Appendix, or on a similar form approved by the Occupational Safety and Health Administration, U.S. Department of Labor.

Section 5 — *Work Practices and Engineering Controls*

(a) A no-smoking rule shall be strictly enforced in all areas where there is occupational exposure to the decomposition products of fluorocarbon polymers. As a further precaution, the carrying of smoking materials into such areas shall be prohibited. Employees shall be instructed to wash their hands before smoking.

(b) In sintering or molding operations where the fluorocarbon polymer is heated above its melting point, temperatures in excess of the manufacturers' recommended range should be avoided whenever possible. To prevent overheating, ovens shall be fitted with an automatic temperature cutout set at the manufacturers' recommended temperature for the fluorocarbon polymer.

(c) If necessary to prevent accumulation or recirculation of the decomposition products of fluorocarbon polymers in the workplace, ovens shall be fitted with a local exhaust ventilation system. An appropriate alarm shall be incorporated into any exhaust system in case of its failure.

(d) Local exhaust ventilation, located as close as possible to the operation, shall be used whenever welding, cutting, or related high-temperature operations are performed.

(e) Exhaust systems and ductwork shall be kept in good repair so that design airflows and pressures are maintained. Airflow and pressure should be measured at least twice a year. Continuous airflow indicators (oil or water manometers) are recommended. A log shall be kept showing design airflow or pressure and the results of periodic inspection.

(f) Ventilation systems discharging to outside air must be designed to conform to applicable local, state, and federal air pollution regulations and must not constitute a hazard to employees or to the general population.

(g) General Housekeeping

(1) Spills of fluorocarbon polymers shall be cleaned up, preferably by vacuuming. Care shall be taken that polymer dust is not blown onto steampipes or other heated equipment.

(2) Emphasis shall be placed on prompt and frequent cleanup of dust to prevent accumulation of fluorocarbon polymers.

(3) Equipment shall be maintained regularly, and necessary repairs shall be made promptly.

(4) Fluorocarbon polymer scrap and waste shall be collected in special containers and, if not reused, shall be disposed of by high temperature incineration or by burying.

Section 6 — *Sanitation*

(a) Smoking shall be prohibited in all areas where fluorocarbon polymers are handled and used, and smoking materials shall not be carried into such areas.

(b) The employer shall provide hand-washing facilities with soap and clean towels. Employees who work in fluorocarbon polymer areas shall be instructed to wash their hands thoroughly before eating, smoking, or handling smoking materials.

(c) In the interest of good industrial safety and hygiene practices, preparation and consumption of food in areas where fluorocarbon polymers in bulk are handled and used should be discouraged. Employers may designate specific areas for these activities.

(d) Where excessive contamination of clothing with fluorocarbon polymer dust is likely, employers shall provide employees with launderable clothing for repeated use or disposable outer garments for one-time use.

(e) Laundry personnel should be informed of the hazards and of safe procedures if they are likely to encounter clothing contaminated with fluorocarbon polymers.

NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH RECOMMENDATIONS FOR WORKPLACE EXPOSURE TO POLYCHLORINATED BIPHENYLS (PCBs)

The National Institute for Occupational Safety and Health (NIOSH) recommends that employee exposure to polychlorinated biphenyls (PCBs) in the workplace be controlled by adherence to the following sections. The standard is designed to protect the health and provide for the safety of employees for up to a 10-hour workday, 40-hour workweek, over a normal working life time. The standard is measurable by techniques that are valid, reproducible, and available to industry and governmental agencies. Compliance with the standard should substantially reduce any risk of reproductive or tumorigenic effects of PCBs and prevent other adverse effects of exposure in the workplace. Employees should regard the recommended workplace environmental limit as the upper boundary for exposure and make every effort to keep exposure as low as possible.

Evidence indicates adverse reproductive and tumorigenic effects in experimental animals exposed to certain commercial PCB preparations. Currently available information is not adequate to demonstrate that other commercial PCB preparations do not have these effects. Should sufficient information become available to indicate that the standard offers greater or lesser protection from some chlorobiphenyl isomers or commercial preparations than is needed, it will be considered for revision.

The Toxic Substances Control Act of 1976 (Public Law 94-469) required the US Environmental Protection Agency (EPA) to prescribe marking and disposal regulations for PCBs by July 1, 1977 (*Federal Register* 42:26563-77, May 24, 1977). By this Act, the manufacture, processing, distribution in commerce, or use of PCBs in any but totally enclosed systems is to be banned, effective 1 year after the date of its enactment, October 11, 1976. Two years after the enactment date PCB manufacture is to be banned, and processing and distribution in commerce are to be banned 2.5 years from that date. However, the Act allows the Administrator of EPA to rule otherwise if he finds that manufacture, processing, distribution in commerce, or use in other than totally enclosed systems will not present an unreasonable risk of injury to health or to the environment. The Act does not affect use of equipment already containing

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PCBs in totally enclosed systems, so that a potential for occupational exposure to PCBs will continue to exist for many years as a consequence of their transportation, installation, use, and disposal. The part of the Act specific for PCBs is presented in Figure I-1 [omitted].

"PCBs" are defined for this recommended standard as commercial preparations of chlorinated biphenyl compounds, including those preparations which may be described as single isomers or classes of isomers, such as Decachlorodiphenyl. Biphenyl and its monochlorinated derivatives occurring in commercial preparations of PCBs shall be measured along with the polychlorinated derivatives, and shall be treated in this standard as the polychlorinated compounds of the preparations. "Occupational exposure to PCBs," is defined as working with PCBs or with equipment containing PCBs that can become airborne or that can spill or splash on the skin or into the eyes, or the handling of any solid products that may result in exposure to PCBs by skin contact or by inhalation. The term "PCB work area" is defined as an area where there is occupational exposure to PCBs. In areas where no occupational exposure to PCBs occurs, but where PCBs are present in equipment in the workplace, adherence is required only to Section 8(a).

Section 1 — *Environmental (Workplace Air)*

(a) Concentration

Occupational exposure to polychlorinated biphenyls (PCBs) shall be controlled so that no worker is exposed to PCBs at a concentration greater than 1.0 microgram total PCBs per cubic meter of air (1.0 *ug*/cu *m*), determined as a time-weighted average (TWA) concentration, for up to a 10-hour workday, 40-hour workweek.

(b) Sampling and Analysis

The recommended TWA occupational exposure limit for PCBs has been determined to be the lowest reliably detectable limit by the sampling and analytical methods recommended in this document. Environmental samples shall be collected and analyzed as described in Appendices I and II, or by any methods shown to be at least equivalent in accuracy, precision, and sensitivity to the methods specified.

Section 2 — *Medical*

Medical surveillance shall be made available to all employees subject to occupational exposure to PCBs.

(a) Preplacement or initial medical examinations for workers shall include:

(1) Comprehensive medical and work histories with special emphasis on hepatic function, skin condition, and reproductive history.

(2) Comprehensive physical examination with particular attention to the skin and to hepatic function including determinations of serum glutamic-oxaloacetic transaminase (SGOT) and serum glutamic-pyruvic transaminase (SGPT) activities. The responsible physician may also wish to obtain measurements of serum triglyceride concentrations or of other indices of fat metabolism.

(3) A judgment of the employee's ability to use positive pressure respirators.

(b) During examinations, applicants or employees having medical conditions that could be directly or indirectly aggravated by exposure to polychlorinated biphenyls or formulations containing polychlorinated biphenyls shall be counseled on the increased risk of impairment of their health that might result from working with these substances.

(c) Women in the work force who are of child-bearing age shall be advised of the potential adverse effects of PCBs on the unborn child. Those who bear children while working with PCBs shall be counseled concerning the advisability of nursing their babies.

(d) Initial medical examinations shall be made available to all workers as soon as practicable after promulgation of a standard based on these recommendations.

(e) Periodic examinations shall be made available at least annually and include: (1) interim medical and work histories, and (2) physical examinations as outlined in paragraphs (a)(1) and (a)(2) of this section.

(f) If evidence of adverse effects of exposure to PCBs is suspected or confirmed, appropriate medical care shall be made available to the affected worker(s).

(g) Pertinent medical records shall be maintained for all employees exposed to PCBs in the workplace. Such medical records shall be maintained for the period of employment plus 30 years. These records shall be made available to the designated medical representatives of the Secretary of Health, Education, and Welfare, of the Secretary of Labor, of the employer, and of the employee or former employee.

Section 3 — *Labeling and Posting*

All labels and warning signs shall be printed both in English and in the predominant language of non-English-reading workers. Illiterate workers and workers reading languages other than those used on labels and posted signs shall be otherwise informed regarding hazardous areas and shall be informed of the instructions printed on labels and signs.

(a) Labeling

The following warning label shall be affixed in a readily visible location on PCB-processing or other equipment, and on PCB-storage tanks or containers:

POLYCHLORINATED BIPHENYLS
(PCBs)

DANGER! CONTAINS POLYCHLORINATED BIPHENYLS
CANCER SUSPECT AGENT

Use only with adequate ventilation.
Do not get in eyes, or on skin or clothing.

First Aid: In case of skin or eye contact, flush with running water.

(b) Posting

Warning placards shall be affixed in readily visible locations in or near PCB work areas. The information contained thereon shall be arranged as in the following example.

POLYCHLORINATED BIPHENYLS
(PCBs)

DANGER!

CANCER SUSPECT AGENT

AUTHORIZED PERSONNEL ONLY

Do not enter unless area is adequately ventilated.
Do not get in eyes, or on skin or clothing.

First Aid: In case of skin or eye contact, flush with running water.

Section 4 — *Personal Protective Equipment and Clothing*

(a) Protective Clothing

In any operation where workers may come into direct contact with PCBs, protective clothing impervious to PCBs shall be worn. Gloves, boots, overshoes, and bib-type aprons that cover boot tops shall be provided when necessary.

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Protective apparel shall be made of materials which most effectively prevent skin contact with PCBs where it is most likely to occur. Employers shall ensure that all personal protective clothing is inspected regularly for defects and that it is in a clean and satisfactory condition.

(b) Eye Protection

Chemical safety goggles, face shields (8-inch minimum) with goggles, or safety glasses with side shields shall be provided by employers and shall be worn during any operation in which PCBs are present. If liquid or solid PCBs contact the eyes, the eyes shall be irrigated immediately with large quantities medical personnel. (A drop of vegetable oil on the eye has been found to reduce the resultant irrigation.) Eye protection shall be in accordance with 29 CFR 1910.133 and ANSI Z 87.1-1968.

(c) Respiratory Protection

(1) Engineering controls shall be used when needed to keep concentrations of airborne PCBs at or below the recommended TWA occupational exposure limit. The only conditions under which compliance with the permissible exposure limit may be achieved by the use of respirators are:

(A) During the time necessary to install or test the required engineering controls.

(B) For nonroutine maintenance or repair activities.

(C) During emergencies when concentrations of airborne PCBs may exceed the permissible limit.

(2) When the use of respirators is permitted by paragraph c(1) of this section, respirators shall be selected and used in accordance with the following requirements:

(A) The employer shall establish and enforce a respiratory protection program meeting the requirements of 29 CFR 1910.134.

(B) The employer shall provide respirators in accordance with Table I-1 and shall ensure that employees properly use the respirators provided. The respirators shall be those approved by NIOSH or the Mining Enforcement and Safety Administration. The standard for approval is specified in 30 CFR 11. The employer shall ensure that respirators are properly cleaned, maintained, and stored when not in use.

TABLE I-1

RESPIRATOR SELECTION GUIDE

Concentration of PCBs	Respirator Type Approved under Provisions of 30 CFR 11
Greater than 1.0 mg/cu m or Emergency (entry into area of unknown concentration)	(1) Self-contained breathing apparatus with full facepiece operated in pressure-demand or other positive pressure mode. (2) Combination Type C supplied-air respirator with full facepiece operated in pressure-demand or other positive pressure mode and an auxiliary self-contained breathing apparatus operated in pressure demand or other positive pressure mode.

Section 5 — *Informing Employees of Hazards from PCBs*

(a) All new and present employees in any area in which PCBs are used shall be informed of the hazards, relevant symptoms, and effects of overexposure to PCBs, and the precautions to be observed for safe use and handling of these materials.

(b) All employees involved with the manufacture, use, transport, or storage of PCBs shall be informed that PCBs have been found to induce tumors in experimental animals after repeated oral ingestion and that because of these findings it is concluded that PCBS are potential human carcinogens; employees shall also be informed that adverse reproductive effects may result from occupational exposure to PCBs.

(c) The employer shall institute a continuing education program, conducted by instructors qualified by experience or training, to ensure that all employees occupationally exposed to PCBs have current knowledge of job hazards, proper maintenance and cleanup methods, and proper use of protective clothing and equipment, including respirators. The instructions shall include a general description of the medical surveillance program and of the advantages to the employee of participation. Special attention shall be given to women in the workplace. They shall be made aware of the potential adverse effects of PCBs on the unborn child, and of the known transport of PCBs to breast milk. Elements of the program shall also include:

Emergency procedures and drills;
Instruction in handling spills and leaks;
Decontamination procedures;
Firefighting equipment location and use;
First-aid procedures, equipment location, and use;
Rescue procedures;
Confined space entry procedures;
Low warning (odor) properties of PCBs.

(d) The information explaining the hazards of working with PCBs shall be kept on file and be readily accessible to workers at all places of employment where PCBs are manufactured, used, stored, or transported. Required information shall be recorded on the "Material Safety Data Sheet" shown in Appendix III [omitted] or similar form approved by the Occupational Safety and Health Administration, US Department of Labor.

Section 6 — *Work Practices and Engineering Controls*

(a) Regulated Areas

Access to PCB work areas shall be regulated and limited to authorized persons. A daily roster shall be kept of persons entering such areas.

(b) Handling of PCBs and General Work Practices

(1) Operating instructions shall be formulated and posted where PCBs are handled or used.

(2) Transportation and use of PCBs shall comply with all applicable local, state, and federal regulations.

(3) PCBs shall be stored in tightly closed containers in well-ventilated areas.

(4) When PCB storage containers are being moved, or when they are not in use and are disconnected, valve protection covers shall be in place. Containers shall be moved only with the proper equipment and shall be secured to prevent dropping or loss of control during transport.

(5) Storage facilities shall be designed to contain spills completely within surrounding dikes and to prevent contamination of workroom air.

(6) Ventilation switches and emergency respiratory equipment shall be located outside storage areas in readily accessible locations which will remain minimally contaminated with PCBs in an emergency.

(7) Process valves and pumps shall be readily accessible and shall not be located in pits or congested areas.

(8) Containers and systems shall be handled and opened with care. Approved protective clothing as specified in Section 4 shall be worn by employees engaged in opening, connecting, and disconnecting PCB containers and systems. Adequate ventilation shall be provided to minimize exposures of such employees to airborne PCBs.

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(9) PCB-operating and storage equipment and systems shall be inspected daily for signs of leaks. All equipment, including valves, fittings, and connections shall be checked for leaks immediately after PCBs are introduced therein.

(10) When a leak is found, it shall be repaired or otherwise corrected immediately. Work shall resume normally only after necessary repair or replacement has been completed, the area has been ventilated, and below the recommended TWA concentration limit.

(c) Control of Airborne PCBs

(1) Suitable engineering controls, designed to maintain exposure to airborne PCBs at or below the limit prescribed in Section 1(a), shall be used. Complete enclosure of processes is the recommended method for control of PCB exposure. Local exhaust ventilation may also be effective, used alone or in combination with process enclosure. When a local exhaust ventilation system is used, it shall be so designed and operated as to prevent accumulation or recirculation of airborne PCBs in the workplace environment and to effectively remove PCBs from the breathing zones of employees. Exhaust ventilation systems discharging to outside air must conform to applicable local, state, and federal regulations and must not constitute a hazard to employees or to the general population. Before maintenance work on control equipment begins, the generation of airborne PCBs shall be eliminated to the extent feasible.

Enclosures, exhaust hoods, and ductwork shall be kept in good repair so that designed airflows are maintained. Airflow at each hood shall be measured at least semiannually and preferably monthly. Continuous airflow indicators are recommended, such as water or oil manometers properly mounted at the juncture of fume hood and duct throat (marked to indicate acceptable airflow). A log shall be kept showing design airflow and the results of semiannual airflow measurements.

(2) Forced-draft ventilation systems shall be equipped with remote manual controls and shall be designed to shut off automatically in the event of a fire in the PCB work area.

(b) Special Work Areas

(1) PCB Hazard Areas

A hazard area shall be considered as any space having physical characteristics and containing sources of PCBs, such as transformers, that could result in PCB concentrations in excess of the recommended airborne PCB exposure limit. Exits shall be plainly marked, conveniently located, and open outwardly into areas which will remain minimally contaminated in an emergency.

(2) Confined or Enclosed Spaces

Entry into confined or enclosed spaces, such as tanks, pits, process vessels, and tank cars where there is limited egress, shall be controlled by a permit system. Permits shall be signed by an authorized representative of the employer and shall certify that appropriate measures have been taken to prevent adverse effects on the worker's health as a result of his or her entry into such space.

Confined or enclosed spaces which have contained PCBs shall be thoroughly ventilated to assure an adequate supply of oxygen, tested for PCBs and other contaminants, and inspected for compliance with these requirements prior to each entry. Adequate ventilation shall be maintained while workers are in such spaces. Leakage of PCBs into such confined or enclosed spaces while work is in progress shall be prevented by disconnecting and blanking the PCB supply lines. Each individual entering such confined or enclosed space shall be furnished with appropriate personal protective equipment and clothing and be connected by a lifeline harness to a standby worker stationed outside of the space. The standby worker shall also be equipped for entry with approved personal protective equipment and clothing and have contact with a third person. The standby person shall maintain communication (visual, voice, signal line, telephone, radio, or other suitable means) with the employee inside the confined or enclosed space.

(e) Emergency Procedures

For all PCB work areas where there is a potential for the occurrence of emergencies, employers shall take all necessary steps to ensure that employees are instructed in, and follow, the procedures specified below as well as any others appropriate to the specific operation or process.

(1) If PCBs leak or are spilled, the following steps shall be taken:

(A) All nonessential personnel shall be evacuated from the leak or spill area.

(B) The area of the leak of spill shall be adequately ventilated to prevent the accumulation of vapors.

(C) If the PCBs are in liquid form, they shall be collected for reclamation or sorbed in vermiculite, dry sand, earth, or similar nonreactive material.

(2) Personnel entering the spill or leak area shall be furnished with appropriate personal protective equipment and clothing. All other personnel shall be prohibited from entering the area.

(3) Only personnel trained in the emergency procedures and protected against the attendant hazards shall shut off sources of PCBs, clean up spills, control and repair leaks, and fight fires, in areas where PCBs are used.

(4) All wastes and residues containing PCBs shall be collected in PCB-resistant containers and appropriately disposed of (*Federal Register* 42:26563-77, May 24, 1977).

(5) Safety showers, eyewash fountains, and washroom facilities shall be provided, maintained in working condition, and located so as to be readily accessible to workers in all areas where the occurrence of skin or eye contact with PCBs is likely. If liquid or solid PCBs are splashed or spilled on an employee, contaminated clothing shall be removed promptly and the skin washed thoroughly with soap and water for at least 15 minutes. Eyes shall be irrigated immediately with copious quantities of running water for at least 15 minutes if liquid or solid PCBs get into them. A drop of vegetable oil may be applied to the eye to relieve the irritating effect of PCBs.

Section 7 — *Sanitation Practices*

(a) Employees occupationally exposed to PCBs shall be provided with separate lockers or other storage facilities for street clothes and for work clothes.

(b) Employees occupationally exposed to PCBs shall not wear work clothing away from their place of employment.

(c) Employees occupationally exposed to PCBs shall be provided clean work clothing daily, and cleaning establishments shall be informed as to the hazards of handling PCBs and proper disposal procedures for PCB-contaminated waste water.

(d) Facilities for shower baths shall be provided for employees occupationally exposed to PCBs. Workers should shower before changing into street clothes.

(e) Employees exposed to PCBs shall be advised to wash their hands and exposed skin before eating, drinking, smoking or using toilet facilities during the work shift.

(f) Food, drink, or smoking materials shall not be permitted in areas where PCBs are handled, processed, or stored.

Section 8 — *Monitoring and Recordkeeping Requirements*

(a) Monitoring

(1) As soon as practicable after the promulgation of a standard based on these recommendations, each employer

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who manufactures, processes, handles, stores or otherwise uses PCBs shall determine by an industrial hygiene survey whether occupational exposure to PCBs may occur. Surveys shall be repeated at least once every year and within 30 days of any process change likely to result in occupational exposure to PCBs. Records of these surveys, including the basis for any conclusion that there may be no occupational exposure to PCBs, shall be retained until the next survey has been completed.

(2) If occupational exposure to PCBs is determined to be possible, a program of personal monitoring shall be instituted to measure or permit calculation of the exposures of all employees.

(A) In all personal monitoring, samples representative of the employees' breathing zones shall be collected.

(B) For each TWA concentration determination, a sufficient number of samples shall be taken to characterize each employee's exposure during each work shift. Variations in work and production schedules and in employees' locations and job functions shall be considered in choosing sampling times, locations, and frequencies.

(C) Each operation in each work area shall be sampled at least once every 3 months.

(3) If an employee is found to be exposed to PCBs in excess of the recommended TWA concentration limit, control measures shall be initiated, the employee shall be notified of the exposure and of the control measures being implemented to correct the situation, and the employee shall be monitored every 30 days. Such monitoring shall continue until two such consecutive determinations indicate that the employee's exposure no longer exceeds the recommended TWA concentration limit. Routine monitoring may then be resumed.

(b) Recordkeeping

Environmental monitoring records shall be maintained for at least 30 years after the employee's last occupational exposure to PCBs. These records shall include the dates and times of measurements, job function and location of employees within the worksite, methods of sampling and analysis used, types of respiratory protection in use at the time of sampling, TWA concentrations found, and identification of exposed employees. Each employee shall be able to obtain information on his or her own environmental exposures. Daily rosters of authorized persons who enter regulated areas shall be retained for 30 years. Environmental monitoring records and entry rosters shall be made available to designated representatives of the Secretary of Labor and of the Secretary of Health, Education, and Welfare.

Pertinent medical records for each employee shall be retained for 30 years after the employee's last occupational exposure to PCBs. Records of environmental exposures applicable to an employee should be included in that employee's medical records. These medical records shall be made available to the designated medical representatives of the Secretary of Labor, of the Secretary of Health, Education, and Welfare, of the employer, and of the employee or former employee.

APPENDIX I
SAMPLING PROCEDURE FOR COLLECTION OF POLYCHLORINATED BIPHENYLS

General Requirements

(a) Air samples representative of the breathing zones of workers must be collected to determine the exposure from each job or from the specific operation in each work area.

(b) Suggested records:

(1) Date and time of sample collection;

(2) Pump model and serial number;

(3) Sample tube type and number;

(4) Sampling duration;

(5) Total sample volume;

(6) Location of sampling;

(7) Temperature, pressure, and relative humidity at time of sampling;

(8) Other pertinent information.

Calibration

Since the accuracy of environmental sampling can be no greater than the accuracy of the air volume measurement, the accurate calibration of the sampling pump is essential to the correct estimation of the volume of the sample that is collected. The required frequency of calibration is dependent on the use, care, and handling to which the pump is subjected. Pumps should be calibrated initially and recalibrated if misused or repaired. If pumps receive hard usage, more frequent calibration may be necessary. Regardless of use, maintenance and calibration should be performed on a regular schedule and records of these should be kept.

The accuracy of calibration depends on the type of instrument used as a reference. The choice of calibration instrument will depend largely upon where the calibration is to be performed. Ordinarily, pumps should be calibrated in the laboratory. For laboratory testing, primary standards, such as a spirometer or a soapbubble meter, are recommended, although other standard calibration instruments, such as a wet-test meter or dry gas meter, can be used. The calibration setups will be similar for all instruments.

Instructions for calibration with the soapbubble meter follow. If another calibration device is selected, equivalent procedures should be used. Since the flowrate of a pump depends on the pressure drop across the sampling device, in this case a "Florisil" tube, the pump must be calibrated while operating with a representative tube in line. The calibration system should be assembled in series following this order: soapbubble meter, water manometer, Florisil tube, and pump.

(a) Check the voltage of the pump battery with a voltmeter to ensure adequate voltage for calibration, and change or charge the battery if necessary.

(b) Turn on the pump and moisten the inside of the soapbubble meter by immersing the buret in the soap solution and drawing bubbles up the inside until they travel the entire buret length without bursting.

(c) Adjust the pump rotometer to provide the desired flowrate.

(d) Check the water manometer to ensure that the pressure drop across the sampling train does not exceed 2.5 inches of water at 0.2 liter/minute.

(e) Start a soapbubble up the buret and measure with a stopwatch the time required for it to move between calibration marks.

(f) Repeat procedure (e) at least twice, average the results, and calculate the flowrate from the volume between the preselected marks divided by the time required for the soapbubble to traverse the distance.

(g) Record the volume measured, elapsed time, pressure drop, air temperature, atmospheric pressure, serial number of pump, date, time, and name of person performing the calibration.

(h) The rotometer reading should be corrected for temperature and pressure, if necessary.

Sampling

(a) Samples should be collected as near as practicable to the faces of workers without interfering with freedom of movement.

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(b) Samples should be collected to permit determination of TWA exposures for every job involving exposure to PCBs and in sufficient numbers to express the variability of the exposures in the work situation.

(c) Apparatus for Breathing Zone Sampling

(1) Pump, battery-operated, with clip for attachment to the worker's clothing. Airflow through the pump should be controlled within 5% of the desired rate during the entire sampling period.

(2) Sorbent Tubes

Glass tubes at least 7 cm long with 4 mm I.D. and containing two sections of 30/48 mesh deactivated Florisil. (Florisil, 30/60 mesh, is sieved to the proper mesh size.) The front section, preceded by a glass wool plug, contains 100 mg adsorbent, and the backup section contains 50 mg. A urethane foam plug is placed between these sections and also behind the backup section. The ends of the tube are flame-sealed to prevent contamination before use.

Deactivate the Florisil before packing the tubes by drying a weighed amount at 105 C for 45 minutes. After cooling to room temperature, add the Florisil to a round bottom flask which can be attached to a rotary evaporator. Add water at 3ml/100 g of Florisil (i.e. 3% W/W water) and turn the mixture in the rotary evaporator for 1 hour or until it is uniformly mixed (free-flowing).

(d) Collection and Shipping of Samples

(1) Immediately before sampling, break each end of the sorbent tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

(2) The smaller, or backup, section of Florisil should be positioned nearest the sampling pump.

(3) The sorbent tube must be vertical during sampling. Tubes should not be placed in a horizontal position since this may lead to "channeling" of the sorbent bed.

(4) Do not pass air being sampled through any hose or tubing before it enters the tube.

(5) Collect the air sample at a flow rate of 200 cc/minute or less to obtain the total sample volume required. The recommended maximum sampling volume for this method is 50 liters.

(6) Cap the sorbent tubes with inert plastic caps immediately after sampling. Under no circumstances are rubber caps to be used. Label tubes and note precise location assignments.

(7) Handle one additional tube in the same manner as the sample tubes except that no air is to be drawn through it. Label this tube as a blank.

(8) If the tubes are to be shipped, pack them tightly to minimize breakage in transit.

(9) Do not subject the tubes to extremes of temperatures or to low pressures.

(10) Provide bulk samples of the PCB preparation whose presence in the environment is suspected to the analytical laboratory. Do not transport these bulk materials in the same container as the samples or blank tubes. If possible, also provide a bulk air sample to use for qualitative identification.

APPENDIX II

ANALYTICAL METHOD FOR POLYCHLORINATED BIPHENYLS

Principle of the Method

A known volume of air is drawn through a tube containing Florisil to adsorb the PCBs present in the air sample. The collected PCBs are desorbed with hexane, and the resulting solutions are analyzed using gas-liquid chromatography with electron capture detection. The concentration of PCBs relative to a standard PCB preparation is read from a standard curve. If the air sample is found to differ significantly in composition from available PCB standards, then use the alternate procedure of perchlorination described in paragraph (b)7 of *Procedure*.

Range and Sensitivity of the Standard Analysis

NIOSH has found with Aroclor 1016, that the minimum detectable amount of PCB is 32 pg/4ul. With a total desorption volume were 5 ml, this would represent a total sample of 40 ng of Aroclor 1016. Thus the method is capable of detecting a concentration of 40 ng in a 1 cu m air sample, or a concentration of about 1 ug/cu m in an air sample of 80 liters. The upper range of the analytical method is apparently limitless depending only upon the degree of dilution needed to maintain the concentration of the sample within the linear range of the electron capture detector (32 pg to 3 ng/injection). In practice, concentrations in workplace air have been found to be as high as 1.5 mg/cu m.

Interferences

(a) Strict measures to avoid contamination are required when using the electron capture detector. Foremost, the syringe must be thoroughly cleaned after each injection. Hexane to be used in the analytical procedure should be periodically analyzed by GLC for purity. It should show no chromatographic peaks later than 45 seconds, if less than 5 ul have been injected.

(b) Any compound which has nearly the same retention time on the GLC column as one of the PCBs is an interferent. This type of interference can often by overcome by changing the GLC operating conditions or by selecting another column. Retention time data on a single column, or even on a number of columns, cannot be considered as proof of chemical identity. It is important, therefore, that a sample of the bulk mixture of PCBs be analyzed at the same time as the contents of the sample tubes so that chemical identification of possible interferences can be made.

(c) The interferences which have been reported in the literature in the GLC analysis of PCBs are not expected to be important for this method. Chlorinated pesticides, such as DDT, DDE, etc, have been reported as interferences due to coextraction with PCBs during workup of samples such as water, tissue, soil, or biologic fluids. In the case of personal air sampling in an industrial environment, these interferences would not be present in amounts that would significantly interfere unless they were manufactured in the same area. Thus, unless these chlorinated pesticides are specifically known as potential interferents, extra cleanup or separation steps for these materials are not necessary.

(d) Sulfur-containing compounds in petroleum products have been reported as interferences.

(e) If present in the PCB mixture, biphenyl will be an interference when samples are analyzed by perchlorination; however, PCBs for the purpose of this recommended standard include biphenyl.

(f) Brominated impurities in antimony pentachloride have also been found to lead to interferences in perchlorination procedures. Results from NIOSH laboratories indicate, however, that these brominated impurities may be removed by vacuum distillation of the antimony pentachloride.

Precision and Accuracy

The performance characteristics of the method as found by NIOSH are presented below.

(a) The volume of air sampled can be measured to ±1% if a pump with a calibrated volume indicator is used. Volumes

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calculated from initial flow rate settings may be less accurate (±5%) because of changes in flow rate during sampling.

(b) At airborne PCB concentrations of up to 10 mg/cu m, the front section of the Florisil tube has a 100% collection efficiency for 50-liter air samples.

(c) Recovery of known amounts of PCBs adsorbed on Florisil is quantitative (100%).

(d) Sealed tubes or desorbed sample solutions can be stored for 2 months without PCB loss.

(e) The precision of the analysis is dependent upon the precision and sensitivity of the technique used to quantitate the GLC peaks of the samples and standards. The precision of the standard analytical procedure has a relative standard deviation of 4.4%.

(f) The average conversion of PCBs to decachlorobiphenyl is about 100% with a relative standard deviation of about 2%.

(g) Recovery of decachlorobiphenyl subjected to the decachlorination procedure is 99% with a relative standard deviation of 1.8%.

(h) The accuracy of these procedures is not known; accuracy depends on the ability to separate and identify each compound in the PCB mixture and to compare each with a known standard. Many of the isomers in commercial PCB mixtures have not been separated or identified, and standards for many of the isomers are not available.

Advantages of the Sampling and Analytical Methods

(a) The sampling device is small, portable, and involves no liquids.

(b) The capacity of the solid sorbent sampling device for PCBs is large and recovery of PCBs from the sorbent is quantitative.

(c) The contents of the sample collection tubes are analyzed by means of a rapid instrumental method.

(d) Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions.

(e) The perchlorination procedure provides qualitative confirmation and quantitative measure of PCBs, since it is based on measurement of the single GLC-EC detection response of decachlorobiphenyl.

Disadvantages of the Sampling and Analytical Methods

(a) The precision of the sampling method is limited by the reproducibility of the pressure drop across the tubes. Pressure drop changes will result in variability in the flow rate and cause the sampling volume to be imprecisely known because the pump is usually calibrated for only one tube.

(b) A substantial difference between the composition of PCBs in the air sample and that of the commercial PCB mixture being used as a standard will result in a large error in accuracy when the standard analytical procedure is used, since estimation of the PCB content of the sample is based on comparison with such a PCB mixture.

Apparatus

(a) Gas liquid chromatograph equipped with an electron capture detector capable of maintaining a detector temperature of 350 C.

(b) Glass column (6 feet x 2 mm I.D.) packed with 1.5% OV-17/1.95% QF-1 on 80/100 mesh Supelcoport.

(c) Vials (20-ml), with aluminum-lined caps.

(d) Microliter syringe (10-ul).

(e) Volumetric flasks (10-ml for standards) with glass stoppers.

(f) Method for determining peak areas.

(g) Culture tubes, 13 x 100 mm, with unlined screw top caps.

(h) Oven, capable of maintaining 160 C ± 5 C.

(i) Sand bath.

(j) Vortex mixer.

Reagents

(a) Hexane, pesticide-grade quality.

(b) Nitrogen carrier gas, prepurified.

(c) PCB mixture under study.

(d) Antimony pentachloride, distilled under vacuum.

(e) Decachlorobiphenyl.

(f) Sodium sulfate, anhydrous.

(g) Hydrochloric acid, 20% aqueous.

Calibration and Standards

(a) Standardization Procedure

Use the particular PCB mixture as the standard that was being used in the work area in which air samples were taken. Prepare standards in hexane at concentrations ranging from 8 to 500 ng/ml. Calibration curves should be established daily since the electron capture detector response may vary from day to day. Plot the standard curve in terms of concentration (ng/ml) versus area. Since the injection volumes of the standard and the sample are identical, the concentration of the sample can be read directly from the standard curve.

(b) Alternative Standardization Procedure (Perchlorination)

The product of the perchlorination of the PCB mixture with antimony pentachloride is decachlorobiphenyl. Standards of decachlorobiphenyl are prepared in hexane at concentrations ranging from 70 to 440 ng/ul. Calibration curves are established daily since the electron capture detector response may vary from day to day. The standard curve is plotted in terms of concentration (ng/ml) versus peak area. Since the injection volume of the standard and the sample are identical, the concentration of the sample can be read directly from this curve.

Procedure

(a) Cleaning of Equipment

All glassware used for the laboratory analysis should be washed with a detergent, thoroughly rinsed with tap water, distilled water, pesticide-grade acetone, and finally pesticide-grade hexane and then dried.

(b) Analysis of Samples

(1) Preparation of Samples

Score each tube with a file and place the glass wool and front section in a clean, dry vial. Place the separating urethane foam plug, the back section of the sorbent, and the retaining urethane foam plug in a second clean, dry vial. The front and back sections are analyzed separately.

(2) Desorption of Samples

Prior to analysis, pipet 5.0 ml of hexane into each vial. Florisil particles should not be allowed to cling to the glass above the solvent. A minimum desorption time of 10 minutes is required before analysis.

(3) Gas-liquid chromatographic conditions for PCB determination by this procedure are:

(A) Nitrogen carrier gas flow rate, 60 ml/minute.

(B) Injector temperature, 300 C.

(C) Interface and detector temperatures, both 325 C.

(D) Column temperature, 180 C.

(4) Sample Injection

The solvent-flush technique is recommended for injection of materials into the GLC apparatus. With this method, the

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following procedure would be used to inject 4 μl of sample solution. Three microliters of hexane would be drawn into the syringe, followed by 1 μl of air, followed by 4 μl of sample solution. After the needle is removed from the sample solution, 1 additional μl of air is drawn into the syringe to minimize evaporation at the tip of the needle. The plunger now rests at the 9-μl mark. Inject at least 7 μl of the syringe contents into the gas chromatogram. Not less than 1 μl of flush-solvent should be used. Larger volumes of flush may give a solvent peak which interferes with sample component peaks. The syringe must be cleaned with hexane after each injection.

(6) Preliminary Analysis

Using the solvent-flush method of subsection b(4), inject 1 μl of sample and 1 μl of flush-solvent at the conditions specified under subsection b(3). If the sample is too concentrated, further dilutions will be necessary to bring the concentration of the sample solution into the linear range of the electron capture detector. Once the concentration of the sample is appropriately adjusted, its chromatogram should be compared to that of a standard to determine if the air sample is qualitatively different in composition from the standard. If there is little difference between the two chromatograms, then proceed with the standard analysis using the PCB mixture for standardization, subsection b(6). On the other hand, should there be a significant difference between the two chromatograms (such that comparison with the PCB mixture could result in gross error), then use the alternate procedure for standardization, subsection b(7).

(6) Standard Analysis

Select at least five prominent peaks in the sample chromatogram and compare their heights or areas with those of the standard. Calculate the concentration of PCBs by comparing the heights or areas of the selected peaks in the sample chromatogram of those in the standard chromatograms of known amounts of material.

(7) Alternate Standardization Procedure

A 200-μl aliquot of the sample is placed in a 13-mm x 100-mm culture tube and the hexane is slowly evaporated with dry nitrogen until 10 μl or less remain. Do not allow hexane to climb the tube during evaporation and do not allow the sample to evaporate to dryness. Immediately add 0.2-0.5 ml of distilled antimony pentachloride with a disposable pipet as rapidly as possible (antimony pentachloride decomposes rapidly in air) and cap the tube. The sample should remain light yellow after this addition, but if the sample turns dark brown or black, it must be discarded and another aliquot of that sample must be used. All samples are placed together in a sand bath. There should be no liner in the cap of the tube, since most liners are attacked by antimony pentachloride. A sample of decachlorobiphenyl is treated in a manner similar to the samples. The sand bath containing all of the treated samples is placed in a preheated oven at 160 C for a least 3 hours. Samples may also be treated in a preheated oven at 160 C for at least 3 hours. Samples may also be treated overnight. After perchlorination, the sand bath is removed from the oven and the samples are removed from the sand and allowed to cool to room temperature. To each sample is added dropwise 0.5 ml of 20% hydrochloric acid. This mixture is then extracted four times with 1-2 ml of hexane each time. Each extract is passed through a funnel containing approximately 0.5 g of anhydrous sodium sulfate (retained by a glass wool plug) into a 10-ml volumetric flask. The volume of the sample is brought to 10 ml by rinsing the pipet, sodium sulfate, and funnel tip with hexane. The funnel should not rest on the lip of the flask during filtration. The glass wool plug and sodium sulfate in the funnel are replaced after each sample. An aliquot of the sample solution is injected under the GLC conditions described above. The solvents flush technique is recommended using 2 μl of solvent back flush and 6 μl of standard or sample solution. The syringe must be cleaned with hexane after each injection. The height or area of the decachlorobiphenyl peak is compared to that of the decachlorobiphenyl standard and the weight of decachlorobiphenyl present is calculated.

(8) Gas-liquid chromatographic conditions for decachlorobiphenyl determination:

(A) Nitrogen carrier gas flow rate, 90 ml/minute.

(B) Injector temperature, 300 C.

(C) Interface and detector temperature, 325 C.

(D) Column temperature, 220 C.

(c) Determination of Desorption Efficiency

NIOSH has found average desorption efficiency is −99.3%, thus results of sample analyses need not be corrected for desorption efficiency.

Calculations

(a) Standard Analytical Procedure

The following are the steps in the calculation of concentrations of PCBs in air when determined with a PCB mixture as the standard.

(1) Add the heights or areas of several selected prominent peaks (at least five) in the chromatogram, compare with the total heights or areas of those same peaks in the standard, and read the concentration of the sample solution (ng/ml) from the standard curve.

(2) Multiply the concentration, in ng/ml, of the sample solution by the total volume, in ml, of the sample solution and calculate the weight of PCBs in the sample. Make corrections for the blanks if necessary.

(3) Add the weights found on the front and the back sections of the tube to find the total weight of PCBs in the air sample.

(4) Divide the total weight of the PCBs in the air sample by the volume, in liters, of air sampled and report the PCB concentration in ng/liter or its equivalent in μg/cu m.

(b) Alternate Standardization Procedure

The following are the steps in the calculation of concentrations of PCBs in air using the perchlorination method.

(1) The height or area of the decachlorobiphenyl peak in the chromatogram of the sample aliquot is compared to the height or area of the decachlorobiphenyl peak in the chromatograms of the standard. The concentration of decachlorobiphenyl in the sample aliquot is read from the standard curve.

(2) The concentration of decachlorobiphenyl in this aliquot (ng/ml) is multiplied by the total volume (ml) of the sample solution to give the total weight of PCBs in the sample as decachlorobiphenyl.

(3) The weights of PCBs, as decachlorobiphenyl, found on the front and back sections of the tube are summed, corrections for blanks are made, and the total weight of PCB, as decachlorobiphenyl, in the air sample is calculated.

(4) The total weight of PCB is divided by the volume of air sampled and the air concentration is reported in ng/liter or its equivalent in μg/cu m.

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