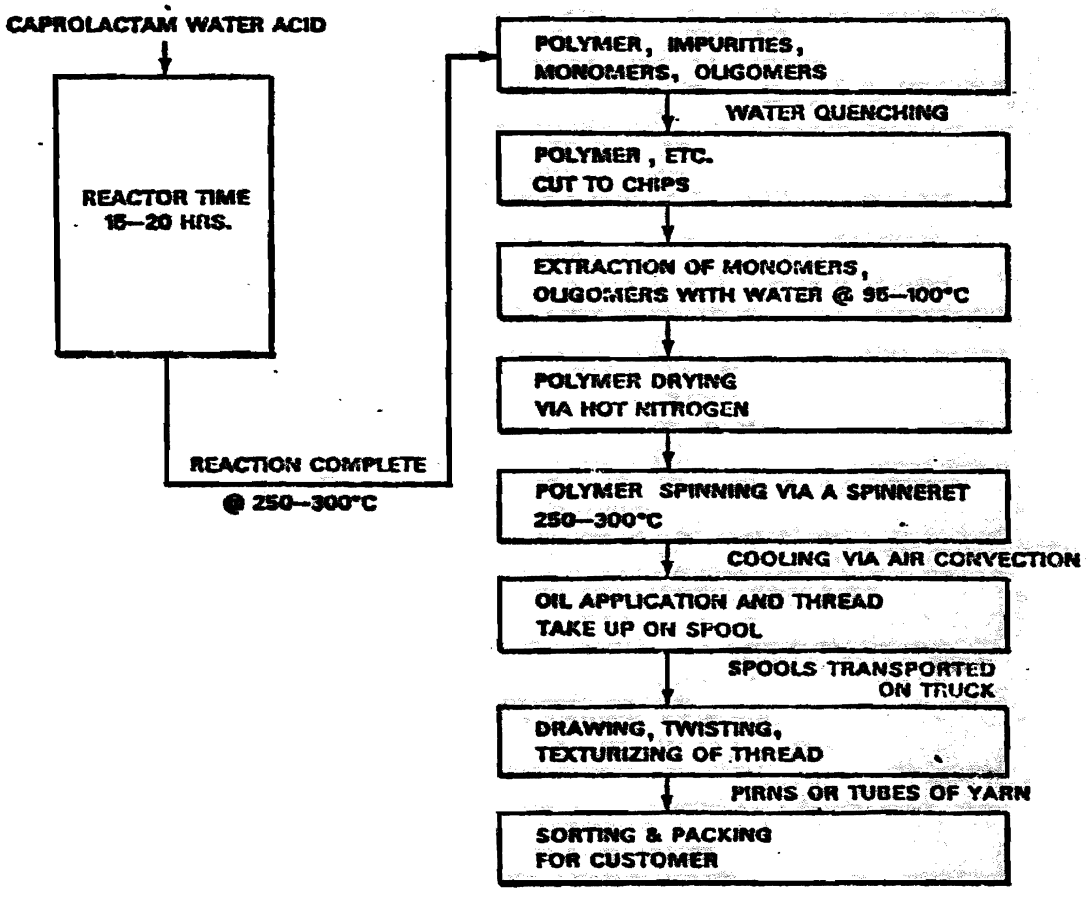
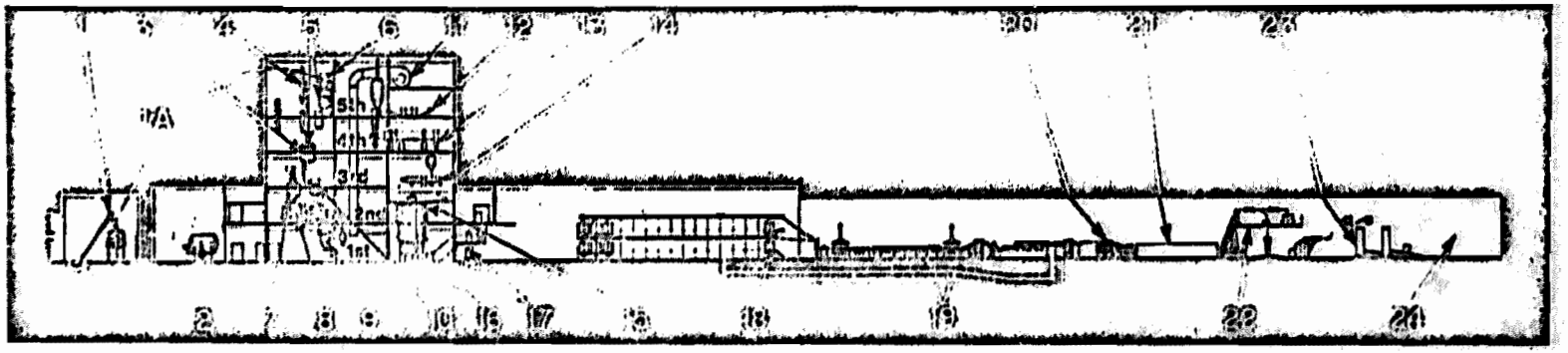
APPENDIX 1

SYNTHETIC FILAMENT PLANT
NYLON 6

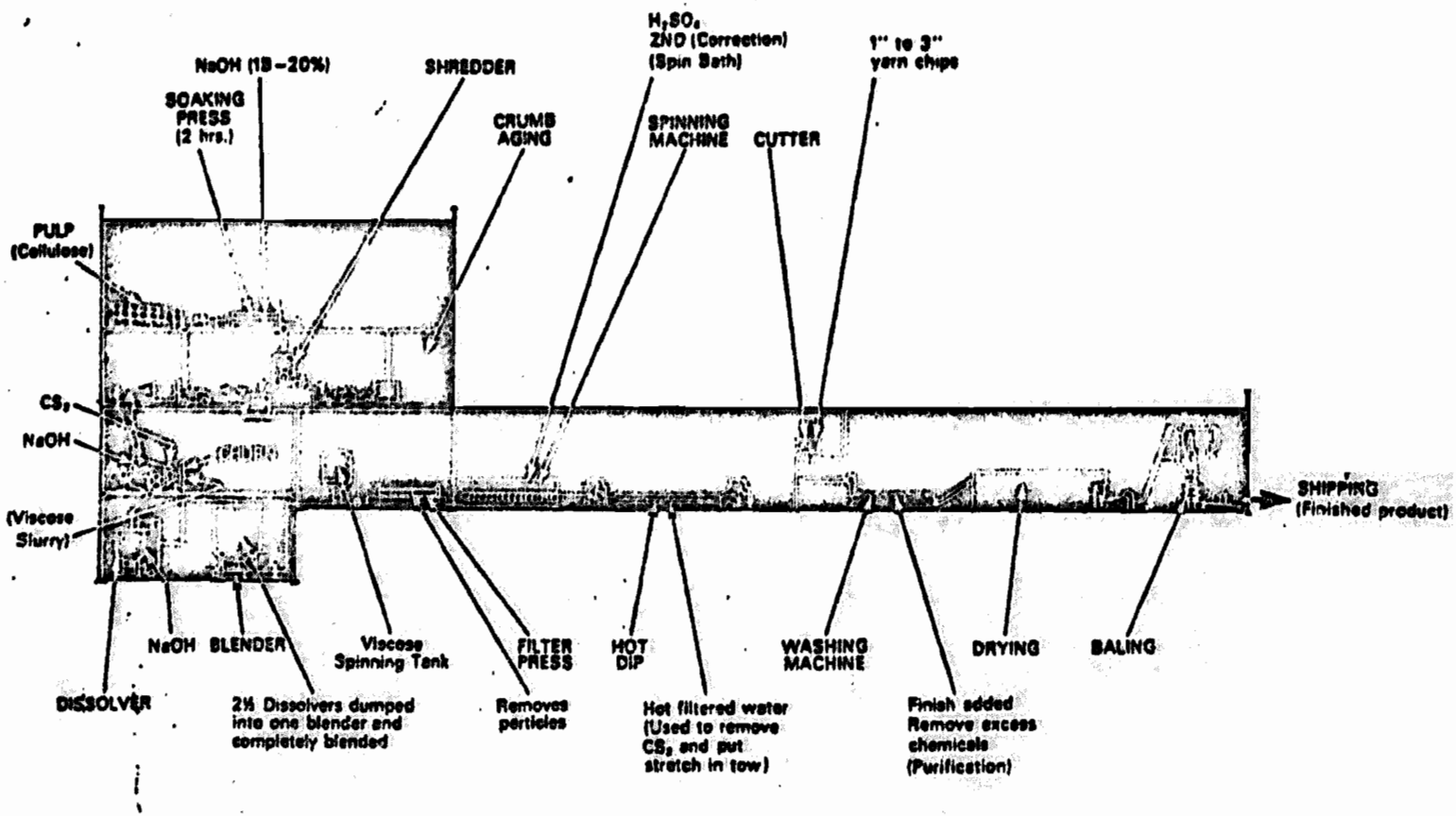


TYPICAL MANUFACTURE OF POLYESTER STAPLE



1. DMT (DIMETHYL TEREPHTHALATE) STORAGE
1A. PUMPED TO OVERHEAD TANK
2. DOWTHERM BOILER (HEATING AGENT)
3. TRANSESTERIFICATION REACTORS (E.I. VESSELS) CATALYSTS ADDED TO E.I. (DEPENDING ON PRODUCT). MANGANESE ANTIMONY ; COBALT ; TITANIUM OXIDE; TIME – APPROX 180 MIN.
4. METHANOL CONDENSER (BY-PRODUCT FROM DMT)
5. ETHYLENE GLYCOL, OVERHEAD STORAGE TANK ADDED TO E.I. VESSEL
6. DMT OVERHEAD STORAGE TANK
7. POLYCONDENSATION REACTOR (AUTOCLAVE) MOLTEN POLYMER AT THIS POINT
8. CHIP CUTTING POLYMER COOLING INTO SHEET AND CUT INTO CHIPS (55 MINS./BATCH)
9. CHIP BUFFER TANKS
10. GLYCOL CONDENSER
11. CHIP BLOWER (CHIP BLOWN FROM BUFFER TANK TO STORAGE TANKS – 5th FLOOR)
12. CYCLONE (REMOVES EXCESS DUST FROM CHIPS)
13. ROTARY CHIP DRYER
14. EXTRUDER (MELTS CHIPS)
15. POLYMER PUMPED TO SPINNING MACHINE & FORCED THROUGH SPINNERETTE FORMING FILAMENTS. FILAMENTS COOLED BY AIR CONVECTION & FORM FILAMENT YARNS.
16. TAKE-UP MACHINES (FILAMENT YARN)
17. PIDDLER (TOW CANS)
18. CREELING AREA TOW CANS W/YARN TAKEN FROM PIDDLER AREA.
19. DRAWING OF YARN OVER HEATED ROLLERS, THROUGH FINISH BATHS, ETC. THIS PROCESS STRETCHES YARN TO DESIRED LENGTH.
20. CRIMPER MACHINES (YARN IS CRIMPED) VARYS W/PRODUCT
21. DRYER (REMOVES EXCESS MOISTURE)
22. CUTTER DECK (YARN TOW IS CUT INTO VARIOUS LENGTHS) (DEPENDS ON PRODUCT)
23. BALERS (YARN IS BALED IN CARDBOARD CONTAINER FOR SHIPMENT)
24. FINISHED PRODUCT STORES

TYPICAL RAYON STAPLE PLANT



APPENDIX 4

February 1976

DETERMINATION OF H_2S AND CS_2 IN AIR USING SPECTRONIC 20

PROCEDURE

A. Reagents

1. $Bi(NO_3)_3$ Solution - Dissolve 5.00 gms. $Bi(NO_3)_3 \cdot 5 H_2O$ in 300 ml. of glacial acetic acid. Dilute with 1.4 liters of distilled water. Add 1.0 gms. of gelatin dissolved in 100 ml. of warm distilled water. Mix well and filter into a glass stoppered bottle.

2. Modified Diethylamine Solution - Dissolve 0.05 gms. $Cu(CH_3COO)_2 \cdot H_2O$, 1 ml. diethylamine, 20 ml. of triethanolamine, and 25 ml. of conc. NH_4OH in 1 liter of 90% ethyl alcohol. (Keep in a brown bottle and stoppered when not in use.)

B. Procedure

1. Three gas absorption bottles and a 1-liter aspirating bottle are mounted on a special carrying rack equipped with holders and a neck strap.

2. Pipette 10 ml. of $Bi(NO_3)_3$ reagent into the first absorption bottle to absorb the H_2S.

3. Pipette 10 ml. of the diethylamine reagent into each of the second and third absorption bottles to absorb the CS_2.

4. Measure 1 liter of water into the aspirating bottle.

5. 1 liter of air to be tested is drawn through the gas absorption bottles by opening the stopcock on the 1-liter aspirator bottle containing the water.

6. After returning to the laboratory, aspirate the air in the intake tube (if used) and the first absorption bottle on through the second and third absorption bottles.

7. Transfer to 1/2" test tubes, and using $Bi(NO_3)_3$ as a blank, read at 435 mu wavelength the % transmittance of the solution in the H_2S absorption bottle.

8. Using diethylamine solution as a blank, read at 435 mu wavelength the % transmittance of the solution in the second and then the third absorption bottles.

9. Using the % transmittance on the Spectronic 20, read the concentration of H_2S and CS_2 from the attached charts.

10. Concentrations of CS_2 from the 2nd and 3rd bottles are added together.

TERMINATION OF H_2S AND CS_2 IN USING SPECTRONIC 20

ANALYTICAL NOTES

1. Since H_2S is less sensitive at low concentrations, less than 1 ppm should be indicated <1.0 ppm instead of calculating the exact amount.

2. If the H_2S absorption bottle has been standing a considerable length of time after sampling, the colloidal precipitate should be agitated.

3. If the H_2S content is expected to be over 25 ppm or the CS_2 content over 50 ppm, then 20 ml. of reagent should be used and the mgms. found would be multiplied by 2.

4. For highly abnormal samples, ($H_2S > 60$ ppm, $CS_2 > 100$ ppm), it is recommended that the older iodometric method be used.

5. The intake tube in the H_2S absorption bottle should be cleaned in cleaning acid after each sample to help prevent Bi_2S_3 from precipitating on the tube.

Reference: Colorimetric Methods of Analysis, Volume II, page 759, Snell and Snell

Poisons, Hazards, and Solvents, page 330, Jacobs.

AIR SAMPLING TECHNIQUE

I. PREPARATION

A. The analytical procedure is attached.

B. All equipment must be thoroughly clean.

C. The aspirating bottle and absorption bottles are mounted in the special carrying rack provided.

D. When taking the sample, the flow of water from the aspiring bottle is adjusted to give a time interval of approximately 7 minutes for a 1 liter sample.

II. GENERAL AIR SAMPLES

A. Carry the prepared rack at chest height, using the neck strap, during sampling.

B. Do not use intake tubing on the air intake of the first absorption bottle.

C. Walk slowly through the area of interest so that the sample will be representative of the entire area. See the attached diagrams.

D. Samples should be labeled to identify area sampled, date and time taken, and activities performed in area.

III. SAMPLES OF AIR BEING BREATHED BY AN OPERATOR

A. Attach a clean, dry, transparent plastic tube to the intake of the first absorption bottle. The tube should be approximately 6 feet long. A clothes pin is attached to the end opposite the absorption bottle using a rubber band.

B. When taking the sample, the plastic tubing is to be pinned to the operator's shirt, extended over his shoulder and the intake positioned near his face so that the air sample will be comparable to the air being breathed. The actual positioning of the tube may be varied so as to interfer as little as possible with the operator but the intake must be maintained near his face.

C. Samples should be labeled to identify date and time taken, operator's activities while sample was being taken, and area in which operator was working.

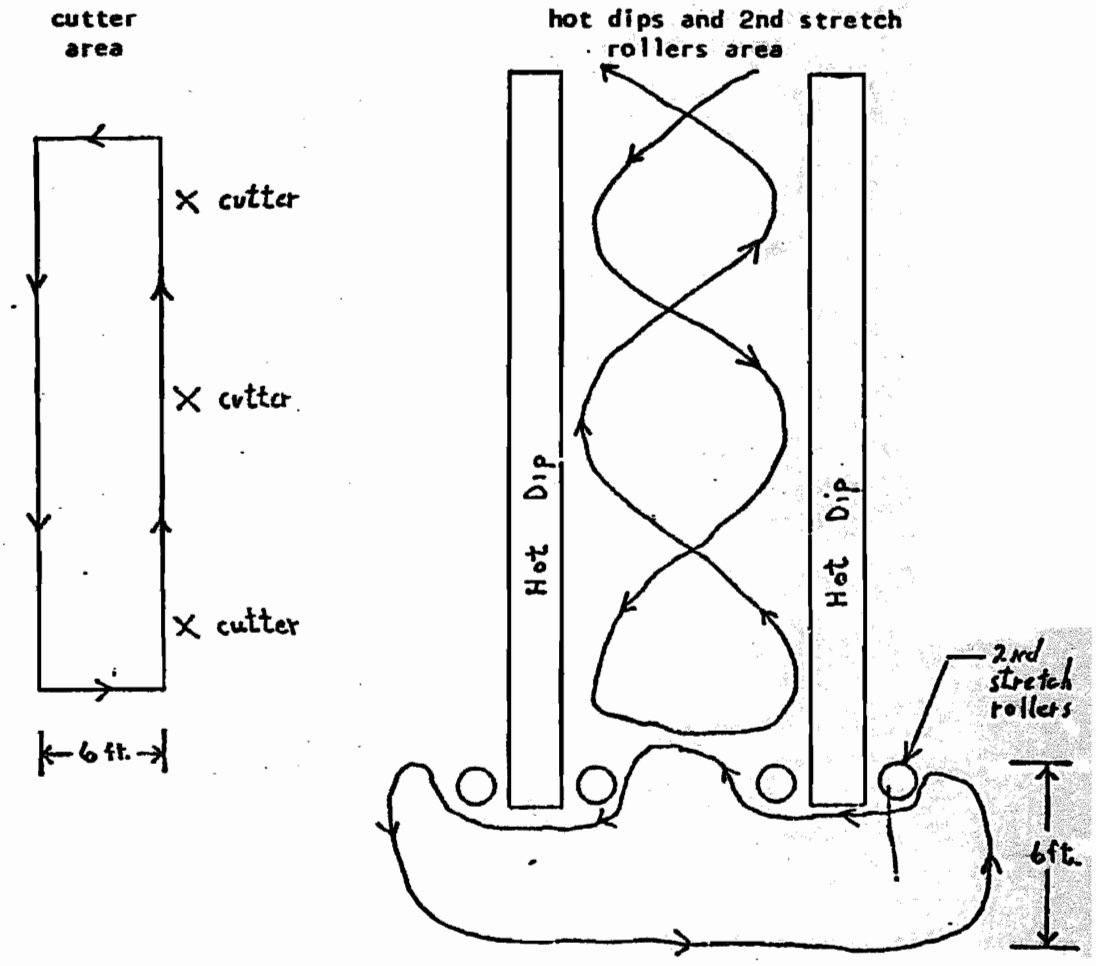
D. Care should be taken not to interfer with the operator in performance of his normal duties.

IV. SPECIAL AIR SAMPLES

A. A variety of special samples may be required. The techniques for these samples will be determined and specified by laboratory management prior to taking the sample.

B. If necessary to use an extended intake tube to reach inaccessible areas, the air in the tube should be displaced by air from the area to be sampled before taking the sample. This may be done by measuring the volume of the intake tube and adding this volume of water to the 1 liter of water in the aspiring bottle before taking the sample. Disconnect the intake tubing from the absorption bottle immediately after taking the sample. DO NOT aspirate the air remaining in the intake tubing through the absorption bottles.

DIAGRAM OF PATH TO FOLLOW IN SAMPLING AIR AT STAPLE PLANT



NOTE: 1. Walk as close to cutter as possible when passing in one direction. Air will sampled at shoulder height.

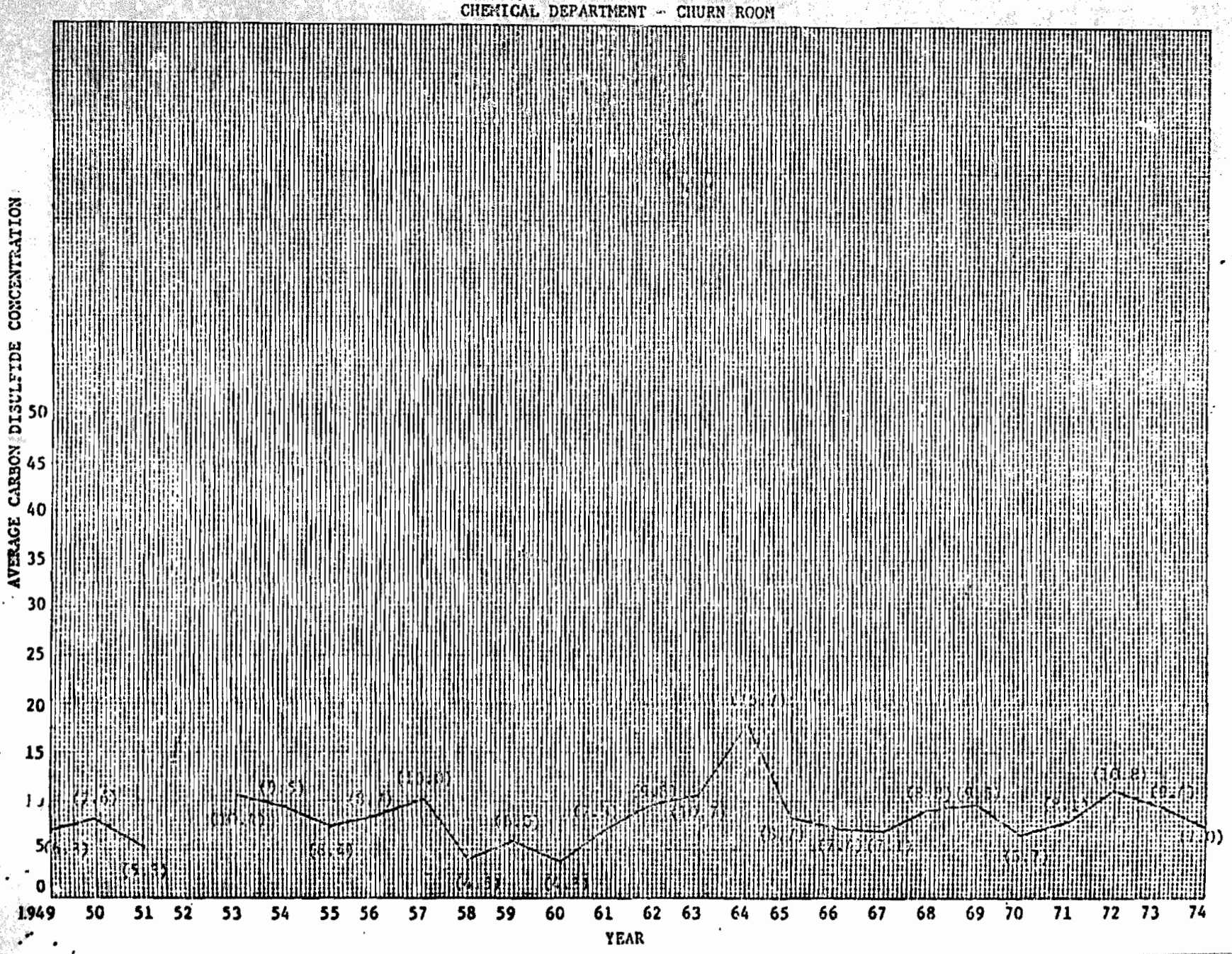
2. Walk as close to 2nd stretch rollers as practical when passing in one direction. Samples will be taken at shoulder height.

Wavelength - 435 mμ) H_2S 1/2" Test Tube
(1 liter sample)

% Transmittance	ppm H_2S	% Transmittance	ppm H_2S
99	0.5	78	7.1
98	0.7	77	7.4
97	1.0	76	7.8
96	1.3	75	8.1
95	1.6	74	8.5
94	1.8	73	8.9
93	2.1	72	9.3
92	2.4	71	9.7
91	2.8	70	10.1
90	3.0	69	10.5
89	3.4	68	10.9
88	3.7	67	11.3
87	4.0	66	11.7
86	4.3	65	12.2
85	4.7	64	12.6
84	5.0	63	13.0
83	5.3	62	13.5
82	5.7	61	14.0
81	6.0	60	14.5
80	6.3	57	15.0
79	6.7		

Wavelength - 435 mu. CS_2 (1 liter sample) 1/2" Test Tube

% Trans.	ppm CS_2	% Trans.	ppm CS_2	% Trans.	ppm CS_2	% Trans.	ppm CS_2
99	0.3	77	4.5	55	10.0	33	18.5
98	0.6	76	4.7	54	10.3	32	18.9
97	0.8	75	5.0	53	10.6	31	19.4
96	1.0	74	5.2	52	11.0	30	20.0
95	1.1	73	5.4	51	11.3	29	20.5
94	1.2	72	5.7	50	11.6	28	21.0
93	1.4	71	5.9	49	11.9	27	21.6
92	1.6	70	6.1	48	12.2	26	22.3
91	1.8	69	6.3	47	12.6	25	23.0
90	2.0	68	6.6	46	13.0	24	23.7
89	2.2	67	6.8	45	13.3	23	24.3
88	2.4	66	7.0	44	13.7	22	25.1
87	2.6	65	7.2	43	14.1	21	25.8
86	2.8	64	7.6	42	14.4	20	26.6
85	3.0	63	7.8	41	14.8	19	27.4
84	3.1	62	8.0	40	15.2	18	28.3
83	3.3	61	8.3	39	15.7	17	29.2
82	3.5	60	8.6	38	16.1	16	30.2
81	3.7	59	8.8	37	16.6	15	31.2
80	3.9	58	9.1	36	17.0	14	32.4
79	4.1	57	9.4	35	17.4	13	33.7
78	4.3	56	9.7	34	18.0	12	35.0
						11	36.4
						10	38.0


CHEMICAL DEPARTMENT - CHURN ROOM
AVERAGE CARBON DISULFIDE CONCENTRATION
50
45
40
35
30
25
20
15
10
5
0
1949
50
51
52
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54
55
56
57
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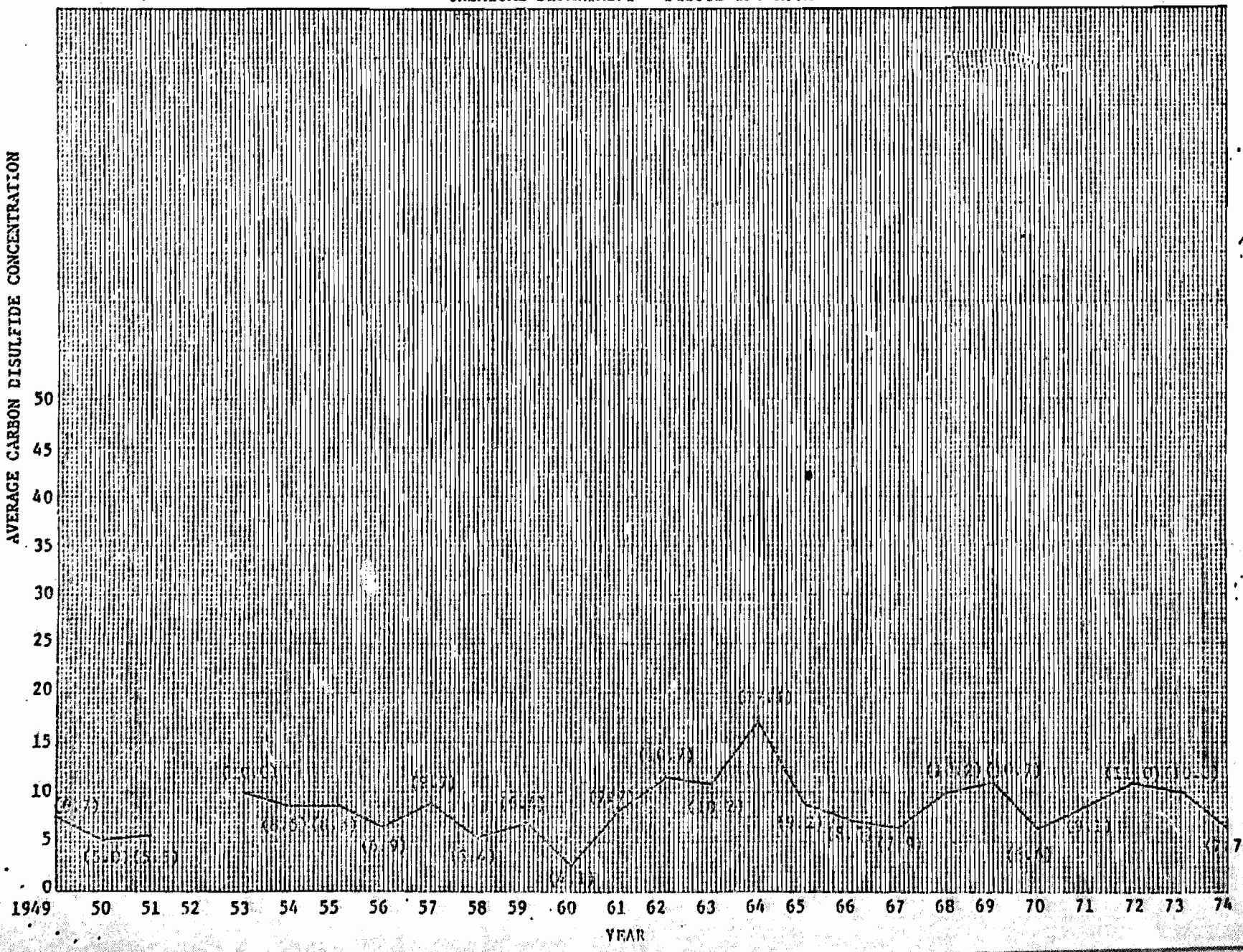
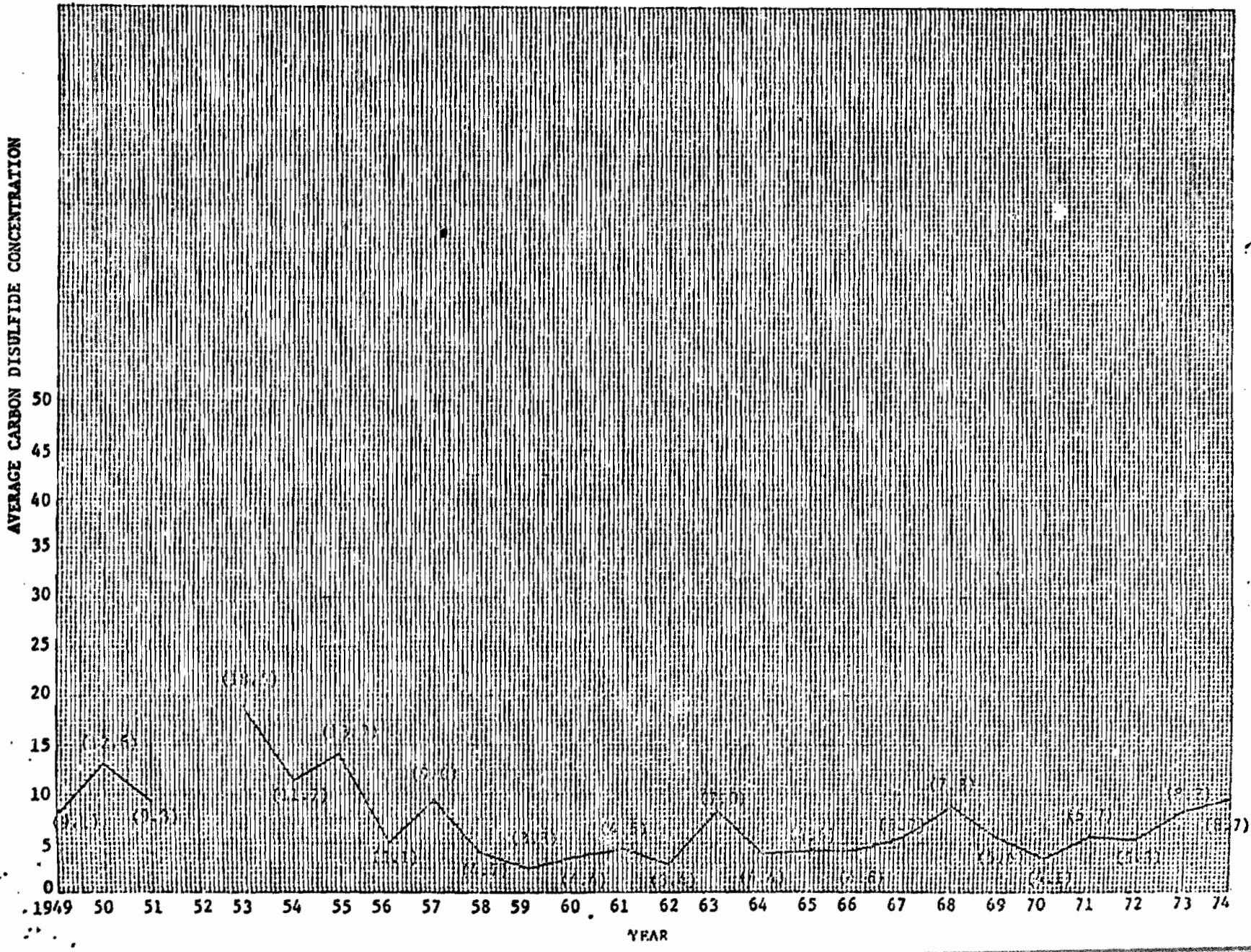
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
YEAR

APPENDIX 5

RAYON FILAMENT PLANT

CHEMICAL DEPARTMENT - DISSOLVING ROOM




FINISHING DEPARTMENT - CAKE LOADING
AVERAGE CARBON DISULFIDE CONCENTRATION
50
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15
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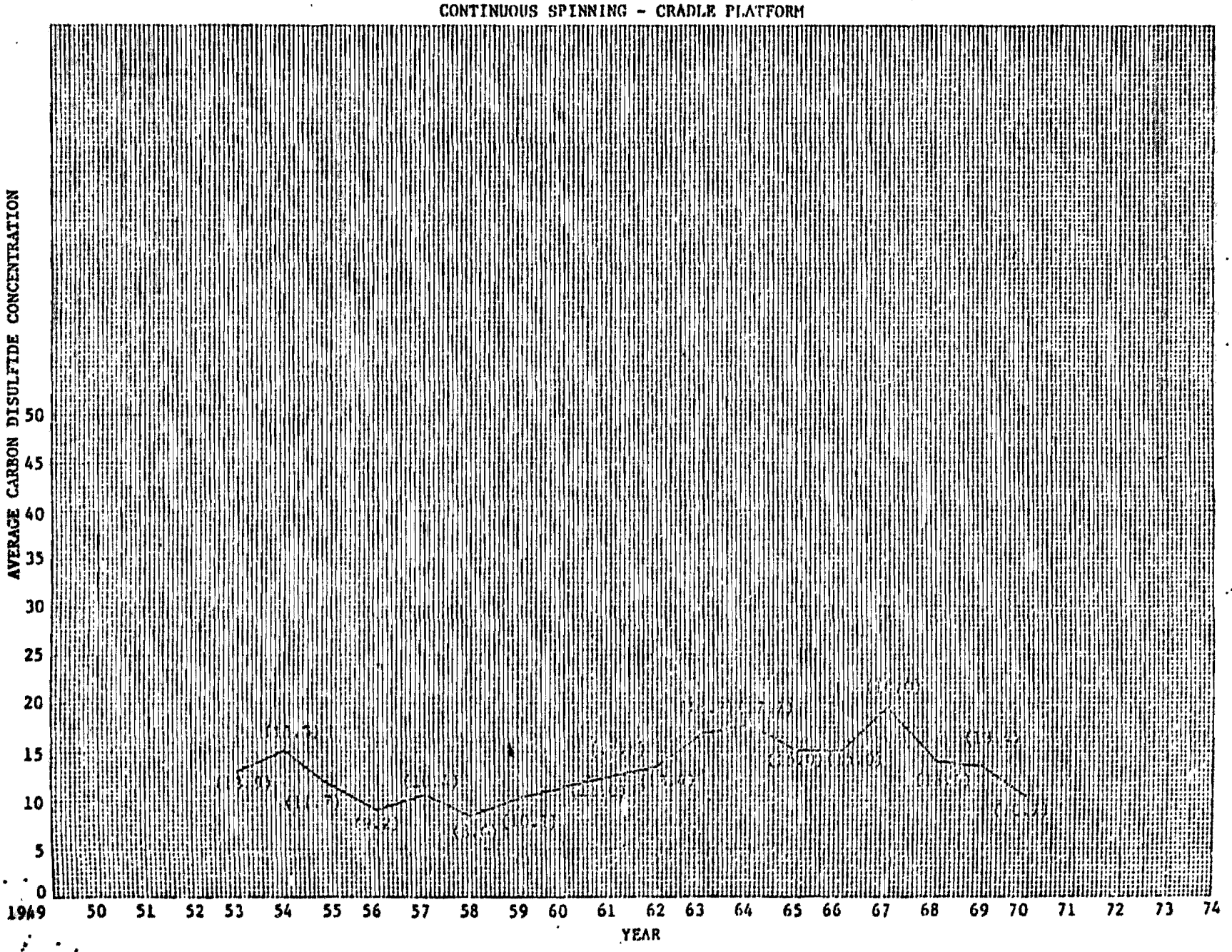
5
0
1949 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74
YEAR


CONTINUOUS SPINNING - CRADLE PLATFORM
AVERAGE CARBON DISULFIDE CONCENTRATION
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45
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35
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25
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15
10
5
0
1949
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51
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53
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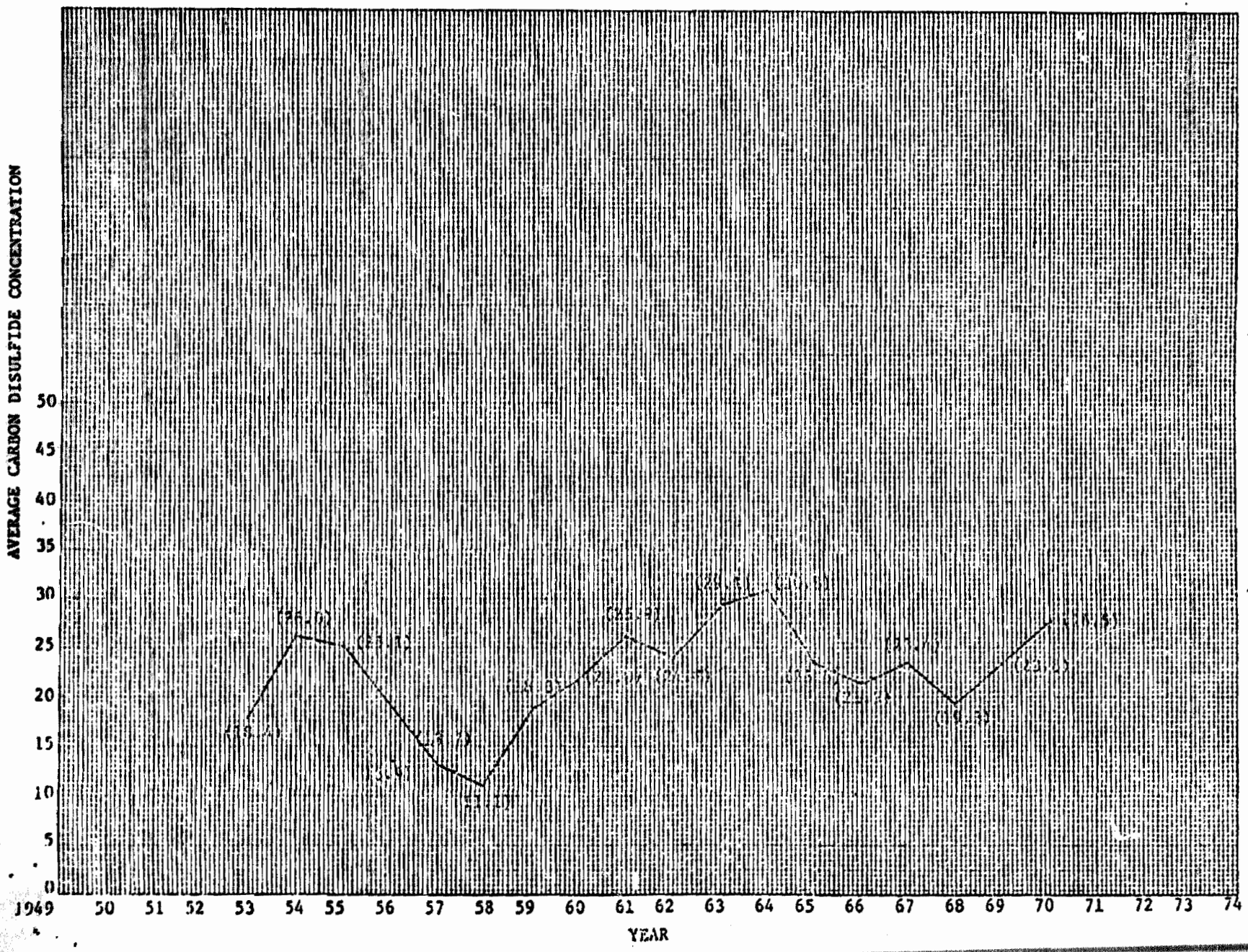
74
YEAR


CONTINUOUS SPINNING - SPINNING IN POINTS
AVERAGE CARBON DISULFIDE CONCENTRATION
50
45
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35
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25
20
15
10
5
0
1949
50
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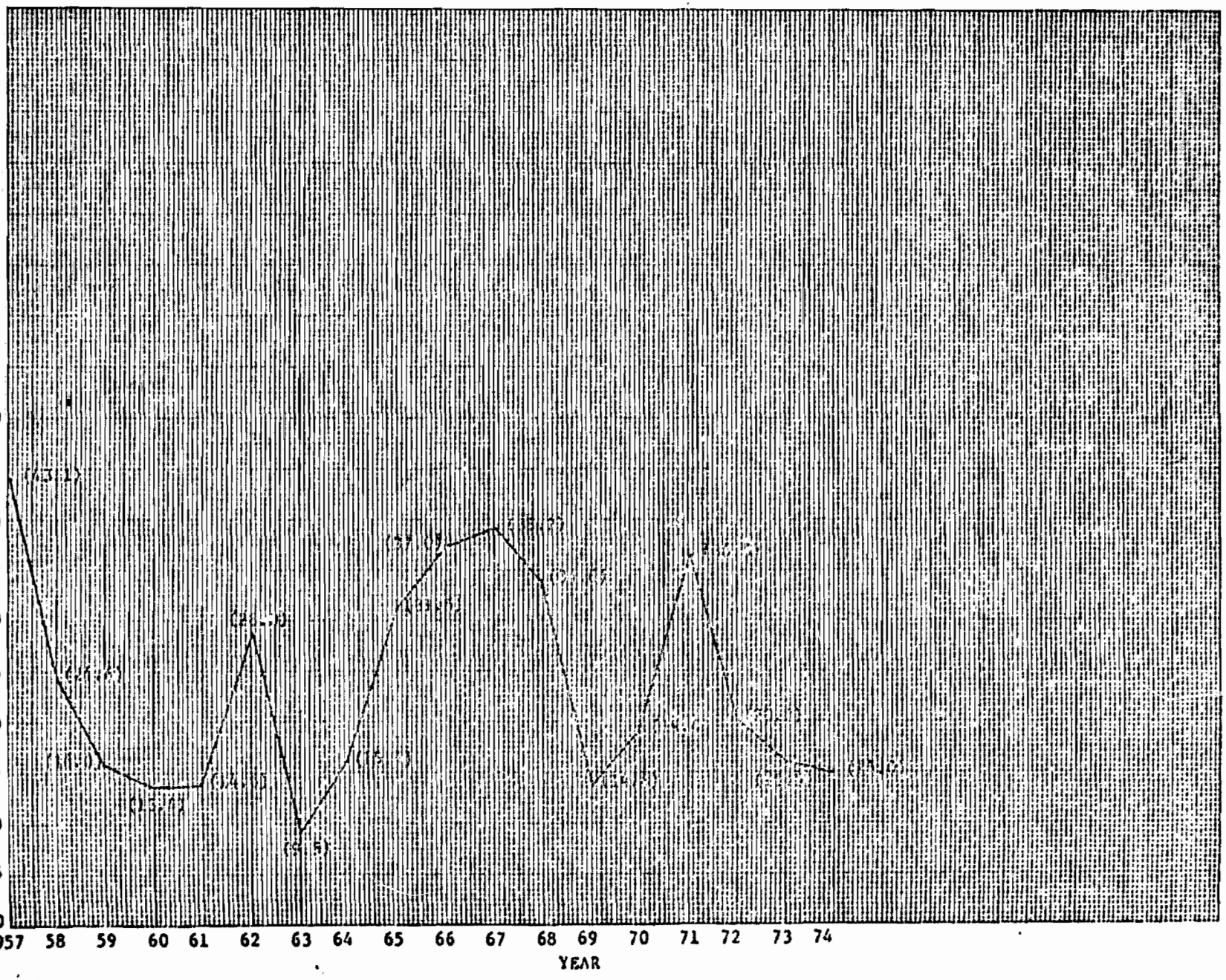
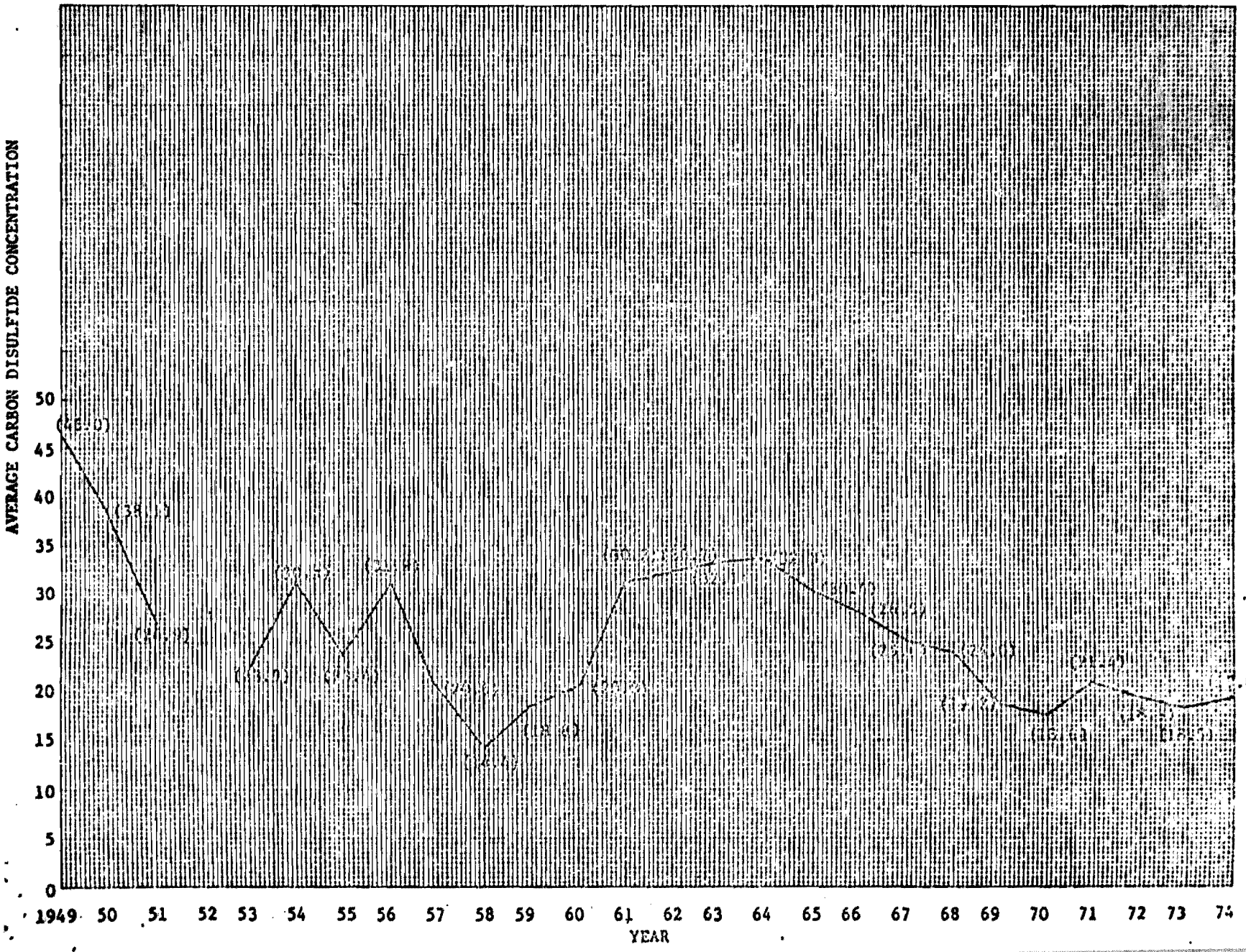
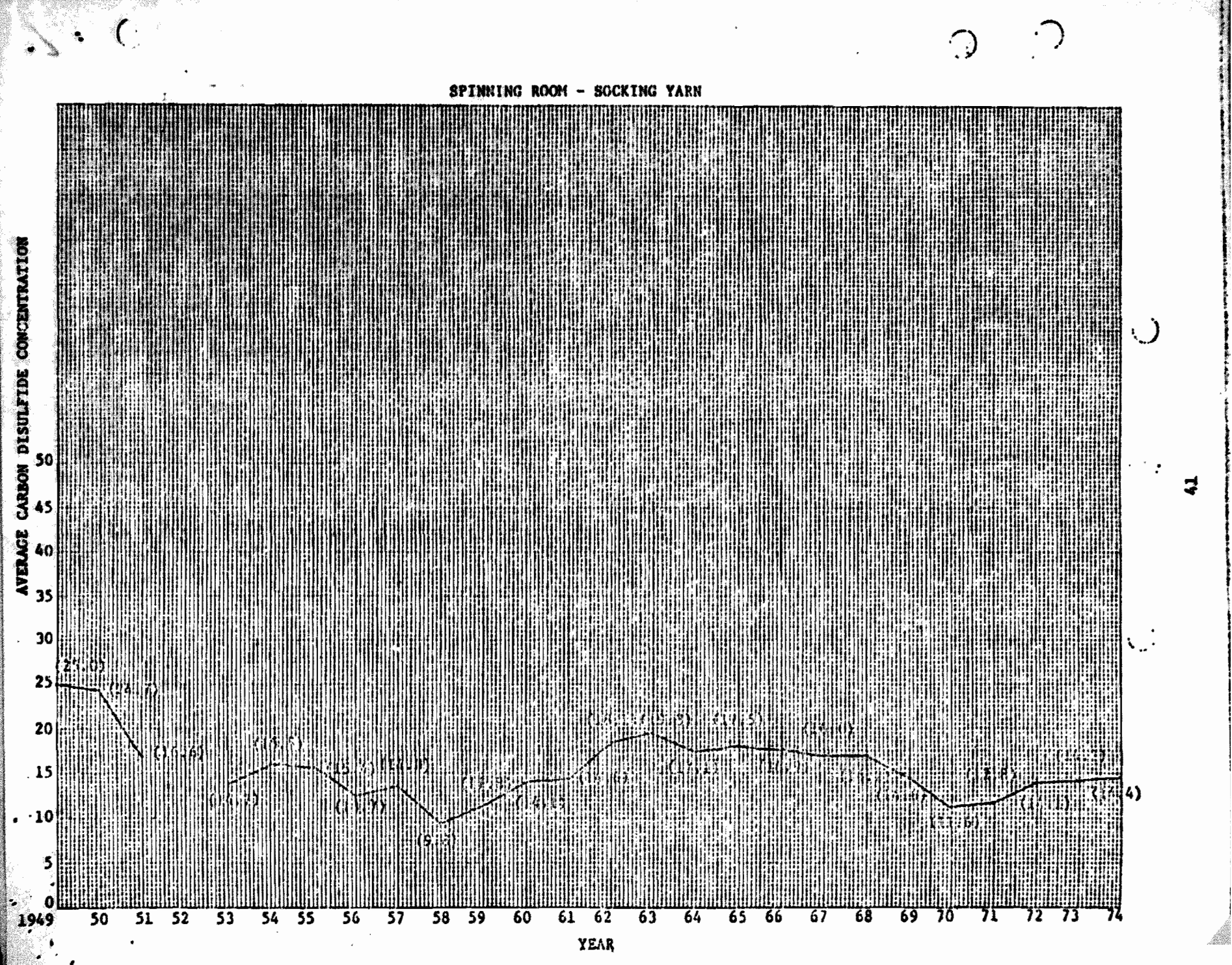
YEAR

FINISHING DEPARTMENT - WASTE CUTTER



SPINNING ROOM - DOFFING YARN




SPINNING ROOM - SOCKING YARN
AVERAGE CARBON DISULFIDE CONCENTRATION
50
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25
20
15
10
5
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1949
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53
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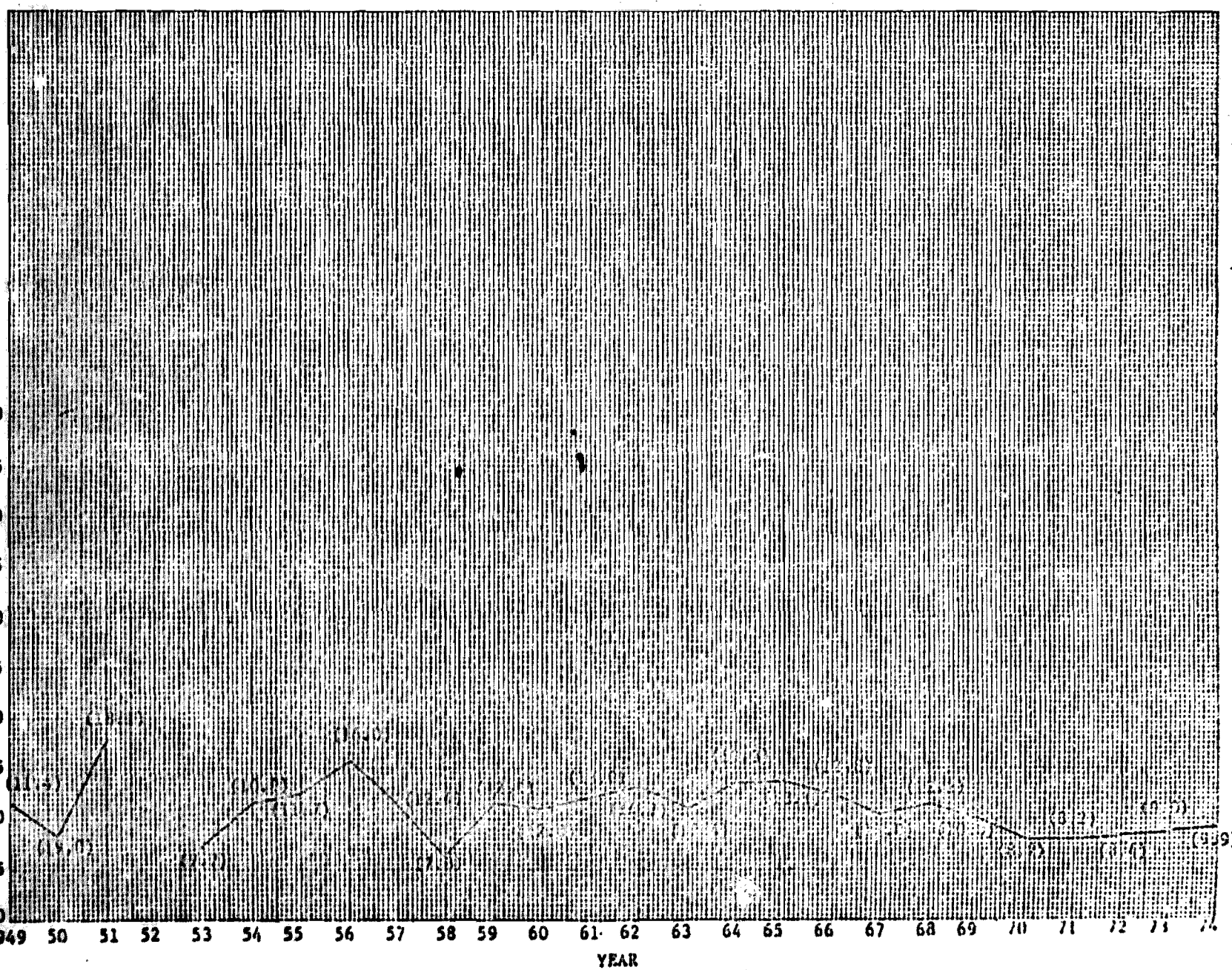
YEAR

SPINNING ROOM - WALKWAY BETWEEN MACHINES



APPENDIX 6

AVERAGE AREA SAMPLING DATA (PPM) BY AREA IN THE RAYON STAPLE PLANT FROM 1957 THROUGH 1978*

AREA	NUMBER OF SAMPLES	AVERAGE (PPM) 1957-1978
Churn Room	297	8.02
Dissolving Room	309	8.97
Spinning Machines	226	7.34
At 2nd Stretch Rollers	1281	26.09
Along hot dip	960	17.2
At the cutter	1256	19.2
Chip Conveyer	393	33.5
Waste Cutter	166	7.16
Correction Operator Desk	273	4.58
Basement Receiving Tank	157	4.99
2nd Bath Tanks	158	6.22
Cooling Tower	1	2.2
Spinning Room	1	12.4

* Samples taken by the company.

APPENDIX 7

NIOSH PERSONAL SAMPLING RESULTS FOR DIMETHYLTEREPHTHALATE (DMT) AT THE POLYESTER STAPLE PLANT ON APRIL 9-10, 1979

JOB DESCRIPTION	SAMPLE NUMBER	PPM DIMETHYLTEREPHTHALATE*
DMT Operator	SF-1-6	<0.015
TiO_2 Operator	SF-1-4	<0.015
	SF-2-3	<0.015
Miscellaneous Cleaner	SF-1-5	<0.015
General Replacer Spinning	SF-1-2	<0.015
	SF-2-6	<0.015
Spinner	SF-1-1	<0.015
	SF-2-2	<0.015
	SF-2-5	<0.015
DMT Relief Operator	SF-2-4	<0.015
Caster	SF-2-2	<0.015

* Limit of Detection 0.1 mg/sample

APPENDIX 8

NIOSH PERSONAL SAMPLING RESULTS FOR CAPROLACTAM AT THE SYNTHETIC FILAMENT PLANT ON APRIL 9-10, 1979

JOB DESCRIPTION	SAMPLE NUMBER	PPM CAPROLACTAM*
Caprolaptam	FF-1-6	<0.14
Unloader	FF-2-3	<0.14
Caprolaptam Operator	FF-1-1	<0.14
Spinner	FF-1-2	<0.14
Chip Cutter	FF-1-4	
	FF-2-4	3.93
	FF-1-5	<0.14
Pneumatic	FF-1-3	<0.14
Blender Operator	FF-2-6	<0.14
Dowtherm Operator	FF-2-7	<0.14
Spinner	FF-2-8	<0.14
	FF-2-1	<0.14
Chip Handler	FF-2-5	<0.14

* Limit of Detection 0.5 mg/sample

\PPENDIX 9

NIOSH SAMPLING RESULTS FOR ETHYLENE
GLYCOL AT THE SYNTHETIC FILAMENT PLANT ON APRIL 10, 1979

AREA DESCRIPTION	SAMPLE NUMBER	PPM ETHYLENE GLYCOL
Polymerization - 5th Floor	S-EG-1-1	5.12
	S-EG-1-2	1.22
Control Room	S-EG-1-3	0.41
Parts Cleaning (between vats)	F-EG-2-10	0.94
Ethylene Glycol Recovery	S-EG-2-1	0.32
Polymerization-5th Floor East End	S-EG-2-2	1.47
Polymerization-5th Floor West End	S-EG-2-3	10.10
Parts Cleaning Room	S-EG-1-4	1.21

APPENDIX 10

NIOSH SAMPLING RESULTS FOR METHANOL
AT THE SYNTHETIC FILAMENT PLANT ON APRIL 9, 1979
AND THE POLYESTER STAPLE PLANT APRIL 10, 1979

AREA DESCRIPTION	SAMPLE NUMBER	PPM METHANOL*
Polymerization-4th Floor Center Section	S-1-3	<0.9
Polymerization-4th Floor West Section	S-1-2	<0.9
Polymerization-5th Floor West Section	S-1-4	<0.9
Polymerization-4th Floor East Section	**S-2-3	<0.9
Polymerization-4th Floor	**S-2-2	<0.9

* Limit of Detection 0.10 mg/sample
** Polyester Staple Plant

APPENDIX 11

NIOSH SAMPLING RESULTS FOR
DOWTHERM AT THE SYNTHETIC FILAMENT PLANT ON APRIL 9, 1979
AND THE POLYESTER STAPLE PLANT APRIL 10, 1979

JOB/AREA DESCRIPTION	TYPE OF SAMPLE	SAMPLE NUMBER	PPM DOWTHERM*
Dowtherm Storage	Area	** F-2-1	<0.01
Continuous Street Oper.	Personal	F-2-3	<0.01
Dowtherm Operator	Personal	F-2-2	<0.01
Polymerization Cleaner 5th Floor	Personal	*** S-2-7	<0.01
Dowtherm Boiler Room	Area	S-2-6	<0.01
Polymerization 4th Floor	Area	S-2-5	<0.01
Polymerization 4th Floor East End	Area	S-2-4	<0.01

* Limit of Detection 0.01 mg/sample
** Synthetic Filament Plant
*** Polyester Staple Plant

APPENDIX 12

NIOSH'S PERSONAL SAMPLING RESULTS FOR HYDROGEN SULFIDE (H_2S) AT THE RAYON STAPLE PLANT

JOB DESCRIPTION	SAMPLE NUMBER	DATE OF SAMPLING	RESULTS H_2S PPM
Spinner	AE-2	4-4-79	0.3
Dissolving Room	AE-1	4-4-79	0.1
Spinner	AE-9	4-5-79	0.7
Wash Track Oper.	AE-11	4-5-79	0.7
Crystallizer and Evaporator Operator	AE-12	4-5-79	1.9
Spinner	AE-10	4-5-79	0.6
Wash Track Oper.	T-4	4-5-79	0.3
Spinner	T-7	4-5-79	0.6
Cutter Operator	T-2	4-5-79	0.2
Spinner	T-8	4-5-79	0.6
Cutter Operator	AE-18	4-6-89	0.13
Wash Track	AE-19	4-6-79	0.68
Churn Room Operator	AE-20	4-6-79	0.14
Crystallizer and Evaporator Operator	AE-15	4-6-79	0.52
Spinner	AE-17	4-6-79	0.42
Sand Filter	AE-13	4-6-79	0.79
Crystallizer and Evaporator Operator	AE-14	4-6-79	0.55

APPENDIX 13

PERSONAL CS_2 AIR SAMPLING DATA FROM THE RAYON STAPLE PLANT TAKEN BY NIOSH DURING THE MARCH AND APRIL, 1979 SURVEY

DATE	DEPARTMENT	JOB CODE	JOB DESCRIPTION	TUBE NUMBER	CONCENTRATION PPM
4-2	11	1	Lye Room Operator	405	0.77
4-3		1	" " "	457	1.00
4-3		1	" " "	423	<0.03
4-4		1	" " "	459	0.85
4-5		1	" " "	479	0.31
4-5		1	" " "	483	1.94
4-2	11	4	Soaking Press Operator	408	0.90
4-2			" " "	402	0.29
4-3			" " "	428	2.18
4-3			" " "	427	1.01
4-3			" " "	440	2.24
4-5			" " "	480	1.51
4-5			" " "	477	1.08
4-5			" " "	462	1.15
4-5			" " "	490	1.38
3-11			" " "	233	3.2
3-9			" " "	111	5.4
3-10			" " "	191	4.3
3-12			" " "	281	6.0
3-7	11	5	Shredder Operator	613	7.3
3-11			" "	541	9.7
3-9			" "	120	4.3
3-10			" "	122	3.1
3-9			" "	129	5.2
3-10			" "	171	13.9
3-12			" "	275	10.7
3-12			" "	276	11.2
3-13			" "	394	1.24
4-23			" "	359	4.14
4-2			" "	429	1.00
4-3			" "	447	2.17

DATE	DEPARTMENT	JOB CODE	JOB DESCRIPTION	TUBE NUMBER	CONCENTRATION PPM
4-5	11	5	Shredder Operator	476	2.19
4-5			" "	701	2.25
4-5			" "	467	3.57
4-5			" "	470	2.55
4-4			" "	496	2.18
4-2	11	6	Churn Operator	395	3.11
4-3			" "	434	21.24
4-5			" "	425	3.39
4-2			" "	400	2.48
4-3			" "	420	1.15
4-4			" "	499	2.67
4-5			" "	472	3.86
4-5			" "	473	5.19
4-5			" "	465	5.20
4-5			" "	486	10.09
3-7			" "	34	10.0
3-8			" "	620	6.8
3-10			" "	198	6.9
3-12			" "	282	7.7
3-7			" "	43	8.4
3-8			" "	73	7.0
3-9			" "	117	7.5
3-10			" "	127	8.2
3-12			" "	226	16.1
3-7			" "	43	5.9
3-8			" "	77	6.9
3-9			" "	109	5.6
3-10			" "	106	6.4
3-11			" "	250	7.1
3-12			" "	272	10.8
3-9			" "	133	4.1
3-12			" "	271	5.1
3-9			" "	112	5.3
3-10			" "	172	3.3
3-11			" "	239	3.6

DATE	DEPARTMENT	JOB CODE	JOB DESCRIPTION	TUBE NUMBER	CONCENTRATION PPM
3-7	11	7	Dissolver Operator	32	4.5
3-8			" "	94	4.6
3-9			" "	103	4.1
3-10			" "	180	4.8
3-11			" "	242	6.1
3-12			" "	277	5.0
3-7			" "	40	3.6
3-8			" "	96	7.9
3-9			" "	119	3.9
3-10			" "	176	3.8
3-11			" "	177	4.0
3-12			" "	218	5.9
3-12			" "	280	4.8
4-3			" "	416	2.84
4-3			" "	444	2.38
4-5			" "	703	2.77
4-5			" "	475	1.97
4-5			" "	468	1.89
4-4	11	10	Receiving & Filtration Oper.	492	3.38
4-4			" " "	455	3.32
3-7	11	69	Press Packer	39	4.9
3-8			" "	82	6.4
3-9			" "	107	4.3
3-10			" "	124	3.8
3-11			" "	246	4.0
3-8			" "	87	6.0
3-7			" "	48	6.9
3-9			" "	101	4.3
3-10			" "	142	4.2
3-11			" "	235	3.6
3-7			" "	49	5.4
4-2			" "	407	3.82
4-2			" "	398	3.33
4-3	11	14	Chemical Tank Cleaner	421	15.07
4-6			" " "	719	.96

DATE	DEPARTMENT	JOB CODE	JOB DESCRIPTION	TUBE NUMBER	CONCENTRATION PPM
4-4	11	14	Chemical Tank Cleaner	399	3.3
4-6			" " "	715	9.2
4-5	11	11	Spinning Tank Operator	722	3.51
4-5			" " "	726	3.67
4-6			" " "	748	1.99
4-2	12	29	Correction Operator	417	2.45
4-3			" "	425	1.58
4-5			" "	464	2.62
4-6			" "	718	1.60
4-3	12	30	Crystallizer & Evaporator Operator	412	1.39
4-3			" " "	433	2.32
4-3			" " "	438	11.02
4-5			" " "	463	2.23
4-3	12	49	Chemical Mix Operator	415	0.43
4-4			" " "	495	0.34
4-6			" " "	74	0.98
4-3	12	71	Salt Unit Operator	449	0.37
4-5			" " "	739	<0.04
4-4			" " "	493	0.22
4-6			" " "	712	<0.09
4-2	12	72	Sand Filter & Relief Oper.	401	0.92
4-3			" " " "	452	1.45
4-4			" " " "	500	2.84
4-5			" " " "	707	1.83
4-5			" " " "	488	1.67
4-2	12	73	Staple Spinner	393	5.71
4-2			" "	391	1.85
4-3			" "	418	2.73
4-4			" "	451	22.32
4-3			" "	426	1.65
4-3			" "	435	13.14
4-3			" "	442	2.09
4-3			" "	443	10.83
4-3			" "	432	6.70
4-3			" "	413	217.6

DATE	DEPARTMENT	JOB CODE	JOB DESCRIPTION	TUBE NUMBER	CONCENTRATION PPM
4-5	12	73	Staple Spinner	728	3.67
4-4		"	"	458	9.38
4-5		"	"	705	1.28
4-4		"	"	484	16.14
4-6		"	"	713	3.06
4-5		"	"	708	1.87
4-5		"	"	466	1.88
4-5		"	"	483	1.94
4-5		"	"	485	1.84
4-5		"	"	481	9.27
3-7		"	"	14	2.6
3-8		"	"	612	2.9
3-9		"	"	131	2.0
3-10		"	"	108	3.3
3-11		"	"	17	3.1
3-12		"	"	210	11.8
3-7		"	"	11	11.5
3-8		"	"	89	13.0
3-9		"	"	135	4.7
3-10		"	"	114	31.6
3-11		"	"	18	7.0
3-12		"	"	201	14.1
3-7		"	"	15	8.9
3-8		"	"	91	13.4
3-9		"	"	136	7.0
3-10		"	"	200	22.9
3-11		"	"	244	9.1
3-12		"	"	227	5.4
3-7		"	"	20	9.3
3-9		"	"	104	9.0
3-10		"	"	199	26.2
3-11		"	"	238	8.0
3-12		"	"	223	14.4
3-7		"	"	13	10.4
3-8		"	"	88	13.9

DATE	DEPARTMENT	JOB CODE	JOB DESCRIPTION	TUBE NUMBER	CONCENTRATION PPM
3-9	12	73	Staple Spinner	134	9.6
3-10			" "	192	33.9
3-9			" "	130	2.9
3-10			" "	74	9.4
3-11			" "	231	3.2
3-12			" "	228	4.6
3-10			" "	178	11.2
3-11			" "	249	9.7
3-12			" "	220	8.2
3-9			" "	102	2.0
4-2	12	75	Tow Patroller	409	17.06
4-3			" "	446	6.11
4-5			" "	730	12.4
4-3	12	76	Cutter Operator	450	5.57
4-5			" "	737	3.50
4-6			" "	717	<0.04
3-7			" "	45	9.7
3-8			" "	611	12.0
3-9			" "	132	6.8
3-10			" "	174	30.7
3-11			" "	154	7.6
3-12			" "	207	12.6
3-7			" "	618	12.6
3-8			" "	75	6.3
3-9			" "	113	4.1
3-10			" "	116	10.7
3-11			" "	245	1.3
3-12			" "	205	7.1
3-7			" "	615	11.7
3-8			" "	95	12.4
3-9			" "	126	6.5
3-10			" "	19	16.1
3-11			" "	72	12.6
3-12			" "	208	8.0

DATE	DEPARTMENT	JOB CODE	JOB DESCRIPTION	TUBE NUMBER	CONCENTRATION PPM
3-7	12	80	Washer Operator	35	9.9
3-8			" "	96	8.9
3-9			" "	118	6.5
3-10			" "	194	6.1
3-11			" "	12	10.1
3-12			" "	204	11.1
3-7			" "	16	4.8
3-8			" "	93	6.7
3-9			" "	115	5.6
3-10			" "	106	6.4
3-11			" "	234	7.1
3-12			" "	217	14.4
3-7			" "	37	5.3
3-8			" "	76	7.0
3-9			" "	138	4.8
3-10			" "	197	6.1
3-11			" "	125	6.6
3-12			" "	224	9.5
3-9			" "	105	4.2
3-10			" "	145	4.2
3-11			" "	175	6.4
3-12			" "	229	7.0
4-2			" "	404	3.56
4-5			" "	735	1.92
4-3			" "	441	6.11
4-3			" "	424	159.0
4-4			" "	497	3.15
4-5			" "	702	2.87
4-5			" "	724	3.33
4-5			" "	471	2.55
4-6			" "	710	1.01
4-2	12	78	Dryer Operator	406	0.62
4-3			" "	411	47.65
4-3			" "	436	1.09
4-4			" "	460	<0.06

DATE	DEPARTMENT	JOB CODE	JOB DESCRIPTION	TUBE NUMBER	CONCENTRATION PPM
4-5	12	78	Dryer Operator	704	0.41
4-5			" "	478	<0.05
3-9	12	-- 79	Baler Operator	110	1.0
3-10			" "	179	1.2
3-11			" "	123	1.2
3-10			" "	193	2.1
3-12			" "	203	1.2
4-2			" "	410	2.21
4-2			" "	396	<0.04
4-5			" "	734	1.02
4-3			" "	419	0.60
4-3			" "	437	0.82
4-5			" "	474	0.36
4-5			" "	721	0.28
4-5			" "	489	<0.05
4-6			" "	744	<0.05
4-6			" "	746	1.21
4-3			" "	431	0.95
4-4			" "	498	0.57
4-3	12		Lift Truck Operator	430	0.42
4-4			" " "	494	<0.06
4-5			" " "	706	<0.06
4-6			" " "	743	0.45

APPENDIX 14

Carbon Disulfide

SAMPLING AND ANALYTICAL METHOD

Analyte:	Carbon Disulfide	**Method No.:**	S248
Matrix:	Air	**Range:**	14.7-58.8 ppm
OSHA Standard:	Ceiling - 30 ppm Peak - 100 ppm 8-hr. TWA - 20 ppm	**Precision ($\overline{CV}_T$):**	0.059
Procedure:	Adsorption on charcoal, desorption with benzene, GC	**Validation Date:**	1/30/76

1. Principle of the Method (Reference 11.1)

   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 benzene.

   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 for standards.

2. Range and Sensitivity

   2.1 This method was validated over the range of 14.7-58.8 ppm at an atmospheric temperature and pressure of 22°C and 766 mm Hg, using a 6-liter sample. Under the conditions of sample size (6 liters) the probable useful range of this method is 5-90 ppm. The 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 carbon disulfide and other substances in the air. The first section of the charcoal tube was found to hold 6.0 mg of carbon disulfide when a test atmosphere

11. References

11.1 "Analytical Method for Chloride in Air," Health Laboratory Science, Vol. 12, No. 3, (July 1975), 253-258.

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

APPENDIX 15

Methyl Alcohol

SAMPLING AND ANALYTICAL METHOD

Analyte:	Methyl Alcohol	Method No.:	S59
Matrix:	Air	Range:	140-540 mg/cu m
OSHA Standard:	200 ppm (260 mg/cu m)	Precision ($\overline{CV}_T$):	0.070
Procedure:	Adsorption on silica gel, desorption with water, GC	Validation Date:	1/17/75

1. Principle of the Method

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

1.2 The silica gel in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with water.

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 the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 140-540 mg/cu m at an atmospheric temperature and pressure of 25 C and 748 mm Hg, using a nominal 5-liter sample. Under the conditions of sample size (5 liters) the probable range of this method is 25-900 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 4-mg sample. The 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 silica gel tube. This capacity varies with the concentration of the analyte and other substances in the air. The first section of the silica gel tube was found to hold 5.6 mg of the analyte when a test atmosphere of 540 mg/cu m of the analyte in dry air was sampled at 0.2 liters per minute for 52 minutes. Breakthrough occurred at this time.

i.e., the concentration of the analyte in the effluent was 5% of that in the influent. (The silica gel tube consists of two sections of silica gel 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.

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 specific compound under study 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 140 to 540 mg/cu m was 0.063. This value corresponds to a standard deviation of 16.5 mg/cu m 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 The average values obtained using the overall sampling and analytical method were 8.9% lower than the "true" value at the OSHA standard level.

4.3 The above data are based on validation experiments using the internal standard method. (Reference 11.2)

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 gas 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 compounds 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 silica gel 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 accurately (±5%) at the recommended flow rate, (Reference 11.3)

6.2 Silica gel tubes: glass tube 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 silica gel separated by a 2-mm portion of urethane foam. The absorbing section contains 100 mg of silica gel, the backup section 50 mg. A 3-mm portion of urethane form 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 absorbing section. The pressure drop across the tube 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 (10-ft x 1/8-in. stainless steel) packed with 10% FFAP on 80/100 Chromosorb W-AW.

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

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

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

6.8 Pipets: 1.0-ml delivery type.

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

7. Reagents

7.1 Eluent: Distilled water.

7.2 Methyl Alcohol (reagent grade).

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 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 silica gel 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 tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

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

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

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

8.3.5 A maximum sample size of 5 liters is recommended. Sample at a flow of 0.20 liters per minute or less. The flow rate should be known with an accuracy of at least ±5%.

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

8.3.7 The silica gel 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 tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the suspected compound should be submitted to the laboratory in glass containers with Teflon®-lined caps. These liquid bulk samples should not be transported in the same container as the silica gel tubes.

8.4 Analysis of Samples

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

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of distilled water is pipetted into each sample container. Desorption should be done for 4 hours. Tests indicate that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the water is added to minimize evaporation.

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

1. 30 ml/min (80 psig) nitrogen carrier gas flow.
2. 30 ml/min (50 psig) hydrogen gas flow to detector.
3. 300 ml/min (50 psig) air flow to detector.
4. 200 C injector temperature.
5. 300 C manifold temperature (detector).
6. 80 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-µl 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 µl 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-µl 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 µl to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 µl 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 (see Section 9).

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 silica gel to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process.

8.5.2 Procedure for determining desorption efficiency. Silica gel equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.0-ml sample container. This silica gel must be the same

type as that used in obtaining the samples and can be obtained from unused silica gel tubes. A known amount of the analyte is injected directly into the silica gel with a 10-ul syringe, and the container is capped. The amount injected is equivalent to that present in a 5-liter sample at the selected level.

At least six tubes at each of three levels (0.5X, 1X, and 2X the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the silica gel. These six 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.

The weight of analyte found in each tube is determined from the standard curve (Section 9). Desorption efficiency is determined by the following equation:

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

The desorption efficiency is dependent on the amount of analyte collected on the silica gel. Plot the desorption efficiency versus the 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/ml of eluent. 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 samples. Curves are established by plotting concentrations in mg/ml versus peak area.

Note: Standard solutions should be analyzed at the same time that the sample analysis is done. This will minimize the effect variations of FID response.

10. Calculations

10.1 Read the weights, in mg, corresponding to each peak area (area ratio in case of the internal standard method) from the

standard curve. No volume corrections are needed, because the standard curve is based on mg/ml eluent 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 weights 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 (Section 8.5.2) for the amount of analyte 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 analyte in the air sampled can be expressed in mg per cu m, which is numerically equal to µg per liter of air

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

10.6 Another method of expressing concentration is ppm:

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

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 (g/mole) of analyte
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", Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract No. HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes, September 15, 1972."

APPENDIX 16

Phenyl Ether - Biphenyl Mixture

(vapor)

Dowtherm

SAMPLING AND ANALYTICAL METHOD

Analyte:	**Phenyl Ether-Biphenyl Mixture**	**Method No.: S73**
Matrix:	**Air**	**Range: 3.86-15.7 mg/cu m**
OSHA Standard:	**1 ppm (7 mg/cu m)**	**Precision ($\overline{CV}_T$): 0.089**
Procedure:	**Adsorption on silica gel, desorption with benzene, GC**	**Validation Date: 2/14/75**

1. Principle of the Method

   1.1 A known volume of air is drawn through a silica gel tube to trap the organic vapors present. Flow rate 20cc per minute.

   1.2 The silica gel in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with benzene.

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

   1.4 The areas of the resulting peaks are determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

   2.1 This method was validated over the range of 3.86-15.7 mg/cu m at an atmospheric temperature and pressure of 23°C and 761 mm Hg, using a 10 liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 0.7-21 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 0.2 mg sample. The 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 silica gel tube. This capacity varies with the concentrations of the analyte and other substances in the air. The first section of the silica gel tube was found to hold at least 0.7 mg of analyte when a test atmosphere containing

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.

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 hexane solution of phenyl ether containing 17.3 mg/ml is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

The amount injected is equivalent to that present in a 10 liter air sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and 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 0.5 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

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

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

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/0.5 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 samples. Curves are established by plotting concentration in mg/0.5 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the 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/0.5 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 weights found in the front and backup sections to get 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/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

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
M.W.	= molecular weight (g/mole) of analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

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Determination of Ethylene Oxide, Ethylene Chlorohydrin, and Ethylene Glycol by Gas Chromatography

HARVEY D. SPITZ and JOSEPH WEINBERGER

Abstract □ The technique of gas chromatography was employed for the quantitative determination of ethylene oxide, ethylene chlorohydrin, and ethylene glycol. The simultaneous determination of ethylene chlorohydrin and ethylene glycol in an aqueous solution using a single polyethylene glycol column was accomplished under isothermal conditions, while ethylene oxide was determined employing a styrene–divinylbenzene copolymer column. A key step in obtaining useful and reproducible columns for determining trace quantities of ethylene oxide, ethylene chlorohydrin, and ethylene glycol was found to be related to the aging procedure employed. Experimental data indicate that one can quantitatively recover low levels of ethylene chlorohydrin and ethylene glycol from a water-absorbable fabric. The lower limits of detection of ethylene oxide, ethylene chlorohydrin, and ethylene glycol were found to be in the nanogram range.

Keyphrases □ Ethylene oxide, chlorohydrin, and glycol—determination □ Quantitative recovery from fabric—ethylene oxide, chlorohydrin, and glycol □ GLC—analysis

The increasing demand for ethylene oxide as a sterilizing agent has stimulated a great deal of research on the possible toxicological effects of ethylene chlorohydrin (2-chloroethanol) and ethylene glycol, which are associated side products of this sterilant. Although the literature contains a significant number of reports on the toxicity of ethylene oxide (1–12), ethylene chlorohydrin (13–17), and ethylene glycol (13, 18–24), the large variation in the experimental systems employed and the conclusions reached have prompted further investigations.

Several analytical methods have been reported in the literature for the determination of ethylene oxide (25–33), ethylene glycol (27, 34), and ethylene chlorohydrin (35–39). However, the present analytical requirements with respect to sensitivity, specificity, and time of analysis for the quantitative determination of ethylene oxide, ethylene chlorohydrin, and ethylene glycol in water-absorbable fabrics did not readily adapt to these methods.

Some workers (40) advocated a weighing procedure based on the premise that the loss in weight of a sterilized sample with respect to time represents the amount of ethylene oxide lost. The poor sensitivity one obtains with this approach, coupled with other possible concomitant loss of material (such as a loss due to absorbed gases used in diluting the sterilant or a loss of volatile materials from the sample) or even gain in material (such as the formation of ethylene glycol, diethylene glycol, *etc.*), makes this method less attractive as compared to other techniques.

Since low levels of the three residues may be toxicologically significant, the technique of gas chromatography was chosen over other available analytical methods because of its excellent sensitivity and selectivity.

In this paper, emphasis is placed on the quantitative determination of ethylene oxide, ethylene chlorohydrin, and ethylene glycol in the nanogram range, employing two different gas chromatographic columns. One column is capable of determining trace quantities of ethylene oxide, while the second column is capable of simultaneously determining trace amounts of ethylene chlorohydrin and ethylene glycol.

EXPERIMENTAL

Apparatus—F&M model 5750, equipped with a dual-flame ionization detector, connected to a 1-mv. recorder[1] was used.

Column A—A coiled stainless steel column, 1.83 m. (6 ft.) × 0.32 cm. (0.125 in.) i.d., containing a styrene–divinylbenzene copolymer resin (80–100 mesh, 300–400 $m.^2/g.$ surface area)[2] was employed for the analysis of ethylene oxide.

Column B—A coiled glass column, 1.83 m. (6 ft.) × 2 mm. i.d., containing 3% polyethylene glycol[3] coated on a styrene–divinylbenzene copolymer resin (80–100 mesh, less than 50 $m.^2/g.$ surface area)[4] was used for the analysis of ethylene chlorohydrin and ethylene glycol.

Preparation of Column Packing—To prepare the packing for Column B, the following method was employed. A 1% solution of polyethylene glycol in chloroform was prepared by dissolving 0.6 g. of the polyethylene glycol in 60 ml. of chloroform. To this solution, 19.4 g. of the styrene–divinylbenzene resin[4] was slowly added with gentle stirring. The mixture was allowed to stand for 10 min. before being transferred to a large watchglass. The packing was spread out to a height no greater than 0.64 cm. (0.25 in.). The watchglass was then placed in a ventilation hood with occasional stirring during this drying procedure until all traces of chloroform were removed from the packing.

Column Packing—Column A was vibrated while being packed under vacuum and then coiled to the necessary configuration of the chromatograph oven. The coiled glass column (Column B) was packed in a similar manner.

Column Conditioning—Column B was initially conditioned in the gas chromatograph overnight at 200° with helium flow. The following day, the column was connected to the detector system and 1-μl. injections of distilled water were made approximately every 15 min. for several hours at a column temperature of 180°. Similarly, Column A was aged overnight at 200°, and several 1-μl. injections of acetone were made at this temperature.

With this aging technique, one is able to analyze all three residues in the nanogram range, employing the maximum sensitivity of the instrument.

Instrumental Parameters—For the analysis of ethylene chlorohydrin and ethylene glycol (Column B), the instrument was operated isothermally at a column temperature of 168°, an injector temperature of 195°, and a detector temperature of 220°. Helium was used as the carrier gas with a flow rate of 30 ml./min., while a flow rate of 300 ml./min. was used for air and 30 ml./min. for hydrogen. For the analysis of ethylene oxide (Column A), the instrument was operated at an injector temperature of 125°, a detector temperature of 220°, and a column temperature of 100° for 9 min., then the instrument was temperature programmed at 50°/min. up to a maximum of 200° and held for 4 min. at this temperature. Flow rates for helium, hydrogen, and air were approximately the same as used for Column B. A chart speed of 0.51 cm. (0.2 in.)/min. was used for the determination of ethylene oxide and 1.3 cm. (0.5 in.)/min. for the simultaneous determination of ethylene chlorohydrin and ethylene glycol.

[1] Sargent recorder, model No. SRG.
[2] Chromosorb 102, Johns-Manville Products Corp.
[3] Carbowax 20M, Union Carbide Corp.
[4] Chromosorb 101, Johns-Manville Products Corp.

Figure 1—Typical gas chromatogram of 5.7 ng. of ethylene chlorohydrin (A) and 6.4 ng. of ethylene glycol (B) on Column B. Attenuation range = 1 × 1. Injection volume = 1 µl.

Recovery Study for the Simultaneous Determination of Ethylene Chlorohydrin and Ethylene Glycol—A water-absorbable fabric was simultaneously spiked with known amounts of ethylene chlorohydrin and ethylene glycol at four different levels of concentration. Approximately 1-g. samples of fabric were placed in 20-ml. serum vials to which 5.0 ml. of different standard solutions was added. These standard solutions were prepared (in water) in such a manner that 5.0 ml. of each standard solution contained ethylene chlorohydrin and ethylene glycol in varying amounts. Sample 1 was simultaneously spiked with 0.022 mg. of ethylene chlorohydrin and 0.099 mg. of ethylene glycol, while succeeding samples were spiked with higher levels of both compounds (Table I). After allowing the samples to stand for 15 min., 5.0 ml. of distilled water was added to each vial. The vials were sealed by crimping an aluminum seal over a rubber septum. The samples were then placed in a mechanical shaker[1] and were shaken for 5 min. Duplicate samples were also prepared in the same manner as previously described. Likewise, corresponding standards were prepared in the same fashion, employing the same standard solutions used to spike the samples except that the vials did not contain any fabric.

One-microliter injections of each of the foregoing solutions were injected into Column B in duplicate, the order of injection being: sample, corresponding standard, and duplicate sample. The peak height method was used to calculate all the experimental data.

A lower concentration range of ethylene chlorohydrin as compared to ethylene glycol was chosen as it is presently considered to be more toxic than ethylene glycol.

Table I—Recovery of Ethylene Chlorohydrin and Ethylene Glycol from Spiked Fabric

Samples	ECH[a] and EG[b] Added to Fabric, mg. ECH[a]	EG[b]	ECH[a] and EG[b] Recovered from Spiked Fabric,[c] mg. ECH[a]	EG[b]
Sample 1	0.022	0.099	0.021	0.112
Duplicate Sample 1	0.022	0.099	0.019	0.099
Sample 2	0.044	0.495	0.046	0.476
Duplicate Sample 2	0.044	0.495	0.047	0.540
Sample 3	0.088	1.48	0.085	1.44
Duplicate Sample 3	0.088	1.48	0.084	1.48
Sample 4	0.133	2.97	0.131	2.93
Duplicate Sample 4	0.133	2.97	0.131	2.98

[a] Ethylene chlorohydrin. [b] Ethylene glycol. [c] Average value of duplicate injections for each sample.

RESULTS AND DISCUSSION

The experimental data shown in Table I indicate that low levels of ethylene chlorohydrin and ethylene glycol can be quantitatively determined in the presence of each other. These results also indicate that no detectable irreversible adsorption takes place on the fabric with either compound.

One should keep in mind that 1 µl. of the final sample and standard solutions, which was injected into the gas chromatograph, contained from 2 to 13 ng. of ethylene chlorohydrin and 10 to 297 ng. of ethylene glycol. To obtain respectable peak heights for the lower concentrations of ethylene chlorohydrin and the lowest concentration of ethylene glycol, the maximum sensitivity of the instrument was required (attenuation 1 × 1). As shown in Fig. 1, the separation of the two compounds is good and baseline noise is negligible. Since the concentration of ethylene glycol was much higher in Samples 2, 3, and 4 (Table I), it was necessary to change the attenuation manually after the elution of the ethylene chlorohydrin peak to accommodate properly the ethylene glycol peak. This very minor inconvenience of manual attenuation can be alleviated by having a recorder or integrator equipped with an automatic attenuator.

This experiment was also designed to obtain linearity curves for both compounds based on the different standard solutions injected into the chromatograph (those used for the recovery study). Since each standard solution contained both compounds, one was able to obtain simultaneously from the data the individual linearity relationships for each compound. Plots of the data are shown in Figs. 2 and 3. Figure 2 covers an attenuation range for ethylene chlorohydrin from 1 × 1 to 1 × 2, while the ethylene glycol plot covers an attenuation range from 1 × 1 to 1 × 32.

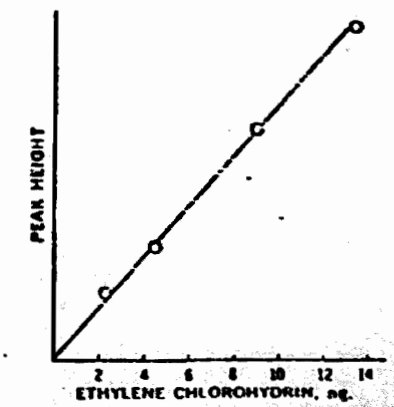

Figure 2—Plot of the concentration of ethylene chlorohydrin versus peak height. Attenuation range = 1 × 1 to 1 × 2. Injection volume = 1 µl.

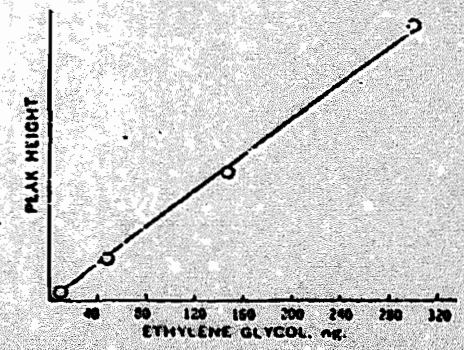

Figure 3—Plot of the concentration of ethylene glycol versus peak height. Attenuation range = 1 × 1 to 1 × 32. Injection volume = 1 µl.

[1] Model No. 3800, Pitchford Manufacturing Corp., Pittsburgh, Pa.

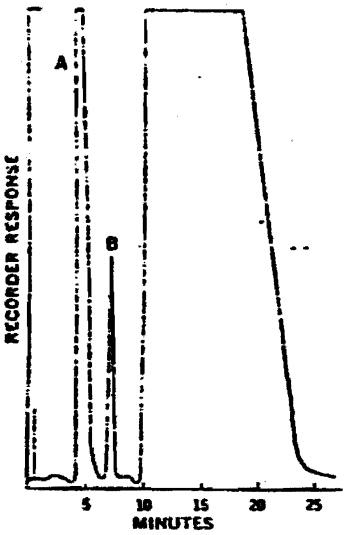

Figure 4—*Typical gas chromatogram of 5.7 ng. of ethylene oxide (B) on Column A. Attenuation range = 1 × 1. Injection volume = 1 μl. (A) is an acetone impurity peak.*

The familiar problem of ghosting (41–43) was observed with ethylene glycol on Column B. Subsequent 1-μL injections of water after previous injections of the higher concentrations of ethylene glycol produced ethylene glycol peaks that were observable only at the most sensitive attenuations of the instrument. The possible error contributed by this ghosting phenomenon was found to be negligible. Details of this work will be discussed in a future paper.

As in the case of ethylene chlorohydrin and ethylene glycol, a gas chromatographic method was developed for determining trace levels of ethylene oxide. The excellent stability of the styrene–divinylbenzene resin, coupled with its ability to resolve ethylene oxide from a solvent such as acetone (and its impurities), makes Column A highly desirable. A typical chromatogram is shown in Fig. 4. The major acetone impurity, as shown in Fig. 4, was observed in several different brands of acetone only at the most sensitive attenuations of the instrument. In most cases, distillation of the acetone will reduce the concentration of this impurity; however, it is usually separated from the ethylene oxide peak. Temperature programming is required to elute the acetone from the column so that a complete analysis can be accomplished within 25 min. As shown in Fig. 5, a linear relationship is present at low levels of ethylene oxide. The analysis for residual ethylene oxide has been carried out successfully in ethylene oxide sterilized samples, such as fabrics and plastics with acetone or tetrahydrofuran as the solvent. Recent private communications with other workers in the field have informed the authors that the method has performed satisfactorily for the analysis of residual ethylene oxide in their sterilized samples.

The approximate lower limit of detection for ethylene oxide on Column A was found to be 0.7 ng./μl. (representing 7% of the chart paper), employing a 1-μL injection of acetone. Similarly, the approximate lower limits of detection for ethylene chlorohydrin and ethylene glycol in aqueous solution on Column B were found to be 0.6 ng./μl. and 1.6 ng./μL. respectively (both representing 8% of the chart paper).

Since more than 1 μl. of solution can be injected into the column without any deleterious effects upon the resolution, the limits of detection are further increased for any given sample. Of course, by decreasing the volume of solvent and increasing the sample size and injection volume, the limits of detection can be increased even further.

Recent experiments in this laboratory showed that all three residues can be determined simultaneously on the polyethylene glycol column in the presence of water and/or acetone. The authors hope to present in the near future the optimum conditions and limits of detection for separating and quantitating all three compounds.

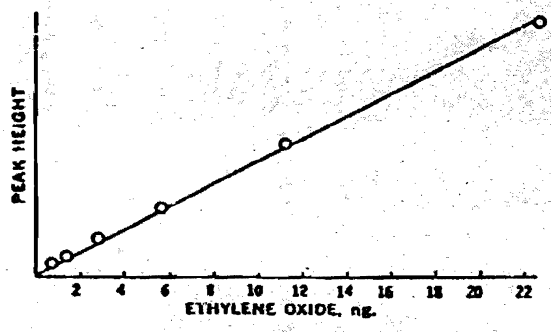

Figure 5—*Plot of the concentration of ethylene oxide* versus *peak height. Attenuation range = 1 × 1. Injection volume = 1 μl.*

Additional work is proposed on separating low molecular weight epoxides and the corresponding glycols and chlorohydrins on the same polyethylene glycol column. Preliminary experiments indicate this is feasible.

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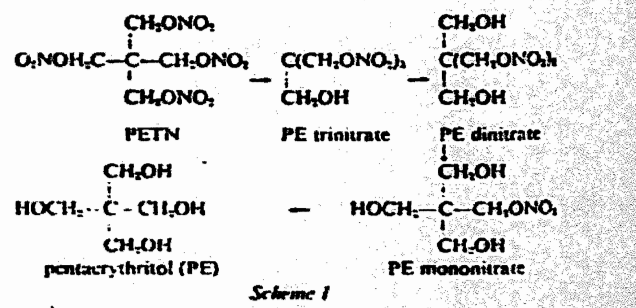
Pharmacodynamics and Biotransformation of Pentaerythritol Tetranitrate in Man

IVAN W. F. DAVIDSON*, HENRY S. MILLER, Jr.*, and FREDERICK J. DiCARLO†‡

Abstract □ The absorption, biotransformation, and excretion of pentaerythritol tetranitrate was studied after oral administration of two dosages, 20 and 40 mg., to patients. The drug was given as ^{14}C-pentaerythritol tetranitrate incorporated into tablets of a type used clinically. The total ^{14}C excretion in 48 hr. was approximately 92% of both doses. However, a greater proportion of the lower dose was excreted in the urine: 60% of the 20-mg. dose and 50% of the 40-mg. dose. Drug radioactivity was detected in the blood within 15 min., and peak levels occurred from 4 to 8 hr. after administration. The only radioactive compounds found in the blood were pentaerythritol, pentaerythritol mononitrate, and pentaerythritol dinitrate. These drug metabolites were also present in the urine and feces. The kinetics of renal excretion of the principal urinary metabolites, pentaerythritol and pentaerythritol mononitrate, were first order. The renal elimination-rate constant, k_e, of pentaerythritol was independent of the dose, but k_e for pentaerythritol mononitrate was dose related and significantly smaller for the higher dose. The ratio of pentaerythritol mononitrate:pentaerythritol excreted in the urine was approximately 1:1 for the lower dose and 3:1 for the higher dose. The findings indicate a rapid denitrification of pentaerythritol tetranitrate by the human to pentaerythritol mononitrate after oral ingestion, but a limited capacity for the conversion of pentaerythritol mononitrate to pentaerythritol.

Keyphrases □ Pentaerythritol tetranitrate and ^{14}C-substituted—human pharmacodynamics, biotransformation □ Biotransformation, pharmacodynamics—pentaerythritol tetranitrate □ Urinary, fecal excretion—pentaerythritol tetranitrate □ TLC—separation □ Scintillometry—analysis

It has been generally assumed that all organic nitrates exert qualitatively similar actions and that the extended duration of action ascribed to the "long-acting" nitrates relates either to differences of absorption and metabolic stability or to specific properties of the drug molecule itself (1). Since little specific information is available on the pharmacodynamics and biotransformation of this group of drugs in man, a study was performed with pentaerythritol tetranitrate (PETN), a "long-acting" organic nitrate in wide clinical use. Biotransformation of PETN (Scheme I) was followed qualitatively and quantitatively by modifying procedures developed earlier using ^{14}C-labeled drug (2). Drug pharmacodynamics were examined at two dose levels, 20 and 40 mg., with a clinical dosage form prepared from ^{14}C-PETN.



Scheme I

EXPERIMENTAL

Subjects—The subjects were 15 male volunteers between the ages of 20 and 68 years who presented no history or evidence of malabsorption, intestinal motility disturbances, or renal disease. For the period of study (4 days), the subjects were restricted to the Clinical Research Unit at Bowman Gray School of Medicine. A complete medical history and physical examination were taken on each subject. Predrug laboratory data included the serum levels of electrolytes (Na^+, K^+, Cl^-, and CO_2), urea nitrogen, uric acid, blood sugar, cholesterol, inorganic phosphate, lactate dehydrogenase, total protein, calcium, bilirubin, alkaline phosphatase, and glutamic-oxalacetate transaminase. Additional laboratory tests performed were EKG, chest X-ray, sedimentation rate, hematocrit, CBC, and urinalysis.

Drug Administration—^{14}C-Labeled and nonradioactive PETN were used to prepare compressed tablets, which contained a total of 20 mg. of PETN and 44 μc. each and met the chemical assay and disintegration-time specifications for the manufacture of a commercial product.[1] After an overnight fast, one tablet was administered *per os* to each of 10 subjects and two tablets were administered similarly to each of five subjects. All subjects remained in the fasting state for an additional 2 hr.

Collection of Specimens—Urine was voided directly into plastic bottles stored in a dry-ice chest. The collection periods were 0–2, 2–4, 4–8, 8–12, 12–24, and 24–48 hr. after drug administration.

Immediately after defecation into a plastic container, each stool collection was covered with cold dioxane and stored in a dry-ice chest. For each subject the feces were pooled from 0–24, 24–48, and 48–72 hr.

Blood specimens (10 ml.) were withdrawn into 15-ml. EDTA-Vacutainers[2] at the following intervals postadministration: 15 and

[1] Peritrate.
[2] Becton, Dickinson Co.

Appendix 18

Exposure Standards for Chemical Substances

Compound Name	ACGIH TLV	
	ppm	mg/m^3
Carbon Disulfide* (skin)	I0	30
Hydrogen Sulfide	10	14
Caprolactam (vapor)	5	20
Ethylene Glycol (vapor)	50	125
Methanol (skin)	200	260
Dowtherm	1	7

*OSHA 8-hour time weighted average is 20 ppm.