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criteria for a recommended standard . . . .
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boron trifluoride

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service Center for Disease Control
National Institute for Occupational Safety and Health

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OCCUPATIONAL EXPOSURE TO BORON TRIFLUORIDE

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health
December 1976

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402

DHEW (NIOSH) Publication No. 77-122

PREFACE

The Occupational Safety and Health Act of 1970 emphasizes the need for standards to protect the health and safety of workers exposed to an ever-increasing number of potential hazards at their workplace. The National Institute for Occupational Safety and Health has projected a formal system of research, with priorities determined on the basis of specified indices, to provide relevant data from which valid criteria for effective standards can be derived. Recommended standards for occupational exposure, which are the result of this work, are based on the health effects of exposure. The Secretary of Labor will weigh these recommendations along with other considerations such as feasibility and means of implementation in developing regulatory standards.

It is intended to present successive reports as research and epidemiologic studies are completed and as sampling and analytical methods are developed. Criteria and standards will be reviewed periodically to ensure continuing protection of the worker.

I am pleased to acknowledge the contributions to this report on boron trifluoride by members of the NIOSH staff and the valuable constructive comments by the Review Consultants on Boron Trifluoride, by the ad hoc committee of the American Academy of Industrial Hygiene, and by Robert B. O'Connor, M.D., NIOSH consultant in occupational medicine. The NIOSH recommendations for standards are not necessarily a consensus of all the consultants and professional societies that reviewed this criteria document on boron trifluoride. Lists of the NIOSH Review Committee members and of the Review Consultants appear on the following pages.

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The Division of Criteria Documentation and Standards Development, National Institute for Occupational Safety and Health, had primary responsibility for development of the criteria and the recommended standard for boron trifluoride. The Division review staff for this document consisted of Keith H. Jacobson, Ph.D. (Chairman), and Richard A. Rhoden, Ph.D., with Robert L. Roudabush, Ph.D.

Stanford Research Institute developed the basic information for consideration by NIOSH staff and consultants under contract CDC-99-74-31. Irwin P. Baumel, Ph.D., had NIOSH program responsibility and served as criteria manager.

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CRITERIA DOCUMENT:
RECOMMENDATIONS FOR AN OCCUPATIONAL
EXPOSURE STANDARD FOR BORON TRIFLUORIDE

CONTENTS

CONTENTS

I. RECOMMENDATIONS FOR A BORON TRIFLUORIDE STANDARD

The National Institute for Occupational Safety and Health (NIOSH) recommends that employee exposure to boron trifluoride in the workplace be controlled by adherence to the following sections. The standard is designed to protect the health and safety of workers for up to a 10-hour workday, 40-hour workweek, over a working lifetime. Sufficient technology exists to prevent adverse effects in workers, but techniques to measure airborne levels of boron trifluoride for compliance with an environmental limit are not adequate. Therefore, an environmental limit is not recommended herein, in part because of the unavailability of adequate monitoring methods. Work practices and engineering controls are recommended for control of exposure since reliable environmental data will not be available. The standard will be subject to review and revision as more information is acquired.

Boron trifluoride is highly reactive in the presence of water vapor. A dense, white mist is formed when boron trifluoride reacts with the moisture present in the air. The hydration and hydrolysis of boron trifluoride appear to be rapid and extensive. The term "boron trifluoride" as used throughout this document refers to the unreacted gas, the products formed by the reaction of boron trifluoride gas upon release into the environment, or both. "Occupational exposure to boron trifluoride" is defined as working in areas where boron trifluoride is manufactured, used, or handled, or is evolved as a result of chemical processes.

Section 1 - Medical

Medical surveillance shall be made available to all workers occupationally exposed to boron trifluoride.

(a) Preplacement examinations shall include:

(1) Comprehensive medical and work histories.

(2) A physical examination giving particular attention to the respiratory system and using appropriate pulmonary function tests such as FEV_1 and FVC. Chest X-rays (14 x 17 inches, PA) should be considered by the responsible physician. Persons with respiratory difficulties should be advised of their possible additional risk from boron trifluoride exposures.

(b) Periodic examinations shall be made available on an annual basis. These examinations shall include at least:

(1) Interim medical and work histories.

(2) A physical examination as outlined in paragraph (a)(2) of this section.

(c) In an emergency involving boron trifluoride, all affected personnel shall be provided with immediate first aid, with emphasis on the respiratory tract, skin, and eyes. In the event of skin or eye contact with boron trifluoride, the contaminated areas shall be flushed with copious amounts of water.

(d) Pertinent medical records, including information on medical examinations with supporting documents, shall be maintained for 20 years after the last occupational exposure to boron trifluoride and shall be available to the designated medical representatives of the employer, of the employee or former employee, of the Secretary of Labor, and of the Secretary of Health, Education, and Welfare.

Section 2 - Labeling and Posting

The cylinder label and warning sign shall be printed both in English and in the predominant language of non-English-reading employees. All employees unable to read these languages shall be informed of the hazardous areas.

(a) Labeling

Cylinders of boron trifluoride gas shall bear the following label in addition to, or in combination with, labels required by other statutes, regulations, or ordinances:

WARNING!

BORON TRIFLUORIDE GAS UNDER PRESSURE

HARMFUL IF INHALED

Avoid inhaling gas, mists, or vapor.
Do not get in eyes, on skin, or on clothing.
Use only with adequate ventilation.

First Aid: CALL A PHYSICIAN AS SOON AS POSSIBLE. If inhaled, remove victim to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. In case of contact, immediately flush skin or eyes with copious amounts of water. Keep at rest.

(b) Posting

The following warning sign shall be affixed in a readily visible location at or near entrances to work areas in which boron trifluoride is present.

DANGER!

BORON TRIFLUORIDE

AUTHORIZED PERSONNEL ONLY!

IF ENTERING VISIBLE MIST, USE RESPIRATOR
HARMFUL IF INHALED
IRRITATING TO EYES AND SKIN

Observe precautions and follow safety procedures as instructed.

Section 3 - Personal Protective Clothing and Equipment

(a) Protective Clothing

Proper impervious protective clothing, including gloves, aprons, suits, boots, goggles, and face shields, shall be worn as needed to prevent skin and eye contact with boron trifluoride.

(b) Respiratory Protection

(1) Engineering controls shall be used to maintain boron trifluoride concentrations at the lowest feasible level. The use of respirators to limit exposure is permitted only:

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

(B) During operations such as nonroutine maintenance or repair activities which may cause exposures at elevated concentrations.

(C) During emergencies when air concentrations of boron trifluoride are sufficient to form a visible mist in the employee's breathing zone.

(D) During the initial charging of a pressurized system with boron trifluoride gas when unsuspected leaks may become evident.

(2) When a respirator is permitted or required by paragraph (b)(1) of this section, it shall be selected and used pursuant to the following requirements:

(A) Only supplied-air positive-pressure respirators shall be provided for work in or entry into boron trifluoride contaminated areas. In addition, for escape purposes only, a full-facepiece gas mask with a combination acid-gas canister and high-efficiency (penetration less than 0.03% against a 0.3-μm dioctyl phthalate aerosol) filter may be used. The employer shall ensure that no worker is exposed to elevated concentrations of boron trifluoride because of improper respirator selection, fit, use, or maintenance.

(B) The employer shall establish and enforce a respiratory protection program meeting the requirements of 29 CFR 1910.134 and of 30 CFR 11, which incorporates the American National Standard Practices for Respiratory Protection Z88.2-1969.

(C) The employer shall provide respirators and gas masks according to paragraph (b)(2)(A) of this section for all potentially exposed employees and shall ensure that the employees use these respirators.

(D) The employer shall ensure that respirators are clean and that employees are instructed on the location and proper use of respirators and on how to test for leakage.

Section 4 - Informing Employees of Hazards from Boron Trifluoride

(a) Each employee with potential occupational exposure to boron trifluoride shall be informed at the beginning of employment or assignment to a boron trifluoride work area, and at least yearly thereafter, of the hazards and relevant symptoms of overexposure and the proper conditions, emergency procedures, and precautions for the safe use of boron trifluoride. Records of such training shall be kept to verify the frequency of training. Each employee shall be instructed as to the availability of information which shall be kept on file and which shall include that prescribed in paragraph (b) of this section.

(b) Information shall be recorded as required on a "Material Safety Data Sheet," as shown in Appendix I, or on a similar form approved by the Occupational Safety and Health Administration, US Department of Labor.

Section 5 - Work Practices

(a) Emergency Procedures

For all work areas, procedures as specified below, as well as any other procedures appropriate for a specific operation or process, shall be formulated in advance and employees shall be instructed in their implementation.

(1) Procedures shall include prearranged plans for obtaining emergency medical care and for necessary transportation of injured workers. Employees trained in the administration of first-aid measures shall be available during each work shift and shall be prepared to render such assistance when necessary.

(2) Approved skin, eye, and respiratory protection as specified in Section 4 shall be used by personnel essential to emergency operations. Protective equipment shall be stored in a manner which will assure access by employees at all times.

(3) Nonessential employees shall be evacuated from exposure areas during emergencies. Perimeters of hazardous exposure areas shall be delineated, posted, and secured. Reentry into exposure areas shall be prohibited until the boron trifluoride mist has been removed.

(4) Only personnel properly trained in emergency procedures

and adequately protected against the attendant hazards shall shut off sources of boron trifluoride and repair leaks. Respirators shall be worn by all workers repairing leaks.

(b) Engineering Controls

Engineering controls shall be designed to prevent the accumulation of boron trifluoride in the workplace and to effectively remove it from the breathing zones of exposed workers. Primarily, closed systems should be used to maintain boron trifluoride concentrations at the lowest feasible level (within the recommended environmental limit when monitoring methods become available), but local exhaust ventilation may also be used. Permanent boron trifluoride storage areas shall also be equipped with adequate exhaust ventilation. Closed systems, exhaust hoods, 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 showing design airflow or pressure and the results of periodic inspection shall be kept. Exhaust ventilation systems discharging to outside air must conform with applicable local, state, and federal air pollution regulations.

(c) Cylinder Handling

(1) Cylinders of boron trifluoride shall be equipped with safety relief devices conforming to 29 CFR 1910.167 and designed to release the gas safely in the event the cylinder is subjected to abnormal temperature or internal pressure. Cylinders shall be handled and stored in accordance with the applicable provisions of 29 CFR 1910.101 relating to

cylinder use, handling, and storage. Cylinders should be used on a first-in, first-out basis. Cylinder maintenance and inspection shall be in accord with applicable provisions of 29 CFR 1910.166.

(2) Cylinders containing boron trifluoride are at high pressure, up to 1,800 pounds per square inch gage (psig), and, therefore, shall never be used without an appropriate pressure regulator which is kept in good condition.

(d) Service Lines

Pressurized service lines connecting boron trifluoride cylinders with reaction vessels shall be constructed from material resistant to boron trifluoride corrosion. Gaskets in such lines shall not contain rubber. The potential for moisture to be introduced into the system shall be minimized, and open service lines shall be purged with dry air or inert gas before charging. These service lines shall be constructed to withstand up to 3,000 psig of pressure.

(e) General Work Practices

(1) In boron trifluoride manufacture and use there is the potential for the development of leaks. Such leaks will be visible since a white mist will be evolved. Adequately protected employees shall repair all leaks immediately.

(2) All boron trifluoride work areas shall be equipped with readily accessible eyewash fountains and safety showers.

Section 6 - Sanitation Practices

(a) Plant sanitation shall meet the requirements of 29 CFR 1910.141.

(b) Food preparation, dispensing (including vending machines), and eating shall be prohibited in boron trifluoride work areas.

(c) Smoking and uncovered smoking materials should be prohibited in boron trifluoride work areas because of the possibility of adsorption of the compound onto smoking materials.

Section 7 - Monitoring and Recordkeeping Requirements

(a) When an adequate sampling and analytical method is developed, the following shall apply:

(1) A program of personal monitoring shall be instituted to identify and measure or permit calculation of the exposure of all employees in boron trifluoride work areas.

(A) In all personal monitoring, samples representative of the exposure in the breathing zone of the employee shall be collected.

(B) For the determination of the exposure of each employee a sufficient number of samples shall be taken to characterize the employee's exposure during each work shift. Variations in work and production schedules shall be considered when samples are collected. The number of representative determinations for an operation or process shall be based on the variations in location and job functions of employees in relation to that operation or process.

(2) If monitoring reveals that an employee is exposed to more than the promulgated environmental limit, the exposure of that employee shall be measured at least once every 30 days, control measures shall be initiated, and the employee shall be notified of his or her

exposure and the control measures being implemented. Such monitoring shall continue until two consecutive determinations, at least a week apart, indicate that employee exposure no longer exceeds the promulgated environmental limit.

(3) When boron trifluoride is used and stored only in a proper exhaust hood, as described in Section 6, paragraph (b), monitoring is not required.

(b) Until adequate environmental monitoring methods are developed, environmental records shall consist of a description of job functions involving exposure to boron trifluoride and indicate any use of personal protective devices. These records shall be maintained for 20 years and shall be made available to designated representatives of the Secretary of Labor and of the Secretary of Health, Education, and Welfare. Pertinent medical records shall also be retained for at least 20 years. Copies of the records of environmental exposures of each employee should be placed into the employee's medical record, and each employee shall be able to obtain information on his own environmental exposures. 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.

II. INTRODUCTION

This report presents the criteria and the recommended standard based thereon which were prepared to meet the need for preventing occupational diseases arising from exposure to boron trifluoride and resultant mists. The criteria document fulfills the responsibility of the Secretary of Health, Education, and Welfare, under Section 20(a)(3) of the Occupational Safety and Health Act of 1970 to "...develop criteria dealing with toxic materials and harmful physical agents and substances which will describe...exposure levels at which no employee will suffer impaired health or functional capacities or diminished life expectancy as a result of his work experience."

The National Institute for Occupational Safety and Health (NIOSH), after a review of data and consultation with others, formalized a system for the development of criteria upon which standards can be established to protect the health of workers from exposure to hazardous chemical and physical agents. These criteria and recommendations for a standard should enable management and labor to develop better engineering controls resulting in more healthful work environments and mere compliance with the recommended standard should not be a final goal.

These criteria for a standard for boron trifluoride are part of a continuing series of criteria developed by NIOSH. The proposed occupational standard applies only to the processing, manufacture, or use of, or other occupational exposure to, boron trifluoride as applicable under the Occupational Safety and Health Act of 1970. The recommended standard was not designed for the population-at-large, and any extrapolation beyond occupational exposures is not warranted. It is intended to protect against development of respiratory effects and against local effects on the skin and in the eyes.

Boron trifluoride, a highly reactive chemical, is used primarily as a catalyst in chemical syntheses. It is stored and transported as a gas but can be reacted with a variety of materials to form both liquid and solid compounds. The gas is very irritating to the skin and respiratory system; inhalation or contact should be avoided. Upon contact with air, the boron trifluoride gas immediately reacts with water vapor to form a mist which, if at a high enough concentration, provides a visible warning of its presence.

The toxicity of boron trifluoride has not been adequately studied. Additional work is needed to evaluate the chemical's potential for carcinogenicity, mutagenicity, and teratogenicity. Studies are needed to identify the composition and properties of the hydrolysis products. Because of present difficulties in the measurement of boron trifluoride in the workplace environment, evaluation for compliance cannot be based on the use of available monitoring methods but will depend primarily on the use of work practices and engineering controls until suitable environmental monitoring methods become available.

III. BIOLOGIC EFFECTS OF EXPOSURE

Extent of Exposure

Boron trifluoride, BF_3 (formula weight 67.81), is a colorless gas, which is stable in dry atmospheres. [1-3] Its physical and chemical properties are listed in Table X-1. [2,4]

Boron trifluoride is known to be produced at the present time as a specialty chemical by only one US company whose production figures are not available. [5 (pp 244,278)] Methods used over the years in the commercial manufacture of boron trifluoride generally have involved a boron-containing compound allowed to react with a fluorine-containing compound in the presence of an acid. [2,4] The current method of synthesis involves combining fluorosulfonic acid and boric acid as in the following reaction [5 (p 13)]:

$$3\ HSO_3F + H_3BO_3 \longrightarrow BF_3 + 3\ H_2SO_4$$

Boron trifluoride, a Lewis acid (electron acceptor), is an excellent catalyst for Friedel-Crafts reactions as well as for many reactions that are also catalyzed by the hydrogen ion, H^+. [2,4] Some of these reactions, including polymerizations, esterifications, and alkylations, are presented in Table X-2. [4] As a catalyst, it readily forms a coordinate covalent bond, accepting a pair of electrons donated by a Lewis base and thereby gaining the additional stability of a full complement of eight electrons in the outermost energy level of the boron atom. In practice, boron trifluoride is often first allowed to form a complex with such compounds as phenol, monoethylamine, ethyl ether, and methyl ether, as listed in Table X-3. [6-12] These complexes generally are liquids or solids at room temperature and, therefore, are often easier to handle than the boron trifluoride gas. The applications of the complexes are similar to those of the gas, ie, as catalysts for Friedel-Crafts and other reactions. Some complexes are unstable and may dissociate to release boron trifluoride under certain temperature and pressure conditions. [7] Although many boron trifluoride complexes are synthesized through the formation of a coordinate covalent bond, a surprisingly small number of different atoms, ie, argon, nitrogen, phosphorus, carbon, oxygen, hydrogen, sulfur, fluorine, and chlorine, have been shown to donate an electron pair to boron trifluoride. [4,13,14]

Although the predominant use of boron trifluoride is as a catalyst, that is not its only use. The magnesium industry utilizes the fire-retardant and antioxidant properties of boron trifluoride in casting and heat treating. [15] Nuclear applications of boron trifluoride include neutron detector instruments, [16,17] boron-10 enrichment, [18] and the production of neutron-absorbing salts for molten-salt breeder reactors (US Patent No. 3,809,762). Boron trifluoride has also been identified as having insecticidal properties. [19]

Boron trifluoride is readily absorbed by water through the formation of a coordinate covalent bond with the oxygen atom of the water molecule. Wamser [20] has reported that, in equilibrated solutions of water and boron trifluoride at various concentrations, the following chemical species were tentatively identified by conductance measurements: fluoboric acid (HBF4), monohydroxyfluoboric acid (HBF_3OH), dihydroxyfluoboric acid ($HBF_2(OH)_2$), boric acid (H_3BO_3), and trihydroxyfluoboric acid ($HBF(OH)_3$). The latter product, however, has not been isolated and was proposed as a transitory intermediate. The mono- and di-hydroxyfluoboric acids, according to Wamser, equilibrate rapidly, while the boric and fluoboric acids are only slowly formed.

The formation of hydrogen fluoride in a mixture of boron trifluoride and water, although likely to occur, has not been conclusively shown. Wamser [20] suggested that the fluoride ion of hydrogen fluoride was not present in the mixture. He theorized that, although hydrogen fluoride may be released through the dissociation of the fluoboric and hydroxyfluoboric acids, it is immediately complexed with the other species present, contributing to the variety of compounds formed. Further support for this theory is found in Halbedel's report [21] that no penetrating burns like those caused by hydrogen fluoride resulted when a person had skin contact with a boron trifluoride-water mixture. Instead, he noted that the resultant surface burns were characteristic of contact with strong acids such as the hydroxyfluoboric acids.

When boron trifluoride gas comes into contact with air, a dense, white mist is formed. [8] As no mist is formed in dried air, [22] the mist in normal air may be assumed to be the product of the reaction of boron trifluoride and water vapor. It is not known if the reaction of boron trifluoride with water vapor in the air results in the same products as its reaction with liquid water. The relative concentrations of boron trifluoride and water vapor are highly variable, and any attempt at identifying the constituents of the mist is speculative. As indicated above, the mono- and di-hydroxyfluoboric acids are formed very rapidly when boron trifluoride contacts water contained in a vessel, [20] but their presence in the mist has not been verified.

Torkelson et al [22] found that, with an infrared analyzer, boron trifluoride was detectable in dry air but not detectable following its reaction with normal room air. This suggested an extensive conversion of the gas to other physical and chemical forms on contact with water vapor. They determined that the average diameter of the droplets in the mist was initially less than 1 μm. The size increased with time to about 1 μm, presumably with the addition of water from the atmosphere. The physical and chemical properties of the mist may depend on the relative humidity (water vapor content) of the air into which the boron trifluoride is released. A slight etching of the glass used in the boron trifluoride exposure chambers was also noticed. [22] Hydrogen fluoride reacts with silica in glass to form volatile silicon tetrafluoride, thereby etching the glass. This observation suggests that some hydrogen fluoride may have been present, at least long enough to react with the silica; however, it is not known whether other products of boron trifluoride hydration may also etch glass.

Employees with potential exposure to boron trifluoride include the initial manufacturers, magnesium founders, organic synthesizers, neutron detector instrument manufacturers, and fumigant producers. [23] NIOSH estimates that 50,000 employees are potentially exposed to boron trifluoride in the United States.

Historical Reports

The discovery and isolation of boron trifluoride date back to the early 1800's and the work of Davy and of Thenard and Gay-Lussac. [4,24] Initially, boron trifluoride was called "fluoric acid" and was confused with hydrogen fluoride since, like hydrogen fluoride, it was released from a mixture of calcium fluoride and boric acid calcined in an iron tube. Commercial production of boron trifluoride was begun in the 1930's in response to interest in its use as a catalyst for which over 400 patents were granted in the 1940's and 1950's. [4] There are no early reports on the toxicity of boron trifluoride.

Effects on Humans

Specific data relating to the toxic effects of boron trifluoride on humans are not available, although, with the advent of water fluoridation and increased uses of fluorides in industry, there is much information on fluorides in general. There are many reviews of the chemistry of boron trifluoride in which its toxicity is alluded to [2,4,8,21]; however, there is little quantitative information to substantiate these views.

The odor threshold of boron trifluoride has not been determined. Torkelson et al [22] reported that a rather pleasant, acidic odor was detected by personnel handling animals exposed to boron trifluoride metered at a concentration of 3.0 ppm (8.3 mg/cu m). Others [25,26] have said that boron trifluoride had a pungent, suffocating odor, but these reports do not contain data on the environmental concentrations. Because of the inadequate information, the use of odor as an indicator is not a sufficient safeguard against excessive exposure.

Halbedel [21] reported, without giving specific details, an attempt by an individual to assess the irritating effect of boron trifluoride on the skin. Cotton soaked with boron trifluoride in water was placed on the skin for "a day or so." The resultant acid burn, according to the author, was not like a typical hydrogen fluoride burn. Halbedel concluded that although burns like those caused by acid might result from prolonged contact with boron trifuoride gas, there was evidently no danger of the more severe hydrogen fluoride-induced burn occurring, since boron trifluoride has the ability to complex the fluoride ion quite effectively.

Epidemiologic Studies

Kirii, [27] in a study found only as a USSR abstract, attempted to determine the effects of chronic boron trifluoride inhalation on chemical workers. Seventy-eight workers were selected on the basis of the chemical exposures they had received in a 10- to 15-year period. Fifty-one of the workers (Group 1) had been exposed to ethylene, isobutylene, and boron trifluoride; the other 27 workers (Group 2) had been exposed only to ethylene and isobutylene. The author stated that the boron trifluoride concentration was quite high, but did not report any specific concentrations in this abstract. Both groups complained of irritability, insomnia, headache, and excessive fatigue. The workers in Group 1 also complained of dryness and bleeding of the nasal mucosa, bleeding gums, exanthema, dryness and scaling of the skin, pain in the joints, and increased fragility of tooth enamel. Additionally, the following objective findings were reported in both groups: slight nasal mucosal changes, apical systolic murmur, bronchitis, emphysema, dryness and reduced turgor of the skin, and a papular rash. The author reported, without supporting data, that these physical findings were more marked in Group 1, suggesting that overexposure to boron trifluoride resulted in joint disease, atrophic nasal mucosal changes, enhanced tendon reflexes, and changes in vascular permeability. However, in the absence of environmental data, it it is not evident that boron trifluoride produced the added effects, since it is not known whether increases in the concentrations of ethylene or isobutylene would also have contributed. If the fragility of tooth enamel was attributable correctly to exposure to boron trifluoride or its hydrolysis products, it seems likely that the fragility would be the consequence of acid products rather than the deposition of fluoride ion.

Physical examinations given to workers employed in a boron trifluoride-manufacturing plant also provided information on workers' exposures. [28] These examinations, instituted in the latter part of 1974, included chest X-rays, urinalyses for fluoride, and pulmonary function tests for forced vital capacity and 1-second forced expiratory volume. Thirteen workers (average age: 47.6 years) with present (7) or past (6) occupational exposures to boron trifluoride and other fluorides ranging from 1 to 27 years (average: 8.84 years) were examined. The X-rays were negative, and no urinary fluoride concentrations were above the acceptable preshift concentration of 4 mg/liter recommended by NIOSH. [34] Eight of the workers (five of seven currently in boron trifluoride areas and three of six with a previous exposure) showed lower pulmonary function volumes than predicted for a normal population. The lower pulmonary function values were judged as minimal in one, moderate in three, and severe in one of the seven workers currently exposed. These five workers had an average exposure of 13.0 years. In the three previously exposed workers with pulmonary function loss (two minimal and one moderate), the exposures ranged from less than 1 year to 20 years. These losses may be related to boron trifluoride exposure, but the data provided are inadequate, especially with regard to the availability of medical histories, and permit no definite conclusions. An air sampling survey of five points throughout the plant showed boron trifluoride concentrations ranging from 0.27 to 0.69 ppm (0.75-1.9 mg/cu m) during one 24-hour period in May 1974, and from 0.1 to 1.8 ppm (0.27-4.99 mg/cu m) in another 24-hour period in August 1974. A midget impinger was used in sampling; distillation and the fluoride-ion-specific electrode was used for analysis. The accuracy and precision of this method are unknown and therefore the data are not known to be true values.

Animal Toxicity

Several investigators have attempted to assess the toxicity of boron trifluoride with animal inhalation studies. However, no investigator has developed an accurate method of verifying the concentrations at which animals were actually exposed. Therefore, throughout this section, nominal or calculated concentrations based on cylinder settings, airflow measurements, and chamber size are used as a probable upper limit of exposure.

The toxicity to animals of boron trifluoride was first investigated during World War II as part of the Manhattan Project. In 1953, Spiegl [29] summarized these studies. Some of the original reports by Weil et al

[30,31] have been declassified and are available, although unpublished.

The studies were initiated with acute mortality range-finding exposures, followed by two 30-day inhalation tests. [29] The acute exposures involved only a few animals and a wide range of calculated concentrations. All 10 guinea pigs, 1 of 10 rats, and 1 of 10 mice died during a 5.5-hour exposure to boron trifluoride at a calculated concentration of 750 ppm (2,100 mg/cu m). Seven of 10 guinea pigs died in a 1.4-hour exposure to boron trifluoride at 350 ppm (970 mg/cu m). A 10.9-hour exposure at 135 ppm (370 mg/cu m) killed only 1 of 10 guinea pigs, while there were no deaths in 10 rats and 10 mice exposed at this concentration. Based on these results, concentrations of 100 and 15 ppm were selected for 30-day exposure studies.

Rats, cats, mice, guinea pigs, dogs, and rabbits were exposed to boron trifluoride at a nominal concentration of 100 ppm for 4-7 hours daily, 5 days/week, for up to 30 days. [30] Daily analyses of the exposure chamber atmospheres were made, and the mean value was determined to be 93.5 ppm (259 mg/cu m) with a range of 38.5-185 ppm (106-512 mg/cu m). These values may not be a true indication of the boron trifluoride levels since separate boron and fluoride determinations did not agree. However, at the conclusion of the experiment it was determined that unknown amounts of boron may have been leached from the glassware used in the sampling and analysis. Moreover, in only a few instances were the measured fluoride levels more than 2-5% of the calculated value.

Although exposure to boron trifluoride at 100 ppm (277 mg/cu m) killed all the animals exposed, [30] the length of exposure necessary to produce death varied with the species. The periods of exposure that resulted in death are given in Table III-1 for animals listed according to species, sex, age, and group size. The guinea pigs were the most susceptible, all dying within the first 2 days of exposure. All of the animals also showed retarded growth as a response to the treatment. However, the weight response was not uniform, and no correlation with the length of exposure was evident.

TABLE III-1

MORTALITY IN ANIMALS EXPOSED TO
BORON TRIFLUORIDE METERED AT 100 PPM

Species	Sex	Number	Age	Hours of Exposure Until Death	
				Average	Range
Dogs	M	3	Adolescent	181.5*	
	F	2	"	181.5*	
Cats	M	4	Adult	135	47.5-174.5
	F	2	"		
Rabbits	M	6	"	139	19.5-181.5
	F	6	"		
Rats	M	25	"	82.5	33.5-146.5
	M	25	Young	88.5	26.5-146.5
	F	25	Adult	92	33.0-167.5
	F	25	Young	134	33.0-202.5
Mice	M	25	"		5.5- 47.5
	M	26	"	24.4	
	F	25	Adult		
	F	25	Young		
Guinea pigs	M	40	Adult	<14	

*Three of the five dogs were killed in moribund condition.

Adapted from Weil et al [30]

Gross examinations of the lungs and kidneys of representative cats, rats, rabbits, mice, and guinea pigs exposed to boron trifluoride revealed moderate to severe damage. [30] Hemorrhage and mucus were consistently noted in the bronchioles of the lungs, and the kidneys showed distortion of the cortical and pyramidal striations. Since there were no controls or followup microscopy, the exact nature and extent of the damage were not ascertained.

The dogs were examined in greater detail. [30] Two of the dogs died from the exposures, and three moribund dogs were killed. Gross examination of the two dogs that died showed patches of dark red airless areas in the lungs, and microscopic examination showed severe bronchopneumonia extending from the bronchial wall into the alveolar walls. The kidneys of one dog showed degeneration of the tubular epithelium, and both dogs had typical and atypical renal regeneration with some dilated tubules. The three dogs which were killed also had bronchopneumonia, but it was evident only on microscopic examination. Again, the pneumonia extended into the alveolar walls; the alveoli were also filled with exudate. The diagnosis of pneumonia caused by boron trifluoride in one dog was questionable since fibrosis was evident, indicating long-standing disease. The kidneys showed interstitial nephritis, but its relation to the exposure is in doubt since the control dog also evidenced nephritis as well as lung changes which, according to the authors, probably resulted from an old case of interstitial pneumonia.

The dogs and rabbits were also tested weekly for biochemical and hematologic changes. [30] Urine sugar, urine protein, blood urea, blood calcium, and blood nonprotein-nitrogen levels were normal. Both species exhibited decreased serum inorganic phosphate levels immediately prior to death. The mean values for dogs were 7.6 mg% initially and 2.4 mg% finally. For rabbits the mean values were 6.3 mg% initially and 4.0 mg% finally. In both species, red and white blood cell counts dropped in the initial weeks of exposure but returned to normal before the animals died.

The teeth and bones of the exposed rats contained 20-25 times as much fluoride as was present in the teeth and bones of unexposed animals. [30] Marked fluorosis based on an observation of the bleaching of incisor teeth was noted in the first week and increased steadily with the length of exposure.

A concurrent phase of this inhalation study used 34 adult male albino rats exposed to boron trifluoride at 100 ppm. [30] One rat was killed each day for serial examination. However, 13 of them died during the second week from the exposure. Therefore the study was continued for only 22 days, in which time 21 rats were killed and examined. These rats showed anatomic changes which were attributed to boron trifluoride exposure. The changes described by the authors, however, did not correlate with the length of exposure. Effects on the lungs apparently started on the fifth or sixth day as pneumonia and peribronchitis. Pronounced pneumonia and bronchitic changes were reported on the 8th, 13th, and 16th days; mild bronchitis and hemorrhage on the 17th and 22nd days. However, the lungs of the rats killed on the intervening days were normal. The author gave no explanation for this phenomenon. The kidneys of the rats were also affected. Degeneration was seen in both the proximal and distal segments of the convoluted tubules, beginning with the third exposure and peaking on the eighth day of exposure. Associated with the degenerative changes, regeneration, often with mitotic figures, was seen in the cortical, midzonal, and pyramidal regions of the kidneys. Mitotic figures were most evident in the pyramidal portion. The 13 rats that died during the second week of exposure were also examined. Bronchopneumonia was present in 6 of these, congestion and edema of the lungs in 1, and renal epithelial degeneration in the medullary and pyramidal areas in 11. The 10 control rats were judged normal, although 2 showed some bronchopneumonia and another showed low-grade interstitial nephritis.

The second boron trifluoride exposure study conducted by Weil et al [31] used a calculated concentration of 15 ppm (41.5 mg/cu m). Subsequent analysis of the chamber atmosphere by a spot-test method, which was a colorimetric reaction between tumeric solution on filter paper and boron, showed a range of 13-31 ppm (36-86 mg/cu m) and a mean concentration of 19.8 ppm (55 mg/cu m). The data, although only semiquantitative, support the metered value of 15 ppm. This test is suitable for detecting order-of-magnitude variability rather than minor fluctuations. [32]

Six species were exposed 4-7 hours/day, 5 days/week, for a maximum of 31 days and were compared with controls. [31] In Table III-2, the animal species, sex, age, and mortality are recorded. The rats, rabbits, guinea pigs, and mice gained weight normally throughout the experiment; dogs and cats showed a 12% weight loss. This exposure resulted in fewer deaths than the 100-ppm exposure; 1 of 30 guinea pigs, 2 of 100 rats, and 15 of 92 mice died; and no deaths occurred in groups of 6 cats, 5 dogs, or 12 rabbits. The higher mortality in mice was thought to have resulted from their accidental exposure to boron trifluoride-contaminated water from the exhaust air scrubber system.

TABLE III-2

MORTALITY IN LABORATORY ANIMALS
EXPOSED TO BORON TRIFLUORIDE METERED AT 15 PPM

Species	Sex	Number	Age	Deaths	Time to Death (hours of exposure)
Dogs	M	4	Adult	0	
	F	1	"	0	
Cats	F	6	"	0*	
Rabbits	M	6	"	0	
	F	6	"	0	
Guinea pigs	M	30	"	1	147
	M	45	"	**	
Rats	M	25	"	0	
	M	25	Young	2	26, 130
	F	25	Adult	0	
	F	25	Young	0	
Mice	M	58	"	12	12-117 (50.1 av)
	F	34	"	3	7, 7, 154

*One cat died of an extraneous cause.
**Used in serial study

Adapted from Weil et al [31]

Blood samples were taken weekly from the dogs, rats, and rabbits. [31] There were no consistent or significant changes in red blood cell and platelet counts. Serum calcium and phosphorus levels in the dogs and rabbits remained normal throughout the experiment.

At the conclusion of the exposure period, 1 control and 5 exposed dogs, 10 exposed rabbits (no controls reported), 10 exposed rats (no controls reported), and 5 exposed and 5 control guinea pigs were examined grossly and microscopically for tissue damage. [31] One exposed dog showed lung hemorrhage, two rabbits showed low-grade interstitial pneumonia, and eight guinea pigs (four exposed and four control animals) showed bronchopneumonia. Three of five exposed and four of five control guinea pigs had interstitial nephritis. No changes related to the treatment were reported in the rats.

In a concurrent phase of this study, 45 adult male guinea pigs were similarly exposed at the 15-ppm concentration. [31] One guinea pig was killed each day for gross lung study, and two guinea pigs were killed each week for gross and microscopic examination of the tongue, cheeks, lungs, kidneys, and liver. In the animals examined daily for gross lung changes, 64% showed evidence of abnormal pneumonic processes, but there was no indication that length of exposure was a factor. Additionally, there was no evidence of edema or hemorrhage characteristically caused by a lung irritant. All of the exposed guinea pigs examined weekly showed interstitial bronchopneumonia, but only one of five control animals showed a similar lesion. The pneumonic process resembled that commonly seen in infection. All other tissues were normal.

Weil and coworkers [30,31] concluded that boron trifluoride was primarily a respiratory irritant which predisposed the exposed animals to respiratory infection. Exposure at 100 ppm (277 mg/cu m) was fatal to all animals. Physiological responses prior to death included respiratory irritation and infection, kidney damage, retarded growth, and severe progressive fluorosis in rat teeth. Exposure at 15 ppm (41.5 mg/cu m) did not produce fluorosis, but did predispose guinea pigs to a rate of respiratory infection greater than that found in controls. The other species were less affected.

Throughout the studies, [30,31] the incidence of kidney disease in the control animals was high. Although the effect in exposed animals was often more marked, it is inappropriate to draw definite conclusions regarding the renal effects of boron trifluoride from these studies.

In 1961, Torkelson et al [22] reported the results of a boron trifluoride inhalation study in rats, rabbits, and guinea pigs. Although boron trifluoride was administered at calculated concentrations of 12.8, 7.7, and 3.0 ppm, analyses of the air in the exposure chambers during the 7.7- and 3.0-ppm exposures showed actual concentrations of only one-half the nominal amounts.

Exposures at calculated concentrations of 12.8 ppm and 7.7 ppm took place in a 160-liter cubical chamber. [22] The exposures metered as 3.0 ppm were in a 3,700-liter vault. Because the rats moved freely in the chambers, they may have received more variable doses of boron trifluoride than the guinea pigs, which were caged. Even though the chambers were not designed originally for exposure to particles, random samples showed that the mist was reasonably well distributed throughout the chambers. Other than the building's air-conditioning system, no devices were used to control moisture. Although variable, the relative humidity was usually about 30%. Boron trifluoride was released into the exposure chamber in a stream of nitrogen to prevent the formation of hydrolysis products in the ducts.

The analytical method used by Torkelson et al [22] was a spectrophotometric reading of the color produced by the reaction of boron and a carminic acid indicator. Total boron in the chamber was determined, and the equivalent boron trifluoride level was calculated. The authors also used infrared analysis to identify the gas, but as previously discussed, this method was not applicable in normal air due to the extensive reactivity of the gas. No data on the precision or accuracy of this method are available.

Ten male guinea pigs and 14 female rats were exposed to boron trifluoride at a nominal concentration of 12.8 ppm (35 mg/cu m), 7 hours/day, 5 days/week, for up to 3 months. [22] On the 19th exposure, the first guinea pigs died. By the 42d exposure, a total of seven had died of respiratory failure and asphyxia. Only one rat died after 34 exposures in 49 days. The 3 surviving guinea pigs and 4 of the 13 rats were killed after 42-45 exposures in 62-65 days. The 9 remaining rats received a total of 60 exposures in 87 days. Four were then killed and examined; the other five were observed without exposure for another month before they were killed and examined. The guinea pigs had difficulty in breathing and appeared asthmatic. Exposed guinea pigs had increased lung weights averaging 0.80 g/100 g of body weight, compared to lung weights of 0.64 g/100 g of body weight for the control animals ($P = 0.01$). Gross examination revealed pneumonitis, which suggested chemical damage, in the hilar region of the lungs. Examined microscopically, the lungs showed areas of collapse and emphysema adjacent to the areas of more severe pneumonitis. The vessels in the alveolar walls were distended with blood cells, and the alveolar walls were thickened and separated from the vascular epithelium. Tissue examinations of control guinea pigs were not reported. The exposed rats were considered to have normal appearance and organ weights, but gross and microscopic tissue examination showed pulmonary changes indicating chemical irritation. The hilar regions of the lungs were the most affected and the injuries were manifested as pneumonitis. Although the fluoride content in some tissues increased (see Table III-3), no abnormal effects were seen by X-ray examination, and the rats which were observed for 1 month after their last exposure continued to gain weight normally.

TABLE III-3

FLUORIDE LEVELS IN TISSUES OF RATS
EXPOSED TO BORON TRIFLUORIDE BY INHALATION

Sex	Number	Nominal Concentration (ppm)	Exposure Duration (hours)	Fluoride Levels (ppm)*		
				Teeth	Bones	Lungs
F	4	0	0	502	-	9.9
F	4	12.8	45	738	-	11.9
F	5	0	0	342	996	-
F	5	7.7	33	643	1,154	-
F	4	0	0	580	1,335	-
F	4	3.0	127	867	1,732	-
M	4	0	0	305	735	-
M	4	3.0	127	506	1,109	-

*Statistical tests were not reported.

From Torkelson et al [22]

In the second phase of this study, [22] 10 male guinea pigs and 5 female rats were exposed 7 hours/day, 5 days/week, to boron trifluoride at a calculated concentration of 7.7 ppm (21.3 mg/cu m). One guinea pig died on each of days 2, 5, 6, and 11. The deaths were accompanied by "what appeared to be an asthmatic attack." On the 29th day, the six surviving guinea pigs were killed accidentally when, because of a faulty flowmeter, there was exposure at an undetermined concentration of boron trifluoride and nitrogen. All five rats in the chamber survived the accident and were exposed to boron trifluoride a total of 33 times in 51 days. No effects were noted in gross appearance, nor did overt fluorosis of the teeth result, although the teeth were light-colored and the fluoride content of the teeth and bones did increase (Table III-3).

In the third phase of the study, [22] 24 rats, 20 guinea pigs, and 6 rabbits, evenly divided as to sex, were exposed 7 hours daily, 5 days/week, to boron trifluoride at a nominal concentration of 3 ppm (1.5 ppm or 4.2 mg/cu m by analysis) for up to 6 months. Since four female guinea pigs died of extraneous causes, six additional female guinea pigs were added and then exposed 88 times in 127 days. Growth, appearance, and mortality were normal for all animal groups except the added guinea pigs, whose weights were lower than those of control guinea pigs, although not statistically significant by the authors' definition (723 g vs 855 g, $p = 0.073$). Microscopic examination of the lungs showed the rats were "very slightly" affected; areas of pneumonitis, peribronchial round cell infiltration, and congestion in the capillaries lining the alveolar walls were evident. Guinea pigs, except for those in the additional group, had a 30% higher incidence of pneumonitis than the rats but exact values were not given. The fluoride content of rat bones and teeth was increased (see Table III-3), although no adverse effects were reported. When examined for microscopic changes, the exposed rabbits did not differ from the controls.

The authors [22] concluded that boron trifluoride was a respiratory irritant to which the guinea pig was the most sensitive of the tested species. Repeated inhalation of boron trifluoride resulted in pneumonitis at all concentrations studied. The earlier mortality of guinea pigs exposed at a nominal concentration of 7.7 ppm than of those exposed at 12.8 ppm was not fully explained in the report. The authors did postulate that since the guinea pigs appeared more uncomfortable on humid days, the uncontrolled humidity may have resulted in varying particle sizes and, therefore, varying lung deposition rates. The authors judged odor threshold an inadequate indicator to provide a safe working environment, and they recommended a TWA concentration of 0.3 ppm.

The most recent boron trifluoride inhalation study found was done in the USSR by Kasparov and Kirii [33] in 1972. Guinea pigs, albino rats, and albino mice were subjected to acute, subacute, and chronic exposures to boron trifluoride. Toxicity was evaluated by mortality rates, body weights, respiratory rates, urine amino acid levels, and radiographic and histologic examinations. Whole blood or serum was tested for total protein content, distribution of protein fractions, levels of cholinesterase and aldolase activities, and pyruvic acid concentration. The authors did not specify whether the air concentrations reported were the results of analysis or calculation. They also did not report how many days each week the animals were exposed, but said only that the animals were exposed daily. They did indicate that dry air was used to deliver the boron trifluoride gas to the chamber, but the moisture generated by the animals' respiration was not measured.

The LC50 was 3,460 mg/cu m (1,245 ppm) for a 2-hour exposure of 70 albino mice, 1,180 mg/cu m (425 ppm) for a 4-hour exposure of 50 albino rats, and 109 mg/cu m (39 ppm) for a 4-hour exposure of 42 guinea pigs. [33] The animals died either during the exposure period or within a few days after exposure, but the exact times were not given. Necropsy of the animals showed cyanosis of mucous membranes and hemorrhage of internal organs, especially the lungs. The lungs also showed increased weight, edema, alveolar-duct destruction, and vascular dilatation. Hemorrhage, edema, and "dystrophy" were seen in the heart and the liver. The kidneys, spleen, and brain were affected with hyperemia and edema. Irritation of the mucous membranes of the eyes was noted.

In subacute tests, 26 guinea pigs and 32 albino rats were exposed to boron trifluoride at a concentration of 32.9 mg/cu m (12 ppm), 4 hours/day, for 15 days. [33] The first guinea pigs died on the 5th day, and all were dead by the 13th day. Examination showed increased hemoglobin levels and pulmonary changes including edema, increased vascular permeability, and dystrophic changes of the parenchyma. All of the rats survived; however, their blood serum protein levels increased significantly. Neuromuscular conductivity (measured by an undescribed method) decreased significantly. Exact test values were not reported. In some rats there were signs of subacute bronchitis and occasional unspecified vascular disturbances. According to the authors, these microscopic changes were not very pronounced.

These researchers [33] also studied the effects of inhalation of boron trifluoride at two concentrations in a 4-month chronic study. Twenty-six guinea pigs and 32 albino rats were exposed 4 hours daily.

Exposure to boron trifluoride at 10 mg/cu m (3.6 ppm) resulted in upper respiratory tract irritation, nose bleeding, and increased serum gamma globulin in rats. Guinea pigs showed a decrease in serum beta globulin levels. Several other results were reported, but the species involved was not identified. These results included leukocytosis, reductions in the levels of serum pyruvic acid and inorganic phosphorus, and fluorosis of the teeth. Respiration also decreased (oxygen consumption was reduced by 36.6%), while signs of chronic bronchitis, sclerosis, moderate alveolar edema, desquamative pneumonia, and emphysema were seen in the lungs. The heart and liver were affected with dystrophy, the spleen with reticuloendothelial-element proliferation, and the brain with pericapillary and pericellular edema.

No signs of toxicity were seen after chronic exposure (4 hour/day, up to 4 months) to boron trifluoride at 3 mg/cu m (1.08 ppm). [33] Guinea pigs showed dysproteinemia, leukocytosis, decreased cholinesterase activity (site of measurement not reported), and subacute bronchitis. These changes were reversible, and no changes were evident 1 month after the last exposure. The internal organs of the exposed rats showed no significant differences from the controls.

Kasparov and Kirii [33] concluded that boron trifluoride was a respiratory irritant, but they also suggested that boron trifluoride caused pathologic changes in other organs such as the kidneys, liver, or heart. The many systemic effects indicated that the compound was absorbed through the lungs. The guinea pig was found to be the most sensitive of the tested species, dying after 5 days of exposure at 32.9 mg/cu m (11.8 ppm) and showing reversible changes at 3 mg/cu m (1.08 ppm).

Correlation of Exposure and Effect

Boron trifluoride exposure in an occupational setting or in an animal inhalation study probably does not usually involve exposure to pure boron trifluoride gas. Boron trifluoride reacts with water vapor in air to form a white mist containing hydration and hydrolysis products. [22]

Sampling and analytical methods are limited to independent measurement of the boron or fluoride levels present in workplace or exposure chamber air, from which the concentration of boron trifluoride gas assumed to have caused their presence is calculated. [22,30] Neither accurate measurement of the gas present nor accurate identification of the products actually inhaled has been possible. For this reason, an accurate correlation of exposure concentration with the resultant effects is not possible at this time.

Kirii [27] compared workers exposed to boron trifluoride, isobutylene, and ethylene with workers exposed only to isobutylene and ethylene. (In the introduction to an animal study by Kasparov and Kirii, [33] it is implied that the boron trifluoride concentration in this study [27] was 18-19 mg/cu m.) Both groups showed nasal mucosal changes, bronchitis, emphysema, insomnia, cardiac effects noted as systolic noise, and dryness of the skin with a fine papulous rash. According to the author, these findings were more marked in workers whose exposure included boron trifluoride. Increased fragility of tooth enamel was also reported, but this is more likely the result of exposure to the acid products than of fluoride deposition. The usefulness of this report is limited because environmental concentrations were not reported; the effects attributed to boron trifluoride are not distinguishable from the potential effects of other chemicals present; and the study was only available in abstract form from which details such as the actual data and statistical analysis of results are missing.

In a boron trifluoride production facility, [28] the environmental concentrations of boron trifluoride were calculated from fluoride levels measured with the fluoride-ion-specific electrode. The 10 determinations made in 1974 showed concentrations ranging from 0.1 to 1.8 ppm (0.27-4.98 mg/cu m). Thirteen workers, with exposures ranging from 1 to 27 years (average, 8.84 years), did not have urinary fluoride levels exceeding the recommended permissable levels, [34] but eight of them showed minimal to severe departures from normal pulmonary function.

The effect of boron trifluoride on the skin of one worker has been reported. [21] A burn similar to that caused by an acid resulted when boron trifluoride (concentration unspecified) in water was placed on the subject's arm for "a day or so."

Animal studies can be used to estimate the effects of boron trifluoride at varying environmental concentrations, but accurate measurement of these concentrations has not been possible. Although animals in these studies were exposed to boron trifluoride and its hydrolysis products by inhalation, it is probable that varying amounts of these products may have been consumed by ingesting the droplets deposited on the cages and their coats. Single-exposure and repeated-exposure effects in animals are summarized in Tables III-4 and III-5.

Single-exposure studies (Table III-4) involved high boron trifluoride concentrations. LC50 values were calculated, [33] as follows: 1,180 mg/cu m (425 ppm) in rats for a 4-hour exposure; 3,460 mg/cu m (1,245 ppm) in mice for a 2-hour exposure; and 109 mg/cu m (39 ppm) in guinea pigs for a 4-hour exposure. The guinea pig, in all mortality studies, was the most sensitive species. [22,29,33]

Repeated-inhalation experiments (Table III-5) involved exposure periods of 1-6 months. [22,30] All the exposed dogs, cats, rats, mice, rabbits, and guinea pigs died in 30 days or less when exposed to boron trifluoride metered at a concentration of 100 ppm (277 mg/cu m) for up to 30 days [30]; all guinea pigs died when exposed at a concentration of 33 mg/cu m (12 ppm) for 15 days; and no rats, guinea pigs, or rabbits died when exposed for up to 6 months to boron trifluoride at concentrations of 3 and 4.2 mg/cu m (1.08-1.5 ppm). [22,33] Lungs and kidneys were adversely affected at all concentrations which caused deaths. Guinea pigs and rats showed pneumonitis and congestion in the lungs after a 6-month exposure to boron trifluoride calculated at a concentration of 3.0 ppm (8.3 mg/cu m), [22] and a 4-month exposure at 3.0 mg/cu m (1.08 ppm) caused reversible tracheitis and bronchitis. [33]

Guinea pigs [31] and rats [30] were killed daily in serial studies performed to determine the time course of adverse respiratory and kidney effects. The variation in response among animals of a single species was extensive. The results indicate that boron trifluoride is a respiratory irritant with no specific progression of effects, since the onset of irritation did not correlate with the length of exposure.

The guinea pig has proved to be the species most sensitive to the effects of boron trifluoride exposure, but rats, mice, rabbits, dogs, and cats also are susceptible. Although the effects of respiratory irritation induced by boron trifluoride have not been adequately demonstrated in humans, animal experiments strongly suggest that the inhalation of boron trifluoride would produce general respiratory irritation in humans.

Carcinogenicity, Mutagenicity, and Teratogenicity

No studies have been found regarding any carcinogenic, mutagenic, or teratogenic potential of this compound.

Summary Tables of Exposure and Effect

The effects on animals from boron trifluoride exposure discussed in detail in Chapter III are summarized in Tables III-4 and III-5.

TABLE III-4

ANIMAL MORTALITY FROM SINGLE ACUTE INHALATION EXPOSURES TO BORON TRIFLUORIDE

Species	Concentration (mg/cu m)*	Exposure Duration (hr)	Mortality Fraction	Reference
Mice	5,570	2	59/70	33
"	3,460	2	35/70	33
"	2,120	2	11/70	33
"	2,078	5.5	1/10	29
Guinea pigs	2,078	5.5	10/10	29
Rats	1,450	4	42/50	33
"	1,180	4	25/50	33
"	1,078	5.5	1/10	29
Guinea pigs	970	1.4	7/10	33
Rats	720	4	8/50	33
Mice	374	10.9	0/10	29
Rats	374	10.9	0/10	29
Guinea pigs	374	10.9	1/10	29
"	149	4	35/42	33
"	109	4	21/42	33
"	40	4	7/41	33

*Converted when expressed as ppm in reference

TABLE III-5

EFFECTS OF REPEATED BORON TRIFLUORIDE INHALATION ON ANIMALS

Species	Nominal Concentration (mg/cu m)*	Exposure Duration**	Effects (including mortality fraction)	Reference
Rats	259	4 - 7 hr/d x 30 d	100/100; 10% weight loss; dental fluorosis; mild renal degeneration; pulmonary edema, hemorrhage, congestion	30
"	55	4 - 7 hr/d x 30 d	2/100; normal growth in others, slight coloring of "incisor enamel"	31
"	35	7 hr/d x 60 d	1/14; pneumonitis, increased fluoride in tissues, dental fluorosis normal whole-body X-ray	22
"	10	4 hr/day for 4 mo	0/32; epistaxis; upper respiratory tract irritation, edema, bronchitis; dental fluorosis	33
"	8.3 - 11	7 hr/d x 33 d	0/5; increased fluoride in teeth and bones	33
"	8.3	7 hr/d x 128 d	0/24; congestion in alveolar capillaries, slight pneumonitis, light-colored teeth	22
"	3	4 hr/d for 4 mo	0/32; no microscopic changes reported	33

TABLE III-5 (CONTINUED)

EFFECTS OF REPEATED BORON TRIFLUORIDE INHALATION ON ANIMALS

Species	Nominal Concentration (mg/cu m)*	Exposure Duration**	Effects (including mortality fraction)	Reference
Mice	259	4 - 7 hr/d x 30 d	101/101; blood and mucus in bronchioles, gross kidney changes	30
"	55	4 - 7 hr/d x 30 d	15/92; high mortality from accidental exposure	30
Guinea pigs	259	4 - 7 hr/d x 30 d	40/40; subnormal weight, blood and mucus in bronchioles	30
"	55	4 - 7 hr/d x 30 d	1/30; bronchopneumonia and interstitial nephritis in control and exposed animals	31
"	35	7 hr/d x 42 - 45 d	7/10; pneumonitis, high lung weight, areas of emphysema	22
"	10	4 hr/d for 4 mo	0/26; low serum inorganic phosphorus levels, bronchitis, emphysema	33
"	8.3 - 11	7 hr/d x 29 d	4/10; asthama-type attacks prior to death; death of remaining animals day 29 from faulty flowmeter	22
"	8.3	7 hr/d x 128 d	4/20; pneumonitis 30% higher than in rats	22
"	8.3	7 hr/d x 88 d	0/6; slight decrease in body weights	22

TABLE III-5 (CONTINUED)

EFFECTS OF REPEATED BORON TRIFLUORIDE INHALATION ON ANIMALS

Species	Nominal Concentration (mg/cu m)*	Exposure Duration**	Effects (including mortality fraction)	Reference
Guinea pigs	3.0	4 hr/day for 4 months	0/26; subacute bronchitis, decreased cholinesterase	33
Rabbits	259	4 - 7 hr/d x 30 d	12/12; decreased serum inorganic phosphorus (from 6.3 to 4.0 mg%)	30
"	55	4 - 7 hr/d x 30 d	0/12; low-grade interstitial pneumonia	31
"	8.3	7 hr/d x 128 d	0/6; no microscopic changes observed	22
Cats	259	4 - 7 hr/d x 30 d	6/6; blood and mucus in bronchioles, mild renal changes	30
"	55	4 - 7 hr/d x 30 d	0/5; 12% body weight loss	31
Dogs	259	4 - 7 hr/d x 30 d	5/5; pneumonia in all, decreased serum inorganic phosphorus (from 7.6 to 2.4 mg%)	30
"	55	4 - 7 hr/day x 30 d	0/5; 12% weight loss	31

*Converted to mg/cu m when expressed as ppm in reference
**Exposures were 5 days/week by Torkelson et al [22] and by Weil et al [30,31] and unspecified by Kasparov and Kirii. [33]

IV. ENVIRONMENTAL DATA

Environmental levels of boron trifluoride have not been determined with an acceptable degree of accuracy and precision. Although analytical methods for total boron or total fluoride may be accurate and precise, reliable environmental monitoring for boron trifluoride is not possible until a sampling method is developed and validated. This section reviews the sampling and analytical methods which have been tested to date.

Sampling Methods

Sampling for boron trifluoride in the workplace environment, in addition to presenting the usual sampling problems, is complicated by the potential presence of both particulate and gaseous forms. The white mist which results from the boron trifluoride reaction with water vapor may contain a variety of compounds. [20,22] Since we do not know the differences between the particulate and gaseous forms of boron trifluoride hydration products, it is important to sample both forms. Filters, absorbers, or combinations of the two have been used. [22,35,36]

Weil et al [30,31,37,38] tested a variety of sampling methods. None of the methods is suitable for personal monitoring, since the equipment was large and up to four impingers were used at the same time. Several absorbents were also tested: 0.4-1.0% potassium hydroxide in absolute alcohol, 4% sodium bisulfite in water, concentrated ammonium hydroxide, 2.5% triethanolamine in alcohol, 10% triethanolamine in water, absolute alcohol, aqueous silver nitrate, water, and dioxane. Only 0.6% potassium hydroxide in absolute ethyl alcohol showed any promise. These methods are not suitable for personal monitoring, and the sampling efficiencies have not been determined.

Torkelson and coworkers [22] developed a sampling method for boron trifluoride gas and mist in moist air during their inhalation toxicity studies. A single fritted-glass scrubber containing 25 ml of distilled water as the absorbent was used to sample the animal exposure chambers. The authors reported that varying the sampling rate from 0.5 to 3 liters/minute caused no loss of sampling efficiency. The efficiency of a single scrubber was established in a trial with two scrubbers, in which essentially all of the boron was retained by the first. They also tested impingers as an alternate absorber and 1% potassium hydroxide in alcohol as an absorbent, but concluded, without giving details, that a scrubber with water gave the best results. A sample of room air was analyzed to correct for boron that might have leached from the glassware used in the sampling. The method, as described, cannot be recommended for environmental monitoring since no details were reported on the efficiency of collection.

Salyamon and Maslyukova [36] used a series of two aerosol filters and an absorber to sample boron trifluoride gas or mist at a rate of 1-2 liters/minute for 10 minutes. They used both the filters and an absorber since they expected boron trifluoride gas to produce an "aerial emulsion" of "hydrolysates" which would readily pass through absorbers containing water. In the absence of filters, they suggested a flowrate of no greater than 0.5 liters/minute. No data were provided, however, to substantiate this method of sampling.

Allied Chemical Corporation, [28] using an adaption of a NIOSH fluoride sampling method, has reported boron trifluoride environmental data; boron trifluoride was collected with a midget impinger containing 10 ml of 0.1 M sodium hydroxide as the absorbent. The method was not used for personal monitoring, and only area samples were obtained. A sampling rate of 2.5 liters/minute and a volume between 10 and 200 liters were used, based on sampling methods for other fluoride compounds. However, no data on the efficiency of collection were developed.

Kasparov and Kirii [35] reported using a series of two porous-plate absorbers for industrial and animal-chamber sampling of boron trifluoride. Water (10 ml) was chosen as the absorbing medium because boron trifluoride is very soluble in water. The air was sampled at 1 liter/minute for 30-60 minutes. The amount of boron collected in the second absorber was not reported, and the efficiency of air sampling was not stated.

Recently, methods for sampling boron trifluoride in animal exposure chambers have been investigated. [39] Large (300-400 ml) plastic impingers in a series fitted with fritted-glass or plastic dispensers were tested. Several solutions were tried as absorbents: 0.3 M hydrogen fluoride, deionized water, 0.01 N sodium hydroxide, and 0.1 N sodium hydroxide. Hydrogen fluoride produced the most efficient collection. Slow sampling rates (1 liter/minute) were required to prevent the carryover of boron trifluoride into the back-up impinger, resulting in a relatively long sampling time of 7.5 hours. Water and sodium hydroxide, according to the authors, produced variable collection efficiencies, but no absolute values were reported.

Previously, NIOSH has recommended a 0.8-μm cellulose acetate membrane filter impregnated with sodium formate for collecting inorganic fluorides. [34] Theoretically, this method would be satisfactory for sampling boron trifluoride since personal sampling is more readily done with a filter than with an impinger and the sodium formate ensures collection of any gases which may be present. However, the method has not been validated for the collection of the boron trifluoride and thus cannot be recommended at this time.

Analytical Methods

Boron trifluoride reacts with the moisture present in air to form hydration products. In dry air, the boron trifluoride gas has been detected by infrared analysis, [22] but the products formed in air of normal humidity were not detected by this method. The hydration products have not been accurately identified but are suspected to be a combination of hydroxyfluoboric acids. [8,20,21] An ideal analytical method, therefore, not only should account for boron trifluoride gas in the environment but also should determine the levels of the hydration products in the mist formed from the release of boron trifluoride gas. Environmental analysis for boron trifluoride has been attempted with surrogate analysis for either the total fluoride or the total boron content in the air. These values are then used to derive the amount of boron trifluoride which would account for the presence of these two elements.

Weil et al [30,31,37,38] investigated analytical methods during their toxicity studies on boron trifluoride, but were unable to develop methods yielding reproducible results for either boron or fluoride. Spectrographic determinations for boron were inconsistent because variable amounts of boron were eluted from the glassware. Colorimetric titrations for boron were not sufficiently sensitive since too little boron was present for volumetric determination. Attempts to determine the fluoride component in the samples were considered impractical because the results were nonquantitative and because there was a reaction of the fluoride with materials present in the chambers. These authors [31] did develop a semiquantitative spot-test method to approximate the boron trifluoride levels in animal chambers. Air was drawn through a filter which contained paper saturated with alcoholic turmeric solution. When the solution reacted with the boron trapped by the filter, the paper developed a color which then was compared visually to previously prepared standards. Although useful for confirming calculated exposure levels of boron trifluoride, the method has limited application because it is not wholly quantitative and because color development is subject to interference by other compounds.

Torkelson and coworkers [22] used the color-producing reaction of boron with carminic acid reported by Hatcher and Wilcox [40] to determine the boron trifluoride concentration in animal exposure chambers. The reaction of boron with carminic acid in a sulfuric acid solution produced a blue color which was subsequently analyzed spectrophotometrically. Solutions containing less than 0.5 ppm boron were concentrated prior to analysis so that boron concentrations in the air as low as 0.48 ppm could be analyzed. The carmine method of boron analysis has recently been reported to be accurate and precise. [39] Boron, either as boric acid or in the tetrafluoborate form, was measurable between 0.4 and 5.0 μg/ml.

Because of sampling difficulties, the precision and accuracy have not been tested in environments containing boron trifluoride.

Kasparov and Kirii [35] have reported the analyses of industrial and chamber atmospheres for boron trifluoride based on boron determination. Samples were collected by an absorber containing water and were distilled in the presence of quartz (silica) to remove the fluoride. The boron content was then determined spectrophotometrically from the color produced by the addition of dianthramide and sulfuric acid. The sensitivity for 1 ml of sample was reported to be 0.2-0.3 μg of boron, which is equivalent to 1.5-2.0 μg boron trifluoride. The error, based on the recovery of boron trifluoride added to water, and not on environmental boron trifluoride, was not more than 5-10% in any trial. Fluoride ion interfered but was quantitatively removed prior to analysis by the distillation. This method, which involves a lengthy distillation, was not validated with boron trifluoride recovery from air and, again, is only as good as the sampling method associated with it.

Other methods potentially useful for determining boron in samples of boron trifluoride and its hydrolysis products include atomic absorption spectrophotometry, [41] curcumin-acetone colorimetric analysis, [42] ignition-electrometric determination, [43,44] and titration for both borates and boric acid. [45,46] None of these methods has been tried with air samples, nor have they been used to measure boron as found in boron trifluoride gas or mist.

The analysis of fluoride in air samples has been studied, [34,47] and analytical methods have been developed. [48] The more recently developed fluoride-ion-specific electrode has been generally accepted as the most direct method for fluoride determination. [49] The method is suited to both environmental and biologic determinations [49,50] and is recommended by NIOSH [34] for the determination of atmospheric inorganic fluorides. The fluoride-ion-specific electrode has also been used to measure boron trifluoride levels. [28] Although the direct measurement of free fluoride ion is straightforward, the determination of fluorides complexed with other atoms requires the liberation of the fluoride ion, in this case from the boron atom. This has been done by distillation, [28] precipitation with aluminum, [51] or by a similar microdiffusion technique. [34] Data are not available on the recovery of the fluoride ion from boron compounds by any of these methods. Additionally, fluoride from sources other than boron trifluoride, such as hydrogen fluoride used as a cocatalyst, [4] would interfere with the results. For these reasons, fluoride analysis is not recommended for determining environmental boron trifluoride levels.

Tetrafluoborate ion (BF4-) reacts with methylene blue to form a complex which can be extracted with an organic solvent such as dichloroethane. Skaar [52] adapted this reaction for determining boron in solution by adding hydrogen fluoride in amounts sufficient to form the tetrafluoborate ion. The methylene blue-boron complex was extracted with dichloroethane and the color measured with a spectrophotometer. Salyamon and Maslyukova [36] extended this method to analyzing boron trifluoride atmospheric samples. Since the hydrolysis products of boron trifluoride exhibited some of the characteristics of the tetrafluoborate ion, these investigators added methylene blue directly to the aqueous contents of absorbers used to sample for boron trifluoride. The resulting complexes were extracted with dichloroethane and analyzed spectrophotometrically.

The lower limit of detection was determined to be 0.3 μg boron or, expressed as boron trifluoride, 2.0 μg. The authors did not ascertain that all the boron present in the hydrolysis products of boron trifluoride was in the form of tetrafluoborate ion; therefore, quantitative analysis was not established.

Carlson and Paul [53] developed a tetrafluoborate-ion-specific electrode using boric acid as a boron source. Boron was concentrated on a boron-specific resin, converted to tetrafluoborate by the addition of hydrogen fluoride, and analyzed directly with the electrode. The investigators, who determined that all the boron from boric acid was changed to the tetrafluoborate ion, analyzed boron at levels as low as 2.6 μg. The presence of hydrogen fluoride required the placement of a protective sleeve around the electrode since this chemical is capable of attacking the reference electrode usedin the analysis. In its study of this technique for boron trifluoride analysis in animal toxicity studies, NIOSH [39] found the precision adequate when sampling a known concentration from air bags but the values obtained did not correspond to the nominal values. Field trials have not been attempted. The problem of analysis may be coupled with the pH problems associated with the use of hydrogen fluroide as the sampling medium. If these problems can be overcome, the tetrafluoborate-ion-specific electrode could possibly be used in boron trifluoride analysis. The most serious problem with the available analytical methods are the inadequacy of and lack of information on the sampling procedures, the uncertainty about the actual toxic agent which should be analyzed, and the lack of testing in situations comparable to industrial settings.

The methods presented above describe several potential means whereby boron trifluoride may be sampled and analyzed. Additional testing is needed to resolve the problems described above and confirm their applicability to field and personal monitoring.

Environmental Data

Since sampling and analytical methods for boron trifluoride have not been validated, the available environmental data are subject to question. Allied Chemical Corporation [28] reported the results of 10 area samples in its boron trifluoride production plant. The samples were taken in 0.1 M sodium hydroxide, distilled, and analyzed for total fluoride with a fluoride-ion-specific electrode. If it is assumed that boron trifluoride was efficiently collected, that all of the fluoride in the samples originated from boron trifluoride, and that all the fluoride in boron trifluoride was liberated, then the environmental concentration of boron trifluoride ranged from 0.27 to 4.98 mg/cu m. As the production facility is outdoors, there was no local exhaust ventilation in operation at the time of sampling.

Boron trifluoride can be formed during the casting and heat treating of magnesium. Fluoborate salts, which release boron trifluoride gas at high temperatures, [54] are added to the sand molds or placed in the furnace. Upon heating, boron trifluoride is released and effectively prevents magnesium fires and oxidation of the molten metal. [15,55] Reports of the boron trifluoride concentrations in these operations have not been found.

Control of Exposure

Prevention of occupational diseases resulting from exposure to boron trifluoride requires the protection of employees from the inhalation of boron trifluoride and from eye or skin contact with the gas or mist. The use of a well-maintained closed system, when compatible with the application involved, is the best method of preventing inhalation. In areas where the escape of boron trifluoride into the environment is likely, the use of a properly designed and maintained ventilation system will prevent the accumulation of the hydrolysis products in the workroom atmosphere. Good ventilation practices, such as those outlined in the current edition of Industrial Ventilation--A Manual of Recommended Practice published by the American Conference of Governmental Industrial Hygienists, [56] should be followed. Where exhaust ventilation is required, adequate makeup air, conditioned as needed for worker comfort, should be provided.

Enclosures, exhaust hoods, and ductwork must be kept in good repair so that design airflows are maintained. Airflow should be measured at each hood at least twice a year. Continuous airflow indicators, such as water or oil manometers properly mounted at the juncture of fume hood and duct throat, are recommended. A log showing design airflow and results of periodic inspection should be kept.

Engineering controls have been applied in several boron trifluoride operations. [5 (pp 13,158,206)] As a gas, boron trifluoride is shipped and stored in cylinders or tube trailers. [8,57] Users have constructed closed systems (which are the best engineering control) for introducing boron trifluoride into the operation. Care is taken to prevent the introduction of moisture into pipelines and storage vessels, as the hydration products are extremely corrosive. Because of its reactivity, boron trifluoride gas introduced below the surface of a liquid may create a hazard from possible back suction into the cylinders. [58] Introducing boron trifluoride below a layer of mercury and the use of traps or check valves are safeguards in this type of system. [2]

Boron trifluoride service lines should be constructed of stainless steel or other corrosion resistant piping and fittings. [8,59] Gaskets made of or containing rubber should not be used but some plastics, such as polytetrafluoroethylene, are corrosion resistant. [59] Pressure fittings are also applicable. The service line should be constructed to withstand pressures of 3,000 psig and should contain a relief valve which is vented in such a way as to prevent worker exposure if it is released. [60]

V. DEVELOPMENT OF A STANDARD

Basis for Previous Standards

Consensus standards were not developed for boron trifluoride in the United States until the 1960's. In their absence, the American Petroleum Institute, in 1948, suggested that until such time as a safe limit was established, the "generally accepted limit for hydrogen fluoride of 3 ppm" could be reasonably applied to boron trifluoride. [3] In addition, it was suggested that 24-hour urine samples from boron trifluoride workers be analyzed semiannually for fluoride content and that annual X-rays of the lungs, ribs, spine, and pelvis be examined for evidence of osseous fluorosis. General safety measures, such as those used for all toxic materials, were also recommended.

In 1957, the American Conference of Governmental Industrial Hygienists (ACGIH) [61] promulgated a tentative threshhold limit value (TLV) for boron trifluoride of 1 ppm, or approximately 3 mg/cu m. This was a time-weighted average (TWA) concentration from which temporary excursions up to 3 times the TLV were permitted, provided an overall TWA concentration of 1 ppm was maintained. The TLV was adopted in 1960 [62] as the first boron trifluoride limit. The 1962 _Documentation of Threshold Limit Values_ [63] based the TLV of 1 ppm on the toxicity studies reported by Spiegl [29] and the theoretical potential for three molecules of hydrogen fluoride to be formed from each boron trifluoride molecule. Since the 1960 TLV for hydrogen fluoride was 3 ppm, [62] the 1-ppm TLV for boron trifluoride represented a reasonable approach at that time. The Documentation also noted the work of Torkelson et al, [22] who had reported the presence of respiratory irritation from the inhalation of boron trifluoride at levels as low as 1.5 ppm.

The TLV of 1 ppm was changed to a ceiling value by the ACGIH in 1963. [64] It was recommended that no employee be exposed to boron trifluoride at concentrations greater than 1 ppm, no matter how short the exposure period. No additional documentation was provided. The ACGIH TLV for boron trifluoride has remained a 1-ppm ceiling value since 1963. [65] The 1974 printing of the third edition of the Documentation of Threshold Limit Values [66] incorporates no new data on boron trifluoride.

Few foreign countries have set boron trifluoride standards. The Soviet Union has adopted 1 mg/cu m (0.36 ppm) as a maximum allowable concentration (MAC). [67] The standard of the Federal Republic of Germany is a Maximum Worksite Concentration limit of 3 mg/cu m (1.08 ppm) as a TWA concentration limit. [68] Although the Italian government has not adopted an environmental limit, it recognizes boron trifluoride as a toxic gas and has placed restrictions on its shipment, storage, and use. [69]

The present federal standard (29 CFR 1910.1000) is a ceiling value of 1 ppm (3 mg/cu m), which was based on the 1-ppm ceiling ACGIH TLV for boron trifluoride adopted in 1968.

Basis for the Recommended Standard

As discussed in Chapters III and IV, the efficiencies of boron trifluoride monitoring methods are questionable. No reports have demonstrated that boron trifluoride gas and hydrolysis products were efficiently collected, and attempts to recover known concentrations have not succeeded. For this reason, the calculated boron trifluoride concentrations have been regarded as an upper limit of exposure in animal inhalation studies. It is doubtful, however, that the animals actually received the full nominal concentration and, therefore, where analytical values are given, the effective concentration may be more realistically considered to lie between the analytical and calculated values.

Toxic effects of boron trifluoride on animals exposed at low levels over time periods up to 6 months have been demonstrated. [22,33] Torkelson et al [22] exposed rats and guinea pigs to boron trifluoride at a nominal concentration of 12.9 ppm (35 mg/cu m) for up to 60 exposures. Microscopic examination showed pneumonitis, suggestive of chemical damage, in the hilar and alveolar areas of the lungs. Areas of emphysema were also seen in guinea pig lungs.

Kasparov and Kirii [33] also tested both rats and guinea pigs. A boron trifluoride concentration of 10 mg/cu m was reported in chambers where the animals were exposed for 4 months. Irritation was seen in the upper respiratory pathways, and emphysema, bronchitis, sclerosis, and edema were noted in the lungs. The authors did not specify whether their concentration data was based on analytical or calculated results, nor did they report which effects were noted in which species.

Torkelson et al [22] also tested boron trifluoride at a calculated concentration of 3.0 ppm (8.3 mg/cu m), which analysis showed as only half that amount, 1.5 ppm or 4.2 mg/cu m. Rabbits, rats, and guinea pigs were exposed for 6 months. Upon microscopic examination, the lungs of the rabbits did not differ significantly from those of the controls, but the lungs of the rats had areas of slight pneumonitis, cell infiltration, and congestion. Thirty percent more pneumonitis was seen in the guinea pigs than in the rats.

Rats did not exhibit significant structural changes when exposed to boron trifluoride at 3.0 mg/cu m for 4 months. [33] Guinea pigs developed subacute tracheitis and bronchitis during the same exposure regimen; however, these effects were not noted 30 days after the last test dose.

These animal studies clearly exhibit the potential of boron trifluoride to cause lung irritation at low exposure concentrations over varying exposure periods. Every concentration tested in animals has produced some effect. The concentration inducing a particular effect can not be reliably determined, but the limited analytical and calculated values provide a probable range over which these effects occur: from 35 mg/cu m down to 3 mg/cu m.

Two incomplete but significant reports indicate that boron trifluoride may also affect workers. [27,28] Kirii, in an abstract of an unavailable report from the USSR, reported that workers exposed to boron trifluoride, isobutylene, and ethylene complained of irritability, insomnia, headache, bleeding noses and gums, and increased fragility of tooth enamel to a greater degree than workers exposed only to isobutylene and ethylene. In persons subjected to boron trifluoride exposures, the author described disturbances of vascular permeability, enhanced tendon reflexes, joint disease, and atrophic changes in nasal mucosa. Details permitting an accurate assessment of this report were not given. In an introduction to a paper on animal toxicity by Kasparov and Kirii, [33] the effect of 18-19 mg/cu m of boron trifluoride on workers is described. This description, similar to and possibly from the same report as the abstract above, notes nasal bleeding, dryness of nasal membranes, increased brittleness of teeth, and an increased incidence of upper respiratory tract disease in workers exposed to boron trifluoride.

Employees in a boron trifluoride production plant have been given physical examinations including X-rays, urinary fluoride determinations, and pulmonary function tests. [28] Boron trifluoride concentrations, the reliability of which are subject to question since they were determined on the basis of an area monitoring method of which details are unavailable, ranged from 0.27 to 0.69 ppm (0.75 to 1.9 mg/cu m) during one 24-hour sampling period and from 0.1 to 1.8 ppm (0.28 to 5.0 mg/cu m) during another. X-ray results were negative. Urinary fluoride levels did not exceed 4 mg/liter in the seven employees currently exposed to boron trifluoride. Pulmonary function tests, however, according to the authors showed lower capacity than that predicted from a normal population. Although, because of the lack of additional medical information, boron trifluoride cannot be labeled as definitely responsible for these effects, it cannot be discounted either.

There is a lack of relevant human toxicity data and of a reliable monitoring method, so accurate correlation of exposure and effect is not possible. Therefore, recommendation of any environmental concentration limit is not justifiable at this time. Nevertheless, based on the evidence of chronic pulmonary effects in animals [22,33] and the available data on pulmonary effects in workers in a boron trifluoride production facility, [28] sufficient information is available to justify concern for worker health in areas where boron trifluoride is manufactured, used, handled or is evolved as a result of chemical processes. It is therefore imperative that workers' exposures be limited by strict adherence to good work practices and the maintenance of adequate engineering controls. Boron trifluoride should be used only in closed systems where feasible. The potential for respiratory, [22] skin, [21] and eye [33] effects indicates that employees must be fully aware of boron trifluoride hazards. Employees must also be trained in the use of personal protective devices such as respirators, especially if they may be exposed to visible boron trifluoride mist. Because cartridge and canister masks have not been tested for boron trifluoride environments, only supplied-air respirators may be used.

It is recommended that preemployment and periodic medical examinations be particularly directed toward respiratory conditions. Employees with these conditions should be advised of their additional risks from boron trifluoride exposure. In addition, to detect the development of chronic effects, pulmonary function tests should be used to evaluate progressive changes in lung function. Employees trained in first aid, including the treatment of acid burns, must be available during each workshift. Records of medical examinations and of any environmental monitoring should be retained by the employer for 20 years to permit proper evaluation of the effects of boron trifluoride exposures, especially since there is the potential for the development of chronic effects.

Although several sampling and analytical methods appear potentially adaptable to boron trifluoride monitoring, there is not enough information to recommend a reliable method at this time. Urinary fluoride levels are potentially adaptable to employee monitoring, but in the current absence of a suitable monitoring method studies to determine a possible correlation of urine fluoride levels with boron trifluoride environmental concentrations cannot be effectively undertaken.

VI. WORK PRACTICES

Prevention of occupational diseases resulting from exposure to boron trifluoride requires protection against the inhalation of, and against eye or skin contact with, the hazardous substance. Good work practices, coupled with engineering controls as described in Chapter IV, are important means of limiting exposure to boron trifluoride.

Respirators must be worn during initial charging of the gas into a system and in repairing all leaks. Only air-supplied respirators are recommended for use during work activities, since canister or cartridge masks have not yet been approved for boron trifluoride. A gas mask may be suitable for escape but not for routine use.

Although the animal toxicity studies available for review involved no testing for skin toxicity, irritation of the mucous membranes of the eye was reported in acute inhalation exposures. [33] The limited human data available [21,27] do suggest that prolonged dermal contact can result in burns probably typical of acid burns. Chemical safety goggles and gloves must be worn by workers servicing a boron trifluoride system. [60] Barrier creams should be tested before use to protect against exposure, since they might trap the hydration mist on the skin where, with time, acid products may form. Fountains and safety showers must be provided in areas of potential boron trifluoride exposure, since skin and eye effects can be minimized with immediate, thorough washing of exposed surfaces.

If a leak develops in a boron trifluoride pressurized vessel, water spray can be used to clear the fumes. [70] All leaks must be immediately repaired by trained personnel. Employees involved in this effort must be provided with personal protective equipment, including respirators and impervious suits.

For entry into a boron trifluoride contaminated area during an emergency situation, especially when entering a visible mist, an impervious suit (many plastics are suitable [59]) and gloves are required in addition to full-face respiratory protection. [60]

Boron trifluoride is commercially available in 60-lb cylinders and in tube trailers containing 5, 6, 7.5, 9, or 10 tons. The gas is shipped at pressures ranging from 1,500 to 1,800 psig. [8]

General guidelines and recommendations for the safe handling of compressed gas cylinders are available in publications of the Compressed Gas Association. [1,71] Current federal standards on the handling of compressed gases have been published in the Federal Register 39:23602-03,23687-92, June 27, 1974 (29 CFR 1910.101,166,167).

Cylinders of boron trifluoride must be secured against dropping, falling, and rupture. Storage areas must be free of excess moisture, and, to minimize corrosion, the cylinders must not be stored on damp ground. [8] No boron trifluoride storage area may contain explosives or flammable materials. [71] Laboratories are advised to store boron trifluoride cylinders in exhaust hoods and to maintain design airflows.

Cylinders must not be exposed to temperatures below -20 F (-29 C) or temperatures exceeding 130 F (54 C). At low temperatures, the steel cylinder walls can become brittle and rupture; at high temperatures, the internal cylinder pressure may trip the relief valve, causing unnecessary exposure. [71]

Permanent storage areas must be equipped with respirators (air-supplied), eyewash fountains, and safety showers. The storage areas must also be well ventilated to prevent the accumulation of boron trifluoride if there is a faulty cylinder. Chances of exposure in such areas can be further reduced if only the quantity of gas necessary for immediate use is stored. [71] Moreover, a first-in, first-out storage system should be developed. Relief valves can be vulnerable to corrosion, which can be minimized by avoiding long periods of storage.

Leaking cylinders which can not be immediately corrected must be removed to a fume hood, a well-ventilated isolated area, or out of doors. If possible, the escaping gas should be trapped, eg, in a mixed solution of caustic soda and slaked lime, and neutralized to prevent the contamination of a wide area. [70]

VII. RESEARCH NEEDS

The result of the release of boron trifluoride into an environment of normal humidity is the immediate production of a white mist. The compounds present in the mist have not been identified, but they are assumed to be the products of boron trifluoride hydration. Accurate identification of the actual compounds present is essential to the determination of boron trifluoride toxicity. In addition, the relationships among aerosol size, relative humidity, and chemical composition must be determined.

No adequate method to sample and analyze the environment for boron trifluoride gas and mist has been developed. Most attempted methods are cumbersome. However, some of the methods (fluoborate-ion-specific electrode and atomic absorption spectrophotometry) are potentially useful, and, therefore, an intensive program to verify a sampling and analysis method should be undertaken.

Torkelson et al [22] noted an increase in the fluoride levels in bones and teeth of rats exposed to boron trifluoride. There is some evidence that boron-fluoride compounds may be excreted more rapidly then they can be deposited. [72,73] The evidence suggests that boron trifluoride has less potential for deposition than the fluoride ion. Confirmation from new research is needed. At the same time, the possibility of boron deposition resulting from boron trifluoride exposures should be evaluated.

Animal inhalation studies have established the effects of boron trifluoride on the respiratory systems of several species. However, the animal data are not sufficient; long term tests are needed to properly evaluate the effects of chronic exposure. Populations occupationally exposed to boron trifluoride have not been studied extensively. Epidemiologic surveys are needed to evaluate dose-response relationships for this compound. Additional testing is needed to investigate any carcinogenic, mutagenic, or teratogenic potential of boron trifluoride.

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IX. APPENDIX I

MATERIAL SAFETY DATA SHEET

The following items of information which are applicable to a specific product or material shall be provided in the appropriate block of the Material Safety Data Sheet (MSDS).

The product designation is inserted in the block in the upper left corner of the first page to facilitate filing and retrieval. Print in upper case letters as large as possible. It should be printed to read upright with the sheet turned sideways. The product designation is that name or code designation which appears on the label, or by which the product is sold or known by employees. The relative numerical hazard ratings and key statements are those determined by the rules in Chapter V, Part B, of the NIOSH publication, An Identification System for Occupationally Hazardous Materials. The company identification may be printed in the upper right corner if desired.

(a) Section I. Product Identification

The manufacturer's name, address, and regular and emergency telephone numbers (including area code) are inserted in the appropriate blocks of Section I. The company listed should be a source of detailed backup information on the hazards of the material(s) covered by the MSDS. The listing of suppliers or wholesale distributors is discouraged. The trade name should be the product designation or common name associated with the material. The synonyms are those commonly used for the product, especially formal chemical nomenclature. Every known chemical designation or competitor's trade name need not be listed.

(b) Section II. Hazardous Ingredients

The "materials" listed in Section II shall be those substances which are part of the hazardous product covered by the MSDS and individually meet any of the criteria defining a hazardous material. Thus, one component of a multicomponent product might be listed because of its toxicity, another component because of its flammability, while a third component could be included both for its toxicity and its reactivity. Note that a MSDS for a single component product must have the name of the material repeated in this section to avoid giving the impression that there are no hazardous ingredients.

Chemical substances should be listed according to their complete name derived from a recognized system of nomenclature. Where possible, avoid using common names and general class names such as "aromatic amine," "safety solvent," or "aliphatic hydrocarbon" when the specific name is known.

The "%" may be the approximate percentage by weight or volume (indicate basis) which each hazardous ingredient of the mixture bears to the whole mixture. This may be indicated as a range or maximum amount, ie, "10-40% vol" or "10% max wt" to avoid disclosure of trade secrets.

Toxic hazard data shall be stated in terms of concentration, mode of exposure or test, and animal used, eg, "100 ppm LC50-rat," "25 mg/kg LD50-skin-rabbit," "75 ppm LC man," or "permissible exposure from 29 CFR 1910.1000," or if not available, from other sources of publications such as the American Conference of Governmental Industrial Hygienists or the American National Standards Institute Inc. Flashpoint, shock sensitivty, or similar descriptive data may be used to indicate flammability, reactivity, or similar hazardous properties of the material.

(c) Section III. Physical Data

The data in Section III should be for the total mixture and should include the boiling point and melting point in degrees Fahrenheit (Celsius in parentheses); vapor pressure, in conventional millimeters of mercury (mmHg); vapor density of gas or vapor (air = 1); solubility in water, in parts/hundred parts of water by weight; specific gravity (water = 1); percent volatiles (indicated if by weight or volume) at 70 degrees Fahrenheit (21.1 degrees Celsius); evaporation rate for liquids or sublimable solids, relative to butyl acetate; and appearance and odor. These data are useful for the control of toxic substances. Boiling point, vapor density, percent volatiles, vapor pressure, and evaporation are useful for designing proper ventilation equipment. This information is also useful for design and deployment of adequate fire and spill containment equipment. The appearance and odor may facilitate identification of substances stored in improperly marked containers, or when spilled.

(d) Section IV. Fire and Explosion Data

Section IV should contain complete fire and explosion data for the product, including flashpoint and autoignition temperature in degrees Fahrenheit (Celsius in parentheses); flammable limits, in percent by volume in air; suitable extinguishing media or materials; special firefighting procedures; and unusual fire and explosion hazard information. If the product presents no fire hazard, insert "NO FIRE HAZARD" on the line labeled "Extinguishing Media."

(e) Section V. Health Hazard Information

The "Health Hazard Data" should be a combined estimate of the hazard of the total product. This can be expressed as a TWA concentration, as a permissible exposure, or by some other indication of an acceptable standard. Other data are acceptable, such as lowest LD50 if multiple components are involved.

Under "Routes of Exposure," comments in each category should reflect the potential hazard from absorption by the route in question. Comments should indicate the severity of the effect and the basis for the statement if possible. The basis might be animal studies, analogy with similar products, or human experiences. Comments such as "yes" or "possible" are not helpful. Typical comments might be:

> Skin Contact--single short contact, no adverse effects likely; prolonged or repeated contact, possibly mild irritation.
>
> Eye Contact--some pain and mild transient irritation; no corneal scarring.

"Emergency and First Aid Procedures" should be written in lay language and should primarily represent first-aid treatment that could be provided by paramedical personnel or individuals trained in first aid.

Information in the "Notes to Physician" section should include any special medical information which would be of assistance to an attending physician including required or recommended preplacement and periodic medical examinations, diagnostic procedures, and medical management of overexposed employees.

(f) Section VI. Reactivity Data

The comments in Section VI relate to safe storage and handling of hazardous, unstable substances. It is particularly important to highlight instability or incompatibility to common substances or circumstances, such as water, direct sunlight, steel or copper piping, acids, alkalies, etc. "Hazardous Decomposition Products" shall include those products released under fire conditions. It must also include dangerous products produced by aging, such as peroxides in the case of some ethers. Where applicable, shelf life should also be indicated.

(g) Section VII. Spill or Leak Procedures

Detailed procedures for cleanup and disposal should be listed with emphasis on precautions to be taken to protect employees assigned to cleanup detail. Specific neutralizing chemicals or procedures should be described in detail. Disposal methods should be explicit including proper labeling of containers holding residues and ultimate disposal methods such as "sanitary landfill" or "incineration." Warnings such as "comply with local, state, and federal antipollution ordinances" are proper but not sufficient. Specific procedures shall be identified.

(h) Section VIII. Special Protection Information

Section VIII requires specific information. Statements such as "Yes," "No," or "If necessary" are not informative. Ventilation requirements should be specific as to type and preferred methods. Respirators shall be specified as to type and NIOSH or US Bureau of Mines approval class, ie, "Supplied air," "Organic vapor canister," etc. Protective equipment must be specified as to type and materials of construction.

(i) Section IX. Special Precautions

"Precautionary Statements" shall consist of the label statements selected for use on the container or placard. Additional information on any aspect of safety or health not covered in other sections should be inserted in Section IX. The lower block can contain references to published guides or in-house procedures for handling and storage. Department of Transportation markings and classifications and other freight, handling, or storage requirements and environmental controls can be noted.

(j) Signature and Filing

Finally, the name and address of the responsible person who completed the MSDS and the date of completion are entered. This will facilitate correction of errors and identify a source of additional information.

The MSDS shall be filed in a location readily accessible to employees exposed to the hazardous material. The MSDS can be used as a training aid and basis for discussion during safety meetings and training of new employees. It should assist management by directing attention to the need for specific control engineering, work practices, and protective measures to ensure safe handling and use of the material. It will aid the safety and health staff in planning a safe and healthful work environment and in suggesting appropriate emergency procedures and sources of help in the event of harmful exposure of employees.

MATERIAL SAFETY DATA SHEET

I PRODUCT IDENTIFICATION	
MANUFACTURER'S NAME	REGULAR TELEPHONE NO. EMERGENCY TELEPHONE NO.
ADDRESS	
TRADE NAME	
SYNONYMS	

II HAZARDOUS INGREDIENTS		
MATERIAL OR COMPONENT	%	HAZARD DATA

III PHYSICAL DATA			
BOILING POINT, 760 MM HG		MELTING POINT	
SPECIFIC GRAVITY (H_2O=1)		VAPOR PRESSURE	
VAPOR DENSITY (AIR=1)		SOLUBILITY IN H_2O, % BY WT	
% VOLATILES BY VOL.		EVAPORATION RATE (BUTYL ACETATE=1)	
APPEARANCE AND ODOR			

IV FIRE AND EXPLOSION DATA

FLASH POINT (TEST METHOD)		AUTOIGNITION TEMPERATURE	

FLAMMABLE LIMITS IN AIR, % BY VOL.	LOWER		UPPER	

EXTINGUISHING MEDIA	
SPECIAL FIRE FIGHTING PROCEDURES	
UNUSUAL FIRE AND EXPLOSION HAZARD	

V HEALTH HAZARD INFORMATION

HEALTH HAZARD DATA

ROUTES OF EXPOSURE

INHALATION

SKIN CONTACT

SKIN ABSORPTION

EYE CONTACT

INGESTION

EFFECTS OF OVEREXPOSURE

ACUTE OVEREXPOSURE

CHRONIC OVEREXPOSURE

EMERGENCY AND FIRST AID PROCEDURES

EYES

SKIN

INHALATION

INGESTION

NOTES TO PHYSICIAN

VI REACTIVITY DATA

CONDITIONS CONTRIBUTING TO INSTABILITY

INCOMPATIBILITY

HAZARDOUS DECOMPOSITION PRODUCTS

CONDITIONS CONTRIBUTING TO HAZARDOUS POLYMERIZATION

VII SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED

NEUTRALIZING CHEMICALS

WASTE DISPOSAL METHOD

VIII SPECIAL PROTECTION INFORMATION

VENTILATION REQUIREMENTS

SPECIFIC PERSONAL PROTECTIVE EQUIPMENT

RESPIRATORY (SPECIFY IN DETAIL)

EYE

GLOVES

OTHER CLOTHING AND EQUIPMENT

IX SPECIAL PRECAUTIONS
PRECAUTIONARY STATEMENTS
OTHER HANDLING AND STORAGE REQUIREMENTS

PREPARED BY

ADDRESS

DATE

X. TABLES

TABLE X-1

PHYSICAL PROPERTIES OF BORON TRIFLUORIDE

Molecular formula	BF_3
Formula weight	67.81
Density at 760 mmHg and 0 C	3.077 g/l
Melting point	-127.1 C
Boiling point	-100.4 C
Solubility	
in ml of gas/ml of water	1,057 at 762 mmHg, 0 C
in g/100 g of water	369.4 at 6 C
Conversion factors	1 ppm = 2.77 mg/cu m 1 mg/cu m = 0.361 ppm

Adapted from Booth and Martin [4] and Martin [2]

TABLE X-2

REPRESENTATIVE BORON TRIFLUORIDE CATALYZED REACTIONS

(1) Synthesis of:

- (a) saturated hydrocarbons
- (b) alcohols
- (c) olefins
- (d) ketones
- (e) ethers
- (f) sulfur compounds

(2) Condensation of:

- (a) acid with olefin
- (b) acid with acetylene
- (c) acid with alcohol
- (d) nitrite with alcohol
- (e) amide with alcohol
- (f) aldols

(3) Dehydration of:

- (a) alcohols
- (b) acids
- (c) ketones

(4) Alkylation of:

- (a) paraffinic hydrocarbons
- (b) alkyl esters
- (c) aromatic hydrocarbons

(5) Polymerization of:

- (a) ethylene
- (b) propylene
- (c) butylene
- (d) isobutylene
- (e) vinyl compounds
- (f) dienes
- (g) cyclic oxides

(6) Isomerization (Beckman rearrangement)

(7) Epoxy resin curing

Adapted from Booth and Martin [4]

TABLE X-3

USES AND PHYSICAL STATES OF SOME
REPRESENTATIVE BORON TRIFLUORIDE COMPLEXES

Complex	Physical State	Use	Reference
BF3 monoethylamine	Solid	Catalyst for epoxy resins	6 12
BF3 dihydrate	Liquid	Catalyst for organic reactions	11
BF3 diethyl ether	"	Catalyst for polymerizations, alkylations, and isomerizations; intermediate chemical	7
BF3 phenol	"	Catalyst	9
BF3 phosphoric acid	"	Polymerization and alkylation catalyst	10
BF3 piperidine	"	Epoxy catalyst	9
BF3 dimethyl aniline	"	"	9
BF3 methanol solution	"	Catalyst	8

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