

## Section 1 Chemicals and handling precautions

### 1 Hazardous, harmful, and general chemicals

This university is engaged in leading and original research as well as advanced technology education. An extensive range of chemical substances are used in research experiments including hazardous chemicals that can lead to human damage and fires and harmful chemicals that cause health problems if not used properly. The former is regulated by the Fire Service Act, and the latter by the Poisonous and Deleterious Substances Control Act., and the Pollutant Release and Transfer Register (PRTR) system of the Act on Confirmation, etc. of Release Amounts of Specific Chemical Substances in the Environment and Promotion of Improvements to the Management Thereof, which aims to control the emission of specific chemical substances into the environment, requires the management and recording of the usage and emissions of such substances (please refer to page 18 and the URL below for each of these laws and regulations).

Fire Service Act URL:

<https://elaws.e-gov.go.jp/document?lawid=323AC1000000186>

These laws and regulations need to be adhered to when handling and storing chemicals, and the supervisor and experimenter must be very careful to ensure that the experimenter and people around them are not at risk. To manage medicines in an effective manner in accordance with these laws and regulations, the university introduced the **management system for lab chemicals** (IASO) in AY2008, which also conducts online management. According to this system, specified poisonous substances, poisonous substances, and deleterious substances must be managed by weight, whereas other chemicals must be managed by unit. It is imperative to comply with these laws and regulations.

System URL: <http://iaso.nagaokaut.ac.jp/iasor7/fw/FW0000/>

System usage URL:

[https://www.nagaokaut.ac.jp/gakunai/designated/jinji\\_romu/yakuhinkanri/index.html](https://www.nagaokaut.ac.jp/gakunai/designated/jinji_romu/yakuhinkanri/index.html)

Before using chemicals, the user is expected to be aware of their physical and chemical properties, the hazards, harm to health and environment, and first aid measures in the case of emergency. These are **listed** in the **Safety Data Sheet (SDS<sup>Note</sup>**, see page 18, “Regarding SDS stock”), which should be read before handling any chemicals. The **SDS** can be viewed in the above chemical management support system, and it

is also posted on the chemical manufacturer’s homepage and can be downloaded. In an unlikely event of a **user needing to visit a hospital or other medical institution due to a chemical accident**, it is advisable to **bring a copy of the first aid measures for the chemical listed on the SDS**. The university’s “Safety inspection list” also requires maintenance and utilization of the **SDS**.

Note: The SDS was called the MSDS in Japan until FY2011, but in accordance with the Globally Harmonized System of Classification and Labeling of Chemicals (GHS), Japan also changed the name to SDS and is also mentioned as SDS in the Japanese Industrial Standards (JIS Z7253).

Furthermore, since June 2016, the Industrial Safety and Health Act has mandated implementation of risk assessments for over 640 types of chemical substances. At our university, we have posted the measures for the risk assessments of the chemical substances in the following URL. When using the substance in question, there is a cautionary statement in IASO about the substance being subjected to risk assessment, therefore it is imperative to ensure that the necessary safety measures are followed before using it.

[https://www.nagaokaut.ac.jp/gakunai/designated/jinji\\_romu/RA/RA.html](https://www.nagaokaut.ac.jp/gakunai/designated/jinji_romu/RA/RA.html)

Table 5–1 shows the hazardous, harmful, and general chemicals considering the actual circumstances of education and research at the university.

Table 5-1 Hazardous, harmful, and general chemicals

A Hazardous chemicals

Name		Fire Service Act: applicable items	Order for Enforcement of Industrial Safety and Health Act, Appendix 1: applicable items
Combustible substances	Strongly oxidizing substances	Category I hazardous materials	Hazardous materials: oxidizing substances Some explosive substances
	Spontaneously combustible substances	Considerable amounts of the category III hazardous materials, yellow phosphorus, hydrides, organometallic compounds and organometallic hybrids	Hazardous materials: combustible substances
	Low-temperature ignitable substances	Category II hazardous materials	Hazardous materials: some combustible substances
	Water-reactive substances	Category III hazardous materials, considerable amounts of spontaneously combustible organometallic hydrides	Hazardous materials: some combustible substances
Explosive substances	Explosives	Category I and V hazardous materials	Hazardous materials: some explosive substances
	Decomposition explosive substances	Explosives, Category I hazardous material peroxides, and other unstable compounds	Hazardous materials: some explosive substances

	Inflammable gases	Among high-pressure gases, inflammable gases, city gas, LPG	Hazardous materials: inflammable gases
Inflammable substances	Special inflammable objects	Category IV hazardous material special inflammable materials	Hazardous materials: inflammable substances
	Highly inflammable substances	Category IV hazardous material Class 1 petroleum and similar amounts of inflammable substances	Hazardous materials: inflammable substances
	Moderate- / low-level flammability substances	Category IV hazardous material Class 2-4 petroleum and similar amounts of inflammable substances	Hazardous materials: inflammable substances
	Decomposition explosive substances	Attention to storage method since this is used in large quantities and constantly	Poisoning countermeasures since this is used in large quantities and constantly
Acids / alkali		Oxidizing liquids are Category 6 hazardous materials	Specified harmful work
Mixed hazardous materials		Regulations on regulations of hazardous materials (Article 46) Important when collecting and treating waste fluid during experiments; take care not to damage bottle during transportation and storage.	Not applicable Often causes an accident. Fire of unknown cause due to chemical, explosion when mixing two types of substances, unknowingly generated unstable substance
Radioactive substances		Act on Prevention of Radiation Hazards due to Radioisotopes, etc.	

## B Harmful chemicals

Name		Poisonous and Deleterious Substances Control Act	Pollution and environment-related laws
Harmful chemicals of importance	Locked storage chemicals	Chemicals, drugs, chemicals designated by the Stimulants Control Act, and chemicals that can be easily changed for which	Refer to the contents of the applicable law section recorded in SDS
	Poisonous gases / highly poisonous vapor	Many are designated as poisonous or deleterious The most common cause of laboratory accidents. Ensure that experiments are conducted with two or more people so that an immediate response can be given in the event of an accident.	Air pollutants Detoxification in each laboratory
	Mercury and mercury compounds	Most are poisonous. A few are deleterious substances, and very few are undesignated chemicals. Do not handle organic mercury compounds alone.	

Harmful chemicals	Inorganic harmful chemicals (including organic compounds containing the corresponding element)	Refer to the contents of the applicable law section recorded in SDS	Refer to the contents of the applicable law section recorded in SDS
	Organic harmful chemicals (excluding ordinary organic compounds and organometallic compounds)	Refer to the contents of the applicable law section recorded in SDS	Refer to the contents of the applicable law section recorded in SDS

### C General chemicals

Name		Poisonous and Deleterious Substances Control Act	Pollution and environment-related laws
General chemicals	Inorganic chemicals	May seem to be unrelated to the above laws and regulations, but some of them are poisonous, so attention should be given regarding the items described in SDS and similar products.	Refer to the contents of the applicable law section recorded in SDS
	Organic chemicals	See above	Classify and transport according to the "Guidelines for Treatment of Experimental Waste Liquid" of the university.

## 2 Risk assessment

A risk assessment is mandatory when using a chemical among over 640 kinds of chemical substances after June 2016 according to the Industrial Safety and Health Act. Accidents and health hazards are prevented efficiently before they happen by identifying various potential hazard sources that are present in laboratories and by putting them in order based on their risk in a risk assessment. A precaution that the chemical substance is included in the list of substances subject to risk assessment is displayed on IASO when using one. It must be used with necessary safety measures. Our measures for risk assessments of chemical substances are presented at the following URL:

[https://www.nagaokaut.ac.jp/gakunai/designated/jinji\\_romu/RA/RA.html](https://www.nagaokaut.ac.jp/gakunai/designated/jinji_romu/RA/RA.html)

The Order for Enforcement of Industrial Safety and Health Act, etc. was amended in February 2022. The rules have been changing from “individual rule for each substance” to rules based on “autonomous management” centered on risk assessments. The future policy has been shown that target substances will be increasing from the initial 674 substances.

Autonomous management of chemical substances means that individuals or organizations themselves properly understand the intrinsic toxicity and danger of chemical substances and risks in handling them, take

measures to mitigate these risks systematically, and prevent accidents such as fire and explosion, health hazards of workers, environmental contamination, and so on.

The Japan Association of National Universities has announced Guidelines for the Autonomous Management of Chemical Substances in Universities: Establishment of Autonomous Management Based on Risk Assessment and Education (Second Edition) in January 2024 as rational measures considering special aspects of studies in universities handling chemicals of various kinds in small quantities. The Guidelines are to be revised corresponding to future amendments made to laws and regulations.

<https://www.janu.jp/univ/guideline/>

Our policy, which maintains research activities and which addresses safety, is under consideration referring to the Guidelines and their future amendments. This chapter cites descriptions in the Guidelines for explanation.

In general, the scope of a risk assessment of a chemical substance covers operating procedures in which it is used and facilities that reduce its toxicity and danger, in addition to its properties (such as toxicity, inflammability and volatility). Operating procedures are also included because the risk posed by a single substance can differ considerably when detailed circumstances of an operation differ. It is therefore important to consider viewpoints of possible trouble in a series of experiment operations, as well as preparations of experimentation facilities to address such trouble, together with the operating procedures of experiments. When a possible risk exists, it is also important to minimize exposure to the target substance. For example, applicable measures include: i) using a substitute; ii) sealing the source of scattering, installing and running a local exhaust ventilation system or general ventilation system; iii) improving the method of operation; and iv) using respiratory protective equipment, etc.

Moreover, some accidents have been caused by substances other than those designated as target substances. It is desirable to identify possible risks of all chemical substances to be handled. Safer environments for experimentation can be made by considering not only chemical substances to be used but also byproducts and wastes to be formed by reaction, etc.

Risks also arise in relation to the storage step. At the times of purchase and storage, consideration of risks such as leakage and fire in cases of disasters such as earthquakes, floods, and power failure is desirable, along with risks of accidents when a room is unattended.

### **3 General precautions for handling chemicals**

A comprehensive plan that starts from purchase to experimentation, storage, treatment, and disposal should be made when a chemical is to be used. Access the university URL shown above and conduct a risk assessment for designated substances. This process leads to prevention of accidents such as fire and

explosion, health hazards of workers, and environmental contamination. Treatment and disposal should follow the rules and directions related to treatment of experimental liquid waste. General precautions for handling chemicals are presented below.

(1) Purchase

- (a) For chemicals designated as hazardous materials in the Fire Service Act, the quantity which can be stored in a laboratory or a building is stipulated in the fire prevention ordinance of the local government. Therefore, do not purchase more than necessary, except for organic solvents that are used regularly.
- (b) For ordinary chemicals, do not purchase chemicals in large quantities, except for chemicals that are used regularly. Data obtained using aged chemicals are not reliable. Some chemicals might deteriorate (by processes such as peroxide formation, moisture absorption, and efflorescence). Purchase a minimum quantity considering disposal after use.
- (c) Prepare a proper experiment protocol. Do not purchase more than necessary.
- (d) After purchase, immediately register in IASO Management System for Lab Chemicals.
- (e) It is desirable to consider risks such as leakage and fire in case of disasters (such as earthquakes, floods and power failure), and risks of accidents when the room is unattended.

(2) Storage

- (a) For storage of chemicals designated as chemicals that must be stored using lock systems, strictly observe the descriptions of the relevant section of toxic chemicals.
- (b) For spontaneously combustible chemicals and water-reactive chemicals such as yellow phosphorus, metallic sodium, metallic potassium and triethylaluminum, store them using a predetermined method, preferably in metallic chemical storage.
- (c) Design the sorting and arrangement of chemical shelves in each laboratory as a whole. Take safety measures for the prevention of danger and fire. At least, store the following chemicals separately from each other: acids and bases; oxidizing agents and reducing agents; and organic chemicals and inorganic chemicals.
- (d) For organic peroxides and special explosive substances, handle with appropriate care. Store them in a cool and dark place separately from other items.
- (e) When substances that must be labeled are transferred into another container and stored, and when they are produced and stored in a container, notify others of their danger and toxicity using methods such as labeling and documents.

(3) Use of local exhaust ventilation system

Measures are needed in a laboratory, such as reduction of the total quantity of chemical substances stored in the laboratory, along with a device to decrease evaporation of volatile chemicals in the room,

in addition to introduction, proper use and maintenance of an exhaust ventilation system. Laboratory control is intended to use these facilities effectively, keep the levels of harmful fumes below the risks of fire and explosion, and maintain an environment that does not affect the health of people who come into the laboratory.

The general performance of exhaust ventilation systems is in the order of local exhaust ventilation system > benchtop hood = scatter preventive measure >> general ventilation fan. Although it is most desirable in a laboratory to conduct all operations using chemical substances in a local exhaust ventilation system, there might be difficulties related to the space, cost or energy consumption. It is therefore important to use a ventilation system that is suitable for the operation methods and for the risk, toxicity, and quantity of the chemical substance to be used.

Evaporation of a single substance can differ depending on factors such as the quantity used, the time of opening the container and contact to the atmosphere, and the area of a container's opening. The exhaust ventilation system should be selected considering the type of use (what kind of container, how it should be handled, etc.). For example, more evaporation occurs and a higher risk of exposure exists when a substance is handled in an open beaker, even for a case in which a substance has less toxicity. For experiment operations that consist mainly of manual operations, selecting and using an exhaust ventilation system that is suitable for the risk level is important for considering the risk assessment based on properties of a chemical substance itself and considering the type of use.

#### (4) Use of personal protective equipment

Accidental contact to the skin, eyes, etc. with chemical substances is very frequent in laboratories because of scatter, leakage, etc. Eye injury particularly might cause effects such as low vision that persist throughout life. Because full prevention of scattering, leakage, etc. is difficult when handling chemical substances, selecting and wearing appropriate protective equipment is important to prevent accidental contact to the skin, eyes, etc. Risk of contact to chemical substances is ever present. Do not forget to wear personal protective equipment not only during experiments but also before experiments, such as when weighing materials, and after experiments, such as during disposal and cleaning. Personal protective equipment is described as the following.

**Safety glasses:** Operators who handle chemical substances must wear safety glasses irrespective of the quantity of the chemical substances used. Glasses for vision correction are not personal protective equipment. Users of glasses for vision correction must wear safety glasses that can cover the area around the eyes, such as protective overglasses.

**Protective gloves:** Operators who handle chemical substances must wear protective gloves of materials selected to reduce the risk of contact to the chemical substances to be handled, considering resistance

to permeation and heat, fitting, grip, etc.

**Protective clothes:** Operators who handle chemical substances must wear protective clothes such as white coats and work clothes. Select protective clothes of a size and shape to avoid skin exposure, assuming protection against scattering of chemical substances. Select clothing while considering fire resistance if a significant risk of fire exists.

**Footwear:** Operators who handle chemical substances must wear appropriate footwear to cover the entire foot. Footwear must be resistant to permeation by the chemical substances to be handled. Sandals, shoes with air vents or high heels, slippers, etc. are inappropriate.

**Respiratory protection:** Respiratory protection is a protective device to wear for the purpose of protecting respiration when chemical substances harmful to the body are present in the environmental air. The work environment should be improved by ventilation, etc. to reduce harmful chemical substances in the environmental air as a prior condition. Wear respiratory protection to prevent substances from entering the body when protection from the chemical substances is insufficient merely by improving the work environment. Various types of respiratory protection against chemical substances can be used, such as protection with fans, facepieces, gas masks, and air-supplied respirators. Select devices that are effective considering the hazards posed by operations.

**Protection during experiments with risk of fire, explosion, bursting, etc.:** For experiments posing a risk of scattering of chemical substances and fragments by fire, explosion, bursting, etc., operators must wear eye, head, and body protection. Select antistatic protection as appropriate. Use measures such as protective screens to minimize damage in the case of an accident.

#### (5) During handling/reaction

When an operator handles the designated chemical substances, etc. for the first time, conduct a risk assessment at the time of planning of the operation (before conducting the operation). The designated substances are indicated as such by our IASO Management System for Lab Chemicals when entered. A risk assessment can be conducted for most of about 670 of the chemical substances using the results disclosed in the university's in-house web. The level of exposure must be minimized using the local exhaust ventilation system, personal protective equipment, etc. based on risk assessment findings. Handle with risk reduction measures shown in the following as appropriate.

- (a) When using a dangerous substance, or when a reaction product is predicted to be a dangerous substance, perform an advance experiment using small quantities.
- (b) When handling volatile chemical substances, avoid handling them to the greatest extent possible in a state that is open to the atmosphere. Use methods to minimize the chances for volatile chemical substances to evaporate. For example: minimally open the lid of the container; and do not use containers with a large opening, such as a beaker, for organic solvents.
- (c) When using dangerous substances, or when conducting dangerous reactions, consider protective



measures against disasters in advance. Conduct them under appropriate arrangements. Wear a face shield, prepare a fire extinguisher, and use the local exhaust ventilation system as appropriate when a risk of fire or explosion exists. Wear rubber gloves and a gas mask when the substances are toxic.

- (d) It is most desirable if all operations using chemical substances are conducted in the local exhaust ventilation system. Use an exhaust ventilation system that is appropriate for the danger, toxicity, and quantity of the chemical substances to be used, and the operation methods. It is desirable to perform operations on a safer side. Control operations to avoid danger such as fire and explosion, and to keep from creating vapors that are harmful to the body filling the space to a level that can lead to difficulties.
- (e) Explosion, fire or acute intoxication might occur during experiments. Do not conduct experiments alone or late at night, but during the daytime.

#### (6) Treatment and disposal

Accidents occur frequently not only during an experiment but also after the completion of an experiment. Risk assessments should include disposal and cleaning up.

- (a) Dangerous chemicals, toxic chemicals, and general chemicals must be treated and disposed of in accordance with the rules and directions of the university based on the intentions of the disaster prevention and fire prevention ordinances of the local government, the Water Pollution Prevention Act, the Air Pollution Control Act, and the Offensive Odor Control Act, referring to the relevant sections.
- (b) Waste that is left over after experimentation presents risks of unexpected accidents. Wear safety glasses during operations of disposal, treatment, transfer, etc. Similarly, wear safety glasses, protective gloves, protective clothes and footwear to cover the entire foot when handling wastes such as transferring containers. During disposal, toxic gases, and other substances might be produced by the unintentional mixing of chemical substances: prepare appropriate respiratory protection, etc. as an effective safety measure.
- (c) When a bottle becomes empty, immediately conduct empty bottle processing in an IASO Management System for Lab Chemicals to delete its registration.

#### (7) Hazardous materials handler qualification

As a general rule, it is necessary for us to record a hazardous materials handler's qualification when handling hazardous materials. Therefore, when in a course or major that involves frequent handling of hazardous materials, it is desirable to obtain a hazardous materials handler license. In particular, universities and research institutes handle a wide variety of chemicals, therefore the Class A license needs to be obtained. The eligibility criteria for the Class A license are that one must have two years of work experience after acquiring the Class B license, or graduated from a chemistry department at a technical college or university or have taken a prescribed number of chemistry courses.

#### 4 Limits on possession and handling of hazardous materials

The storage and handling of hazardous materials is stipulated by the Fire Service Act and local fire prevention ordinances. The Fire Service Act generally prohibits the storage or handling of hazardous materials over a certain quantity. This standard quantity is called the **designated quantity**. Here, a rank of the danger is created according to the properties of the hazardous material, and a quantity is specified by Cabinet Order for each rank, which is then used as the designated quantity.

Hazardous materials are classified by the Fire Service Act from Category I through VI according to their properties, as shown in Table 5-2; and the designated quantity is determined according to the danger of that category. If the quantity of the stored hazardous material is 0.2 times or more than the designated quantity, a notification must be submitted to the fire department; and at our university, with the exception of the hazardous materials storage for which a notification has been sent to the fire department, less than 0.2 times the designated quantity can be stored and handled by each building (strictly speaking, it is “less than 0.2 times the designated amount for each fire protection area”. The fire protection area differs depending on the structure of the building, therefore the case where the scope of the fire protection area is widest is described here). Therefore, the storage and handling of hazardous materials in the laboratory needs to be kept to the minimum necessary amount. Cases where this is exceeded must involve storage in the hazardous material storage.

Multiples of the designated quantity of multiple types of hazardous materials are calculated by the sum of the multiples of each hazardous material, as shown in the following equation, and the sum cannot exceed 0.2.

$$\sum_i m_i / M_i < 0.2 \quad m_i : \text{Possessed quantity of each item, } M_i : \text{Designated quantity of that item}$$

Table 5-2 Appended table of hazardous materials (category, name, and designated quantity are from the Fire Service Act)

Category	Nature	Item	Nature (law)	Designated quantity (law)
Category I	Oxidizing solids	1 Chlorates	Class 1 oxidizing solids	50kg
		2 Perchlorates		
		3 Inorganic peroxides		
		4 Chlorites		
		5 Bromates		
		6 Nitrates	Class 2 oxidizing solids	300kg
		7 Iodates		
		8 Permanganates		
		9 Dichromates		

		<p>10 Other substances specified by a Cabinet Order (periodates, periodic acid, chrome/ lead or iodine oxides, nitrites, hypochlorites, chlorinated isocyanuric acid, peroxydisulfates, peroxyborates, sodium hydrogen carbonate additives)</p> <p>11 Substances containing any of those listed in the preceding items</p>	Class 3 oxidizing solids	1,000kg
Category II	Combustible solids	<p>1 Phosphorus sulfide</p> <p>2 Red phosphorus</p> <p>3 Sulfur</p>		100 kg
		4 Iron powder		500kg
		<p>5 Metal powders</p> <p>6 Magnesium</p> <p>7 Other substances specified by a Cabinet Order</p>	Class 1 combustible solids	100kg
		8 Substances containing any of those listed in the preceding items	Class 2 combustible solids	500kg
		9 Inflammable solids		1,000kg
Category III	Spontaneously combustible substances and water-reactive substances	<p>1 Potassium</p> <p>2 Sodium</p> <p>3 Alkyl aluminum</p> <p>4 Alkyl lithium</p>		10kg
		5 Yellow phosphorus		20kg
		<p>6 Alkali metal (excluding potassium and sodium) and alkaline-earth metal</p> <p>7 Organometallic compounds (excluding alkyl aluminum and alkyl lithium)</p>	Class 1 spontaneously combustible substances and water-reactive substances	10kg
		<p>8 Metal hydrides</p> <p>9 Metal phosphides</p> <p>10 Carbide of calcium or carbide of aluminum</p>	Class 2 spontaneously combustible substances and water-reactive substances	50kg
		<p>11 Other substances specified by a Cabinet Order (chlorinated silicon compounds)</p> <p>12 Substances containing any of those listed in the preceding items</p>	Class 3 spontaneously combustible substances and water-reactive substances	300kg

Category IV	Inflammable liquids	1 Special inflammable materials		50 L
		2 Class I petroleum	Water-insoluble	200 L 400 L
		3 Alcohol		400 L
		4 Class II petroleum	Water-insoluble	1,000 L 2,000 L
		5 Class III petroleum	Water-insoluble	2,000 L 4,000 L
		6 Class IV petroleum		6,000 L
		7 Oil extracted from plants and animals		10,000 L
Category V	Self-reactive substances	1 Organic peroxides 2 Nitric esters 3 Nitro compounds 4 Nitroso compounds 5 Azo compounds 6 Diazo compounds 7 Hydrazine derivatives 8 Hydroxylamine 9 Hydroxylamine salts	Class 1 self-reactive substances	10kg
		10 Other substances specified by a Cabinet Order (metal azides, guanidine nitrate, 1-allyloxy-2,3-epoxypropane, 4-methidene oxetane-2-one) 11 Substances containing any of those listed in the preceding items	Class 2 self-reactive substances	100kg
Category VI	Oxidizing liquids	1 Perchloric acid 2 Hydrogen peroxide 3 Nitric acid 4 Other substances specified by a Cabinet Order (interhalogen compounds) 5 Substances containing any of those listed in the preceding items		300kg

#### Remarks

- 1 The term "oxidizing solids" means solids (substances other than liquids (i.e., substances forming liquids at a temperature of 20 degrees and one atmospheric pressure, or substances liquefied at a temperature exceeding 20 degrees but not higher than 40 degrees and one atmospheric pressure; the same applies hereinafter) or gas (i.e., substances forming gasses at a temperature of 20 degrees and one atmospheric pressure); the same applies hereinafter) that, as a result of an examination for determining the potential risk of oxidation conducted pursuant to a Cabinet Order, demonstrate the nature specified by a Cabinet Order, or that, as a result of an examination for determining the

sensitivity against impact conducted pursuant to a Cabinet Order, demonstrate the nature specified by a Cabinet Order.

- 2 The term "combustible solids" means solids that, as a result of an examination for determining the risk of ignition by fire conducted pursuant to a Cabinet Order, demonstrate the nature specified by a Cabinet Order, or that, as a result of an examination for determining the risk of inflammability pursuant to a Cabinet Order, demonstrate inflammability.
- 3 The term "iron powder" means iron powders excluding those specified by an Order of the Ministry of Internal Affairs and Communications after considering the particle size and other factors.
- 4 Phosphorus sulfide, red phosphorus, sulfur, and iron powder is deemed to demonstrate the nature specified in item 2 of these Remarks.
- 5 The term "metal powders" means powders of metals excluding alkali metal, alkaline-earth metal, iron and magnesium, and also excluding those specified by an Order of the Ministry of Internal Affairs and Communications after considering the particle size and other factors.
- 6 With regard to magnesium and the substances listed in item 8 of the row of Category II containing magnesium, those specified by an Order of the Ministry of Internal Affairs and Communications after considering the form and excluding other factors.
- 7 The term "inflammable solids" means solid alcohol and any other solid whose flash point is lower than 40 degrees at one atmospheric pressure.
- 8 The term "spontaneously combustible substances and water-reactive substances" means solids or liquids that, as a result of an examination for determining the risk of ignition in air conducted pursuant to a Cabinet Order, demonstrate the nature specified by a Cabinet Order, or that, as a result of an examination for determining the risk of ignition or generating combustible gas upon contact with water, demonstrate the nature specified by a Cabinet Order.
- 9 Potassium, sodium, alkyl aluminum, alkyl lithium and yellow phosphorus are deemed to demonstrate the nature specified in the preceding item.
- 10 The term "inflammable liquids" means liquids (with regard to the Class 3 petroleum and Class 4 petroleum and oil extracted from plants and animals, limited to those forming liquids at a temperature of 20 degrees and one atmospheric pressure) that, as a result of an examination for determining the risk of inflammability conducted pursuant to a Cabinet Order, demonstrate inflammability.
- 11 The term "special inflammable materials" means diethyl ether, carbon disulfide, or any other liquid whose ignition point is 100 degrees or lower at one atmospheric pressure, or, whose flash point is minus 20 degrees or lower and boiling point is 40 degrees or lower at one atmospheric pressure.
- 12 The term "Class I petroleum" means acetone, gasoline, and any other liquid whose flash point is lower than 21 degree at one atmospheric pressure.
- 13 The term "alcohol" means saturated monovalent alcohol whose molecules are composed of between one and three carbon atoms (including denatured alcohol), excluding those specified by an Order of

the Ministry of Internal Affairs and Communications after considering its composition and other factors.

- 14 The term "Class 2 petroleum" means heating oil, gas oil, and other liquids whose flash point is 21 degrees or higher but lower than 70 degrees at one atmospheric pressure, excluding paint or other materials specified by an Order of the Ministry of Internal Affairs and Communications after considering the composition and other factors.
- 15 The term "Class III petroleum" means heavy fuel oil, creosote oil, and other liquids whose flash point is 70 degrees or higher but lower than 200 degrees at one atmospheric pressure, excluding paint or other materials specified by an Order of the Ministry of Internal Affairs and Communications after considering the composition.
- 16 The term "Class IV petroleum" means gear oil, cylinder oil, and other liquids whose flash point is 200 degrees or higher but lower than 250 degrees at one atmospheric pressure, excluding paint or other materials specified by an Order of the Ministry of Internal Affairs and Communications after considering the composition.
- 17 The term "oil extracted from animals and plants" means oil extracted from the grease, meat, etc. of animals or the seeds or pulp of plants, whose flash point is lower than 250 degrees at one atmospheric pressure, excluding those stored and retained pursuant to the provisions of an Order of the Ministry of Internal Affairs and Communications.
- 18 The term "self-reactive substances" means solids or liquids, that, as a result of an examination for determining the risk of explosion conducted pursuant to a Cabinet Order, demonstrate the nature specified by a Cabinet Order, or that, as a result of an examination for determining the extent of thermolysis conducted pursuant to a Cabinet Order, demonstrate the nature specified by a Cabinet Order.
- 19 With regard to the substances listed in item (xi) of the row of Category V, those containing organic peroxides and also those containing an inactive solid as specified by an Order of the Ministry of Internal Affairs and Communications are excluded.
- 20 The term "oxidizing liquids" means liquids that, as a result of an examination for determining the potential risk of oxidation conducted pursuant to a Cabinet Order, demonstrate the nature specified by a Cabinet Order.
- 21 With regard to any substance having two or more natures listed in the column of the Nature in this Appended Table, the Item that covers those substances are specified by an Order of the Ministry of Internal Affairs and Communications.

## **5 Hazardous materials storage**

The storage and handling of hazardous materials is strictly stipulated by the Fire Service Act and government ordinances/rules regarding the regulation of hazardous materials. According to these

stipulations, storing hazardous materials in the designated quantity or higher other than at a specified storage location is prohibited. **Each experimental building of the university can hold and handle less than 0.2 times the designated quantity in each fire protection area, and a hazardous material storage is installed to store more than this quantity** (see p.78, “Limits on possession and handling of hazardous materials” for details). Hazardous material storage rooms are divided according to the type and nature of hazardous materials.

**The maximum amount of hazardous materials that can be stored in university storage is 24 times the designated quantity**, and the actual handling method is specified in the Nagaoka University of Technology Hazardous Material Storage Handling Guidelines. **Furthermore, the storage period in the hazardous material storage of the university is set to one year, and storage over longer period is prohibited as a general rule.** Therefore, when purchasing hazardous materials, an experimental plan should be established to avoid purchasing an unnecessarily large amount of hazardous materials. Also, the hazardous material storage is not for storing unnecessary chemicals, therefore chemicals that are not expected to be used should be disposed of immediately in accordance with regulations.

## 6 When starting a new experiment

When starting a new experiment, there is a high possibility of an unexpected accident such as an explosion, hence each experimenter and experiment instructor must observe following precautions before starting an experiment.

- (1) Conduct an extensive investigation of experimental examples.

Investigate the hazards and toxicity of all related substances such as raw materials, products, solvents, and byproducts. Refer to “<Important> Regarding SDS stock”, “Reference URL”, and the relevant parts of this chapter on pp. 18–19.

### A Literature search

The research report is not an experimental guidebook. It should be noted that hazards are not necessarily mentioned.

### B Listen to the stories of experienced people.

- (2) Establish an experimental plan to prevent accidents.
- (3) Furthermore, even in the unlikely event of an accident (e.g., erroneous operation, abnormal reaction, material defect, power outage while absent, water outage, secondary damage from nearby accident, earthquake), exercise caution to prevent casualties.
- (4) Discuss the experimental plan and disaster prevention measures in the laboratory.
- (5) Install the necessary safety protection equipment.
- (6) First conduct a preliminary experiment with small amounts. During this time, ensure to establish sufficient measures such as protective equipment and walls.
- (7) Do not shift to a large quantity in the experiment at once; make a gradual shift.

## 7 General precautions for chemical experiments

There are chemicals, various instruments, and equipment in the chemistry laboratory, and each must be used appropriately. First, carefully read the general handling precautions that are described in Section 1.2 regarding the purchase, storage, use, and disposal of chemicals. Special laboratories require designing of suitable safety precautions. Ensure that laboratory members imperatively obtain safety education and fire prevention training.

### (1) General precautions

- A Keep the laboratory tidy and clean.
- B Always keep fire extinguishers, protective equipment (safety glasses, protective masks, gloves, safety guards, etc.), eyewash stations, first aid tools, and chemicals (first aid kits) available.
- C Regularly inspect for aging electrical wiring, loose terminals, and poor insulation.
- D When handling substances that are expected to be hazardous, thoroughly investigate their hazards and toxicity in advance, consult with experienced people, and consider measures that would minimize damage even in the event of an accident.
- E For hazardous chemicals, specify the product name so that there are no errors.
- F Do not wash containers, equipment, etc., without proper ventilation.
- G The following experiments require special attention.
  - Operations and reactions that include unknown hazards
  - Operations and handling of substances with a wide variety of hazards
  - Experiments wherein the possibility of ignition and harmfulness coexists
  - Experiments under reaction conditions that are close to the limit (high pressure, high temperature, low temperature, and vacuum)
- H When conducting experiments that are expected to be hazardous, inform the surrounding people in advance and take proper measures.
- I Use protective glasses. If further hazards are expected, use protective equipment such as gloves, protective mask, gas mask, and safety screens.
- J Treatment of chemicals and waste after experiments
  - Store solutions containing heavy metals, cyanide compounds, arsenic, strong acids, and strong alkaline solutions in containers according to the guidance of the university's experimental waste liquid processing.**
  - Do not pour organic solvents down the drain.** Collect what can be recovered to the extent possible, and either use or dispose it.
  - Combustible waste such as filter paper should be soaked in water before discarding in a "disposal pot".
- K Even in experiments that are generally expected to be hazardous, students can become inattentive



after repeating it several times owing to familiarity and carelessness. Always carefully examine the equipment used, quantitative relationships, reaction conditions, etc., and start the experiment in a composed yet careful manner.

- L Confirm the position of the fire extinguisher (e.g., carbon dioxide, powder type) and sand (types and characteristics of fire extinguishers are shown in Tables 5-3 and 5-4).
- M Wear lab coats and work clothes to prevent skin exposure. Ensure that nimble movements can be made. Avoid wearing sandals or slippers.
- N Do not purchase more chemicals than necessary. Store all chemicals that are not being used in the experiment in a chemical cabinet that is away from the laboratory table. Keep the organic and inorganic chemicals separated from each other when in storage.  
Place only the necessary items and required amount of chemicals on the laboratory table. Placing extra reagents, solvents, etc., can lead to larger-scale accidents.
- O Before starting an experiment, inspect the laboratory equipment, experimental equipment, piping, wiring, etc., as a safety check.

#### (2) Precautions during experiments

- A When conducting experiments, **do not make a full schedule**. It is better to suspend an experiment if it does not advance according to the plan. Do not rush an experiment.
- B **Do not leave the laboratory during experiments**. When leaving the laboratory, clearly state the experiment content and destination to someone in the same room.
- C When distilling, do not forget to add boiling stones. If they were forgotten, put them in after cooling.
- D When there is a risk of explosion, do not cover the device to seal it. A screen that separates the device from the experimenter is preferable.
- E When opening a lid of a bottle, point the plug in a direction where there is nobody present.
- F When crushing substances, be careful not to cause an ignition or explosion due to friction or impact.
- G Please be careful if a so-called mixed hazardous material (see Section 2.5, p.107) that could ignite or explode is present when mixing two or more types of substances.
- H Do not try to handle an accident alone. Seek help.
- I **Do not pour mercury or its compounds down the drain.**

#### (3) Clean up

- A Cleaning up is also part of the experiment.
- B Immediately wash the used equipment, especially grinding equipment. Be careful when disposing of cleaning waste liquid. Insufficient cleaning can more likely result in accidents by the time the experiment resumes.
- C Dispose of used chemicals according to the specified method. Clarify the content of used chemicals and solutions, and be mindful of the storage method.
- D Ensure that the chemical label on the bottle does not come off. It is preferable to write on the bottom

of the bottle with a permanent marker.

E The disposal of old chemicals is prone to inattentiveness. Patiently dispose of them.

(4) Precautions when leaving and conducting experiments late at night

A Stop the gas, electricity, and water when leaving. Pay particular attention in cases of a day before the weekend.

B Take measures against unexpected water pressure changes, water outages, and power outages. In particular, items for which measures cannot be taken, such as an aspirator (attached backflow prevention bottle) and cooling water, should not be operated unmanned.

C Late night experimentation is not permitted as a general rule, but when such experiments are unavoidable, pay close attention to the use of heating and ventilation.

D There should be at least two people in the laboratory, but if temporarily alone, ensure that the at least person in the laboratory is known. Leaving the door open is an option.

E When conducting experiments or deskwork at night or on weekends, or operating equipment late at night, obtain permission from the academic supervisor by notifying remaining after-hours and unmanned operation late at night, and display them at the designated locations (refer to Appendix 1 on p.3).

Table 5-3 Fire extinguishers to adapt

Class	Type	Main fire extinguishers to adapt
A	Ordinary fire (wood, paper, fiber)	Powder (A, B, C) fire extinguisher, enhanced liquid fire extinguisher, foam fire extinguisher, water fire extinguisher
B	Oil fire (including semi-solid fats and oils)	Powder (A, B, C) fire extinguisher, enhanced liquid fire extinguisher, foam fire extinguisher, inert gas fire extinguisher
C	Electric fire (converter, transformer)	Powder (A, B, C) fire extinguisher, enhanced liquid fire extinguisher, inert gas fire extinguisher

Note) Class A Fire of ordinary combustibles  
 Class B Fire of petroleum or oil  
 Class C Fire of electrical equipment

Table 5-4 Fire extinguisher and fire equipment

Name of fire	Chemical	Applicable fire	Features
Chemical foam fire extinguisher	Agent A: sodium hydrogen carbonate solution Agent B: aqueous aluminum sulfate solution	A, B	Emits bubbles that contain carbon dioxide. Methods for mixing the two liquids involve either tipping over the fire extinguisher or breaking the inner bottle. Range of approximately 5 m, and once released, cannot be stopped partway. Cannot be used for C fires because there is a risk of electric shock.

<b>Powder (A, B, C) Fire extinguisher</b>	Ammonium phosphate	A,B,C	Can be used for various fires and has great fire extinguishing effects. Range of approximately 4 to 6 m and release time is short. Dirty state present after fire is extinguished.
Enhanced liquid fire extinguisher	Liquefied carbon dioxide	A, B	Can also handle C fires when a spray nozzle is attached. Is a strongly alkaline water system and has a cooling effect. Range of 4-8 m.
<b>Carbon dioxide fire extinguisher</b>	Sodium bicarbonate powder	B, C	Inert gas fire extinguisher. Has a short range of 1–2 m and has the disadvantage of a heavy container but results in less dirtiness after fire is extinguished. Large-scale fire extinguishers in hallways are powerful.
B, C powder fire extinguisher	Dried graphite powder, soda ash, salt, etc.	B, C	Great fire extinguishing effect. Range of 3-6 m, somewhat cumbersome to handle, and heavy. Dirtiness present after fire is extinguished.
Water fire extinguisher	Dry sand	A	Can handle C fires if radiated as a mist. Wetting agent added to give it antifreeze properties.
Fire extinguishing sand	Ammonium phosphate	Metal fire	Effective for alkali metals and alkyl metals, but not suitable for three-dimensional fires.

(5) When a fire breaks out

- A Yell “fire” and let surrounding people know.
- B Remove nearby combustibles and turn off the fire source.
- C Turn off the gas source, power supply, etc., as far away from the source as possible.
- D Extinguish small fires without rushing. Do not make a mistake in this procedure and method (the person at the source of the fire should immediately leave that area and loudly call out for help. Panicking and trying to extinguish the fire alone could result in fire spreading to clothes or flipping over the equipment. It is better to entrust this to another person who is calm).  
Be careful when using a fire extinguisher, as the applicable fire extinguisher will differ depending on the fire type. Fire extinguishers can be classified as Class A, B, or C, and their contents are as listed in Table 5-3. Furthermore, the types and features of general fire extinguishers are listed in Table 5-4.  
Apart for some halon-based fire extinguishers (inert gas fire extinguishers, not currently manufactured) in the Information Processing Center / Doctoral Building, the university is equipped with powder (A, B, and C) and carbon dioxide fire extinguishers (two types in bold in Table 5-4), which are placed in each hallway and room.
- E If a lab coat catches fire, do not panic and take an emergency shower (or use a bucket of water if unavailable) (nylon and polyester blends may melt and adhere to the skin if ignited, which can

result in a serious accident. Cotton or wool is desirable for clothing that comes in contact with skin).

- F Fires in a fume hood are usually extinguished by stopping ventilation because of the fire extinguishing effect and prevention of upward spread of the fire. However, there are some cases where ventilation should be continued, such as when accompanied by the generation of poisonous gases or smoke.
- G If gas is ejected from a inflammable gas cylinder due to an accident, first attempt to close the valve. Additionally, quickly turn off the gas burner to turn off the ignition source, then open the windows to improve the ventilation in the room, and move the gas cylinder near the window if possible.
- H If inflammable gas gets emitted from the gas cylinder and ignites, do not extinguish the fire immediately; first remove surrounding combustibles and then extinguish the fire using a fire extinguisher, water, etc.
- I If there is a risk of poisonous gas or generation of large amounts of smoke, extinguish the fire using protective equipment, smoke mask, etc. At a minimum, extinguish the fire from the windward side.
- J Do not be overconfident when using gas masks. Confirm whether the type of absorption tube in the gas mask is appropriate for use. Furthermore, gas masks are not effective when the concentration of the poisonous gas is more than a certain value. Smoke masks and items like the Aqua Lung are useful.
- K After realizing that the generation of the fire or gas is out of control even after the above measures, immediately leave the premise.
- L Dispose of gas sources, heat sources, hazardous materials, etc., to the extent possible, and check if there anyone who has yet not left the premise.

## **8 First aid for chemical injuries**

### (1) Treatment for skin

Immediately wash the affected area with a large amount of clean cold water for at least 15 minutes. For substances that generate heat due to water, such as concentrated sulfuric acid, first wipe off most of the affected area with a dry cloth, paper, tissue paper, etc., as soon as possible, then wash off the rest at once with a large amount of water.

Acids and alkali materials often remain between the folds of the skin and hair, hence neutralize the substance with an aqueous sodium hydrogen carbonate solution for acids and 2-3% acetic acid or lemon juice for alkali materials. Wash phenolic acid with alcohol and neutralize with sodium bicarbonate. Skin ulcers should be treated by a dermatologist.

### (2) Treatment for eyes

Quickly wash eyes with a large amount of water. In particular, alkali materials corrode the eyeballs, therefore wash thoroughly with water, and seek immediate medical attention from an ophthalmologist.

A squirt-type eye wash device is good for washing eyes, but if unavailable, immerse the face repeatedly in a basin overflowing with clean water, keep the eyes closed at first, and then repeatedly blink in the water to wash them. Gentle running water from a rubber tube connected to a faucet may be used. However, be aware that a strong fountain can force the acid on the face into the eyes and peel off of the corroded skin surface.

Do not apply neutralizers. After washing the eyes, apply a thick gauze compress, fix this with an eye patch, etc., and immediately receive treatment from an ophthalmologist.

### (3) Respiratory treatment

Quickly move the patient to fresh air. Remove contaminated clothing, clean the skin, keep the patient warm, and resting. In severe cases, oxygen inhalation or artificial respiration is required.

Concentrated exposure to acid mist, chlorine gas, etc., not only damages the tracheal mucosa but also the alveoli, which causes bronchitis, pneumonia, and pulmonary edema (plasma exudes into lungs), resulting in respiratory distress. This can also lead to shock, therefore treatment by a physician is necessary.

During emergency rescue, use a gas mask to prevent the rescuer from poisoning. Refer to Chapter 2 of these Guidelines for artificial respiration.

### (4) Treatment for accidental ingestion

Have the affected individual drink water or milk in a quantity enough to induce vomiting. Injuries to the stomach and esophagus can lead to death in minutes, therefore an immediate response is required. The amount of water given must be approximately 100 times that of the chemical ingested. Raw eggs can be used for acid, and fruit juice or vinegar can be used for alkali materials. Vomiting can be induced by stimulating the throat with fingers, but there is a choking hazard when the affected individual is unconscious, hence nothing should be done in such cases. Call a physician immediately. Keep the patient warm and resting, and be mindful of shock or respiratory paralysis.

### (5) Treatment in case of poisoning

In the event of poisonous gas inhalation, immediately move the affected individual to fresh air, loosen clothes, and rest. Give artificial respiration if necessary. For phosgene, nitrite gas, and halogen poisoning, be sure to rest for several hours, even if there are no complaints of severe pain after gas inhalation. Afterwards, consult with a physician.

In the event of chemical ingestion, drink warm water or saline solution enough to induce vomiting. However, do not allow unconscious people to drink anything.

## **9 Treatment for various chemicals**

Please refer to IASO or the SDS of each manufacturer. Some examples are shown below.

(1) Hydrofluoric acid

This acid intensely corrodes the skin, therefore wash the skin with water for 30 minutes. Subsequently, cover it with a magnesia mud paste (magnesium oxide 20 g, glycerin 80 g), and apply a dry bandage. When the affected individual's respiratory system is disturbed, ensure that the individual is at rest.

(2) Chlorine, bromine gas

For respiratory disorders, have the affected individual smell cotton wool soaked in dilute ammonia water for short periods at a time. Vapor inhalation of a mixture of alcohol and ether in equal proportion also helps relieve airway irritation.

(3) Carbon monoxide

Take the affected individual out into fresh air (do not let the patient walk), and be mindful of rest and heat retention. Cool with ice in the case of fever. Inhalation of oxygen and 5% CO<sub>2</sub> is desirable.

For severely ill people, an exchange transfusion of 2L or more within 30 minutes is effective, therefore immediately arrange for blood transfusion with a physician. After regaining consciousness, the affected individual will need to remain at rest for 2–3 hours and recover over several days.

(4) Hydrogen cyanide, cyanide compounds

Take the affected individual out into fresh air, and if conscious, have the patient inhale amyl nitrite every five minutes for a total of three minutes, stopping once the systolic blood pressure reaches 80 mmHg. This procedure must be conducted within a few minutes. Respiratory arrest requires artificial respiration with 100% oxygen. Percutaneous respiration is possible with hydrogen cyanide, therefore wash the affected area with soap and water and be mindful of keeping the patient warm. There is also a possibility of shock due to amyl nitrite, therefore seek immediate medical attention.

(5) Nitrogen dioxide

Symptoms occur suddenly with a considerable delay after exposure to nitrogen dioxide. Oxygen inhalation is to be continued even if respiratory symptoms are mild. The main symptom is pulmonary edema. Clean the mouth, nose, mucous membranes of the eyes, and skin with 1% baking soda solution.

(6) Hydrogen sulfide

Oxygen inhalation with 5% CO<sub>2</sub> is effective. If in the eyes, wash the eyes and receive treatment from an ophthalmologist.

(7) Phosgene

This causes severe pulmonary edema. Remove the contaminated clothing and wash with 2% baking soda solution. Begin oxygen inhalation as soon as possible. Inhalation of oxygen through 20% alcohol alleviates respiratory distress.

(8) Yellow phosphorus

This chemical tends to cause difficult-to-heal second- or third-degree burns. Rinse with water or a large amount of running water. For burns, pour 5% sodium bicarbonate water, then wash with 5% copper sulfate solution, later remove the phosphorus in the form of solid copper salts using tweezers; however, do not force them off.

(9) Organic solvent

Dangerous acute poisoning is likely to occur with low-boiling-point solvents. Poisoning is mainly due to invasion from the respiratory tract but can also occur due to percutaneous respiration. This generally has an anesthetic effect, and in severe cases, can cause disturbed consciousness and respiratory center paralysis. Patients can become violent during the recovery period.

First aid is the same as with general methods. Use synthetic detergent and water for cleaning. Be careful as sequelae may remain.

(10) Oxygen deficiency

This can quickly be fatal, therefore immediately rescue the affected individual and move them to fresh air. The oxygen concentration in air under which humans can normally operate is 16% or higher; respiratory distress, nausea, and pallor occur at around 10%; unconsciousness and respiratory arrest occur within a short period of time at around 7%.

Use oxygen respirators, lifelines, etc. to avoid rescuers not to be fellow travelers. Gas masks are not effective.

## Section 2 Hazardous chemicals

Hazardous chemicals cause serious harm such as secondary chemical burns and lifelong injuries resulting from explosions or flames, which stem from their physical or chemical properties, rather than their inherent toxicity. In addition, except for highly toxic substances, chemicals that possess both hazardous and toxic properties are regarded as hazardous chemicals.

### 1 Pyrophoric substances

Pyrophoric substances are materials that generally ignite upon exposure to heat, under impact, on contact, or by mixing. Herein, we present substances that are ignited by heat as well as those that ignite with relative ease in the presence of air or water, resulting in fire.

Table 5-5 Pyrophoric substances

Category	Characteristics	Example substances
Oxidants	Decompose under heating and impact to release oxygen; burn violently with combustibles, occasionally resulting in explosions.	Chlorates and peroxides.
Spontaneous pyrophoric substances	Certain prospective substances for research, which ignite and burn in contact with air at room temperature.	Yellow phosphorus, certain sulfides, and metals produced by the decomposition of certain salts.
Low-temperature pyrophoric substance	Ignites at relatively low temperatures and exhibits a high burn rate.	Red phosphorus and metal powder.
Water-prohibitive substance	Ignites in the presence of water and occasionally explodes.	Metallic sodium and potassium.

#### (1) Oxidants (chemicals)

According to the definition of Class 1 hazardous materials specified in the Fire Services Act of Japan, oxidants are substances that are generally at risk of ignition or explosion from impact, friction, heating, or contact with strong acids. These substances are oxygen carriers, which decompose or explode independently and thus are extremely dangerous. Organic peroxides are particularly dangerous. Potassium chlorate and potassium perchlorate are relatively stable; however, these chemicals may explode when heated in the presence of organic compounds, such as garbage. Such notable substances (chemicals) are listed in Table 5-6; herein, M and R indicate metals and alkyl and aryl groups, respectively.



Table 5-6 Oxidants

Compound	General	Substance (chemical) name	Law or regulation
Chlorates	$M^I ClO_3$ $M^{II} (ClO_3)_2$	Chlorates, such as $NH_4ClO_3$ , $NaClO_3$ , and $KClO_3$ and those of Ag, Hg (II), Pb, and Ba.	Fire Services Act for hazardous materials Class 1.
Perchlorates	$M^I ClO_4$ $M^{II} (ClO_4)_2$	Perchloric acid salts, such as $NH_4ClO_4$ , $NaClO_4$ , $KClO_4$ , Mg, and Ba.	Same as above.
Inorganic peroxides	$MO_x$ or $Ox$ , etc.	$Na_2O_2$ , $K_2O_2$ , $MgO_2$ , $CaO_2$ , $BaO_2$ , persulfuric acid salts [ $(NH_4)_2S_2O_8$ , $Na_2S_2O_8$ ], perboric acid sodium, $H_2O_2$ , and $O_3$ .	Same as above. $H_2O_2$ is a Fire Services Act Class 6 hazardous material.
Organic peroxides	$(RCO_2)_2$ , $RCO_3H$ , $(RO)_2$	Explosively decomposing substances such as acetyl peroxide, benzoyl perchloride, peracetic acid, diethyl peroxide, and cumene hydroperoxide.	Fire Services Act Class 5 hazardous material.
Nitric acid salts	$M^I NO_3$ $M^{II} (NO_3)_2$	Nitric acid salts, such as $NH_4NO_3$ , $NaNO_3$ , and $KNO_3$ and those of Mg, Ca, Ba, Pb, Ni, Co, and Fe.	Fire Services Act Class 1 hazardous material.
Permanganese acid salts	$M^I MnO_4$	$KMnO_4$ and $NaMnO_4$ .	Same as above.
Chlorites	$M^I ClO_2$	$NaClO_2$ and $KClO_2$ .	Same as above.
Bromates	$M^I BrO_3$	$NaBrO_3$ , $KBrO_3$ , and $Ba (BrO_3)_2$ .	Same as above.
Iodates	$M^I IO_3$	$NaIO_3$ , $KIO_3$ , and $AgIO_3$ .	Same as above.
Dichromic acid salts	$M^I_2Cr_2O_7$	$(NH_4)_2Cr_2O_7$ , $Na_2Cr_2O_7$ , and $K_2Cr_2O_7$ .	Same as above.

## Handling precautions:

- 1) These substances are at risk of ignition and explosion upon heating, impact, or contact with strong acids. Store oxidants in a cool and dark place away from fire and heat sources.
- 2) Mixing these substances with reducing substances or organic compounds may lead to heat generation, ignition, or explosions owing to oxidation; thus, do not inadvertently mix or store them with other substances.
- 3) Peroxides generate oxygen ( $O_2$ ) in water and hydrogen peroxide ( $H_2O_2$ ) in dilute acid, which are generating heat and sometimes ignite.
- 4) Alkali metal and alkaline earth metal peroxides readily react with water; hence, moisture proofing is of particular importance.
- 5) Peroxides may be generated by solvents, such as ether, tetrahydrofuran, or ketone, which undergo autoxidation under normal storage conditions for extended periods; therefore, when distilling such chemicals, either decompose them according to regular procedures or retain a considerable amount of the residual liquid.

Likely occurrences:

- 1) While cleaning organic substances off glass funnels with hydrogen peroxide aqueous solution, peroxides may build up in filter flasks and explode, especially during summer.
- 2) Attempts at peroxide distillation and its implementation in heating solutions may result in explosions.
- 3) When hydrogen peroxide in an aqueous solution is added to manganese dioxide ( $\text{MnO}_2$ ) to generate oxygen, the rapid addition of peroxide causes explosions.
- 4) Inadvertent addition of potassium permanganate, rather than potassium dichromate, during the preparation of chromic acid solution produces explosions.
- 5) The decomposition of organic compounds with perchlorate ( $\text{HClO}_4$ ) solution and sulfuric acid is often accompanied by an explosion in the end.

(2) Spontaneous pyrophoric substances

Spontaneous pyrophoric substances primarily react with atmospheric oxygen under storage conditions or during handling to generate heat; in extreme cases, these substances ignite spontaneously. Such substances are listed in Table 5-7, where M and X indicate metals and halogens, respectively.

Table 5-7 Spontaneous pyrophoric substances

Compounds	General expression	Substance (chemical) name	Law or regulation
Yellow phosphorus	P	Yellow phosphorus.	Class 3 hazardous material.
Hydrides	$\text{MH}_n$ $\text{MH}_n\text{X}_{a-n}$	$\text{BH}_3$ , $\text{SiH}_4$ , $\text{PH}_3$ , $\text{AsH}_3$ , $\text{SbH}_3$ , NaH in oil, KH in oil, $\text{BH}_n\text{X}_{3-n}$ , and $\text{SiH}_n\text{X}_{4-n}$ .	Same as above.
Organometallic compounds	$\text{R}_n\text{MX}_{a-n}$	M = Li, Na, K (these substances are RM type), Mg, B, Al, P, Zn, Se, An, Sb, Bi, Ag, Ca, and Ba.	Same as above.
Organometallic hydrides	$\text{R}_n\text{MH}_{a-n}$	M = B, Al, Si, As, and P.	Same as above.
Metal reduction catalysts	M	Ni (including improved Raney nickel), Pt, Pd, and Cu.	
Fine metal powder		Fine metal (such as Pb and Ni) powder made by the thermal decomposition of oxalates and formates in the absence of air. Fine metal (such as Pb, Ni, and Cu) powder made by the thermal decomposition of metal carbonyls and organometallic, etc. in the absence of air.	

Handling precautions:

- 1) These substances are at significant risk of ignition upon contact with air; thus, pay special attention to direct instructions received from a qualified individual.

- 2) Ruptured containers or earthquakes may lead to contact with air and spontaneous ignition; therefore, store these substances in suitable containers by observing appropriate storage methods. The solvents may become volatile and ignite, even after dilution; thus, these chemicals should be used with necessary caution.
- 3) Generally, as yellow phosphorus does not exhibit water-prohibitive properties, place it in glass bottles filled with water, and subsequently store it in a covered metallic container filled with sand. Other commercial organometallic and hydrides thereof are stored in iron containers under an inactive gas atmosphere. When these substances are segregated into flasks, always store them in metallic containers in a sealed metal storage cabinet; this strategy prevents fire by cutting off the oxygen supply.
- 4) Ensure that ignition does not occur when moving or washing the containers. Move or wash containers for yellow phosphorus under an inactive atmosphere of argon or nitrogen and containers for organic metals after dilution with inert solvents or alcohol treatment.
- 5) Because these substances are harmful even after treatment, follow the rules specified by the university.

Treatment:

- 1) It is best to burn incineration of yellow phosphorus each 40-50 g outdoors. Phosphorus pentoxide ( $P_2O_5$ ) immediately transforms into phosphoric acid ( $H_3PO_4$ ) and detoxifies. At this time, an iron plate or concrete structure should be utilized because phosphorous melt and burn. When phosphorous is burned on sand or earth, it turns into molten granules, which remain incombustible and should be handled by using rubber gloves and tweezers.
- 2) Organometallic compounds and hydrides, which emit harmless oxides after burning, are diluted with petroleum naphtha, kerosene, or decalin; these solvents possess high boiling points and do not ignite spontaneously. Subsequently, the substances are burned outdoors in small quantities.
- 3) For toxic oxides (As and Se), detoxify them in a laboratory and follow the rules and instructions specified by the university.

Likely occurrences:

- 1) When a Raney nickel catalyst is employed for hydrogenation, the liquid product is filtered out and subsequently rinsed with a solvent; thereafter, the filter paper is discarded safely because it may ignite after it has dried.
- 2) Organometallic compounds should always be handled as combustible substances; thus, proper care should be taken while cutting the container seals.

(3) Low-temperature pyrophoric substances

These substances oxidize at relatively low temperatures and burn; therefore, a risk of explosion from impact occurs when these substances come into contact with oxidants.

Table 5-8 Low-temperature pyrophoric substances

Compounds	Substance names	Law or regulation
	Red phosphorus, phosphorus sulfide ( $P_2S_3$ and $P_2S_5$ ), and sulfur	Class 2 hazardous material.
Metal powder	Mg and Al powder, grains, and foil ribbon (including photographic flash powder), iron and zinc powder, tungsten and nickel fine powder, and non-Mg and Al powder	Same as above.

Handling precautions:

- 1) These substances oxidize readily and ignite when heated; therefore, store in a cool place away from heat sources or fire.
- 2) These substances ignite readily when mixed with oxidants and explode upon impact; hence, do not mix them oxidants inadvertently (sulfur is used in gunpowder and safety matches, and red phosphorus is used in safety matches).
- 3) Fine sulfur powder generally ignites in air and generates heat.
- 4) Metal powders burn severely when heated in air. In addition, hydrogen gas is generated along with acids and alkalis, which is at risk of igniting and fueling fire. Thus, special care should be taken in the presence of fire in the vicinity when reducing via iron or zinc powder.
- 5) Because phosphorus sulfide is a poisonous and toxic substance, necessary precautions should be taken while handling it.

#### (4) Water-prohibitive substances

In general, these substances (listed in Table 5-9) react readily with water to generate hydrogen or carbon, and the reaction may cause heat generation, ignition, or explosion.

Table 5-9 Water-prohibitive substance

Generic name	S u b s t a n c e s	Law or regulation
Metals and metal compounds	Na, K, Li, Ca, $CaC_2$ (carbides), $Al_4C_3$ (carbonization of aluminum), SiC, $Ca_3P_2$ (phosphorized coal), and CaO.	Class 3 hazardous material.
Hydrides	Metals hydrides of Li, Na, K, Cs, Ca, Ba, Zr, Cu, and Sn, $NaBH_4$ , and $LiAlH_4$ .	Class 3 hazardous material.
Alkali amides	$NaNH_2$ (sodiumamide) and $KNH_2$ (potassiumamide).	
Certain spontaneous combustible organic compounds	Organometallic compounds of Li, Na, K, Mg, Ca, Ba, Al, and Zn. For example, $C_4H_9Li$ , $Al(C_2H_5)_3$ , and $Zn(C_2H_5)_2$ .	A few research field-specific substances, such as $Al(C_2H_5)_3$ , are Class 3 hazardous materials.

Handling precautions:

- 1) These substances react violently with water and generate hydrogen or hydrogen carbide; hence, special precautions should be exercised in the presence of water. Do not inadvertently introduce tap water in the vicinity of water-prohibitive substances because any water spray may cause ignition or explosion.
- 2) Carefully handle metallic sodium when weighing. Quickly remove the surface oxide layer while wiping the storage solvent off the surface with filter paper before weighing. As metallic potassium rapidly reacts with water and atmospheric oxygen and ignites, place it in a wide-mouthed dish or beaker and remove the surface oxide layer with an inert solvent. Subsequently, place it in the pre-weighed inert solvent, and determine the weight from the difference between that before and after placement. Metallic lithium is safe to handle in air.
- 3) Place fragments of metallic lithium, sodium, or potassium into a flask in a water bath using tweezers; thereafter, remove the flask from the water bath without any inadvertent addition of the metal into the water, or cover the water surface with a board or iron plate.
- 4) Carbides react with water and occasionally explode. This phenomenon occurs owing to the high heat generated by the spontaneous ignition of the pure calcium phosphide contained in the raw material carbide.
- 5) Calcium phosphide reacts vigorously with water, occasionally resulting in explosions.
- 6) Raw lime does not ignite in the presence of water; nevertheless, other substances may ignite because of the heat generated.

Likely occurrences:

- 1) When shavings of metallic sodium stored in petroleum are placed in alcohol for an extended period and exhibit no further reactions, the petroleum may ignite when it is poured out for disposal; this ignition results from the small grains of sodium in the petroleum. Therefore, in the interest of environmental protection, never pour out any of the solvents.
- 2) During outdoor attempts to treat bottles containing shavings of metallic potassium stored in petroleum, the shavings may tumble out during transport and ignite; the outcome is more dangerous than that for sodium.
- 3) The inadvertent addition of water to white sodium, which has aged and the surface has oxidized or transformed into sodium carbonate, results in explosions. Always treat white sodium with alcohol.

## **2 Explosive substances**

Explosions consist of explosive decomposition in which substances readily decompose under heat or impact and spontaneously undergo vaporization and expansion. Thermal explosions result from the ignition of flammable gas in air when the concentration crosses the explosion limit; this can occur in relation to the vapor pressure for low-boiling point liquid substances. Both may occur in experiments and

research.

(1) Gunpowder

Gunpowder (black gunpowder, smokeless gunpowder, mercury fulminate, lead azide, carlits, dynamite, and pyrotechnics) consists of molded products with a mixture of explosively decomposing substances; its usage is regulated by the Gunpowder Control Law and Fire Services Act, and its usage should be properly supervised.

(2) Explosively decomposing chemicals (Fire Services Act Class 5 hazardous materials)

These chemicals include nitric acid esters, nitro and nitroso compounds, nitroamines, organic peroxides, and other unstable and readily decomposable compounds.

Table 5-10 Explosively decomposing chemicals

Bond type	Name	Compound examples and Fire Services Act hazardous material class
N-O C-O-NO <sub>2</sub>	Nitric acid esters (A)	Nitroglycerine, nitroglycol, nitrocellulose (those gunpowder: Class 5 of hazardous materials designated under the Fire Defense Law), and monovalent alcohol ester (Class 4).
C-NO <sub>2</sub>	Nitrides (A)	Trinitrotoluene and picric acid, etc. (Class 5 and Class 4 according to the number of other attached nitro groups, respectively).
C-N-NO <sub>2</sub>	Nitroamines (A)	Trimethylene trinitroamine, cyclotetramethylene tetranitroamine (gunpowder) ethyl or phenylnitroamine (Class 5 according to the number of other attached nitro groups).
C-NO	Nitroso compounds (C)	C <sub>6</sub> H <sub>5</sub> NO, CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NO, and C <sub>10</sub> H <sub>7</sub> NO (Classes 5 and 4 according to the number of other attached nitro and nitroso groups).
M-ONC	Fulminates (B)	Hg(ONC) <sub>2</sub> and AgNCO, which are used as triggers for other explosives.
N-N [Ar-N=N]+X	Diazonium salts (C)	C <sub>6</sub> H <sub>5</sub> N <sub>2</sub> X and HOC <sub>6</sub> H <sub>4</sub> N <sub>2</sub> X (normally handled below room temperature).
C-N <sub>2</sub>	Diazo compounds (A)	CH <sub>2</sub> N <sub>2</sub> (diazomethane; a toxic gas) liquid and concentrated solutions, which differ in safety outcomes depending on the type, such as N <sub>2</sub> C (COOH) <sub>2</sub> , N <sub>2</sub> C (COOH <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> , N <sub>2</sub> CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> , and N <sub>2</sub> CHCO <sub>2</sub> C <sub>6</sub> H <sub>5</sub> . C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> O (diazophenol; explodes when dry) Diazonitrophenol (explodes when ignited by electricity or blasting cap).

$MN_3$	Metal azides (B)	Heavy metal azides of Ag, Co, Pb, Hg, Cu, and Cd. Lead azide is used as a trigger for other explosives. Sodium azide was employed in early automobile air bags.
$XN_3$	Halogen azides (B)	Explodes at temperatures below room temperature when X is F, Cl, Br, and I.
$HN_3$	Hydrogen azides (B)	Unstable and explodes readily.
$-CN_3$	Organic azides (B)	Stability differs depending on substances, such as $CH_3N_3$ , $N_3CH_2COOH$ , $C_6H_5N_3$ , $CH_3C_6H_4N_3$ , and $C_{10}H_7N_3$ ; generally, decomposes when heated to room temperature or above (pay special attention to the decomposition point).
$\begin{array}{c} O \\    \\ C-C-N_3 \end{array}$	Organic acid azides (C)	Isocyanate raw materials such as $CH_3CON_3$ and $C_6H_5CON_3$ (Curtius rearrangement).
$MC\equiv CM$	Acetylides (A)	Heavy metal acetylides are unstable (such as silver and copper acetylide)
$\begin{array}{c} O-O \\   \\ H-O-O-R \end{array}$	Hydroperoxides (B)	Refer to Section 2, 1. (1) Oxidants. Isobutylhydroperoxide and cumene hydroperoxide.
$R-O-O-R$	Dialkylperoxides (C)	(Di)ethyl peroxide, (di)isobutyl peroxide, methyl ethyl ketone peroxide, and cyclohexanone peroxide.
$RCO-O-O-H$	Peroxyacids (C)	Peracetic acid, perpropionic acid, and perbenzoic acid.
$RCO-O-OR$	Peroxyacid esters (C)	Peracetic acid t-butyl, persebacic acid t-butyl, and perbenzoic acid t-butyl esters.
$\begin{array}{c} RCO-O-O- \\   \\ OCR \end{array}$	Diacylperoxides (C)	Acetyl peroxide, propionyl peroxide, and benzoyl peroxide.
$\begin{array}{c} O-O \\ / \quad \backslash \\ -C \quad C- \\ \backslash \quad / \\ O \end{array}$	Ozonides (B)	Oily substances that promptly decompose in reaction to ozone and unsaturated compounds.

NOTE: The following letters indicate the severity of hazardousness in the table:

A= Very hazardous; B= Somewhat hazardous; C = Hazardous.

Handling precautions:

- 1) When synthesizing the above-mentioned substances or similar substances, or using them as raw materials or polymerization inhibitors, experiments should be conducted after carefully examining

their properties. In addition, proper care should be exercised when byproducts as well as reaction liquid waste is likely, which should be treated as promptly as possible.

- 2) The above-mentioned substances frequently explode when they are heated or upon contact with acids, alkalis, metals, or reducing substances. Therefore, caution should be exercised, and the proper containers or spatulas should be utilized.
- 3) Explosions may result in the ignition of flammable substances in the vicinity and cause fire; thus, clean the surrounding area and prepare firefighting equipment accordingly.
- 4) Because the above-mentioned substances are highly toxic, protection strategies should be adopted.

Likely occurrences: (oxidants 2–4)

- 1) During the recovery of silver chloride (precipitate of ammonia solution) that has been left standing for an extended period, the dried filtrate is at risk of explosion owing to generation of silver azide.
- 2) An explosion may occur during the synthesis of azide acrylate using chloride acrylate and sodium azide ( $\text{NaN}_3$ ). After the removal of chlorine compounds from vinyl isocyanate following the Curtius rearrangement (similar boiling points of acid chloride and isocyanate), silver precipitate is added for distillation.
- 3) When the products of nitration reaction are distilled, an explosion may occur for a small amount of residual liquid, which is explosive in nature owing to high nitro compound content of the byproduct.
- 4) If a mixture of ethylene and alcohol with dilute nitric acid is left standing for a considerable period, the mixture may ignite (the water and alcohol will evaporate and esterize).
- 5) If the catalyst (metal acetylide) used in alkanol synthesis reaction via Reppe reaction is left standing, it will dry out and explode upon slight impact (i.e., it remains stable in damp conditions).

### (3) Flammable gas

Hydrogen, carbon monoxide (CO), ammonia gas ( $\text{NH}_3$ ), hydrogen sulfide ( $\text{H}_2\text{S}$ ), city gas, and household LPG (mixture of  $\text{C}_3$  and  $\text{C}_4$  hydrocarbons and hydrogen carbide).

Hydrogen carbides:	Methane ( $\text{CH}_4$ ), ethane ( $\text{C}_2\text{H}_6$ ), propane ( $\text{C}_3\text{H}_8$ ), butane ( $\text{C}_4\text{H}_{10}$ ), ethene (ethylene; $\text{C}_2\text{H}_4$ ), propylene ( $\text{C}_3\text{H}_6$ ), butene ( $\text{C}_4\text{H}_8$ ), acetylene ( $\text{C}_2\text{H}_2$ ), cyclopropane ( $\text{C}_3\text{H}_6$ ), and butadiene ( $\text{C}_4\text{H}_6$ )
Amines:	Methylamine ( $\text{CH}_3\text{NH}_2$ ), dimethylamine ( $(\text{CH}_3)_2\text{NH}$ ), trimethylamine ( $(\text{CH}_3)_3\text{N}$ ), and ethylamine ( $\text{C}_2\text{H}_5\text{NH}_2$ )
Alkyl halides:	Methyl chloride ( $\text{CH}_3\text{Cl}$ ), ethyl chloride ( $\text{C}_2\text{H}_5\text{Cl}$ ), vinyl chloride ( $\text{C}_2\text{H}_3\text{Cl}$ ), and methyl bromide ( $\text{CH}_3\text{Br}$ )



Handling precautions:

- 1) Leakage from equipment will accumulate, ignite, and explode when the concentrations cross the explosion limit. Take necessary precautions when using flammable gas cylinders and conducting experiments that generate flammable gas.
- 2) Strictly observe warnings on the handling of cylinders (refer to warning for high-pressure gas and liquefied gas in Chapter 4, Section 4) and regularly inspect the municipal piped-gas cocks.
- 3) Properly address any noticeable gas leaks in cylinder gaskets, pipes, or leaks in municipal gas lines. That is, wear face shields and gas masks as required when conducting experiments that are at risk of explosion or toxic gas generation. In case of a massive gas leak, turn off any flame or gas sources, open the windows for ventilation, and temporarily evacuate the structure. In case of rapid gas leaks (e.g., the safety valve on cylinder of hydrogen or other flammable gas has been blown off), immediately evacuate the building and assess the situation.
- 4) Because acetylene and ethylene oxide decompose explosively, do not heat or allow any impact on these substances in direct sunlight or within the vicinity of a heat source.

Likely occurrences:

- 1) Acetylene cylinders will explode if dropped during transport; all cylinders should be fitted with a safety cap during transport.
- 2) Generally, the mixed gas reaches its explosion limit in oxidation reactions and explodes owing to the rapid heat generation by the reaction; thus, protective walls or screens should be installed.

### **3 Flammable substances**

Combustibles are dangerous substances because they have vaguely described ignition points; the lower the ignition point, the greater is the hazard. The ignition point refers to the lowest temperature at which a liquid becomes a flammable concentrated vapor when its top layer mixes with air. Nevertheless, substances with a high ignition point are also dangerous when heated to temperatures above the ignition point; several accidents have been experienced in laboratories owing to such conditions.

When using flammable substances, ensure that the rooms are well-ventilated and exercise precautions concerning the exhaust. For example, considering that vapor is heavier than air, ventilation holes should be added at the floor level.

Table 5-11 Flammable substance classification

Classification		Definition	Fire Services Act class
Special flammable substances		Liquid at 20 °C or 20–40 °C with ignition temperature* 100 °C or less, ignition point -2 0°C or less, and boiling point 40 °C or less.	Special flammable substances.
Regular flammable substances	High flammability substances	Highly flammable at room temperature; ignition point of 20 °C or less (Fire Services Act Class 1 petroleum and Class 4 compounds exhibiting similar flammability).	Class 1 Petroleum and equivalent flammable substances.
	Moderate flammability substances	Highly flammable; ignition point of 21–70 °C (Fire Services Act Class 2 petroleum and Class 4 compounds with the same flammability).	Class 2 petroleum and equivalent flammable substances.
	Low flammability substances	Ignites when decomposition gases are strongly heated; general ignition point of 70 °C or higher, 70–200 °C for Class 3 petroleum, and 200 °C or higher for Class 4 petroleum. Includes Fire Services Act Class 4 compounds with similar flammability.	Classes 3 and 4 petroleum, animal, and vegetable oils.

NOTE) \*Known as the flash point; refers to the lowest temperature at which combustibles spontaneously ignite when heated in the air.

When storing flammable substances, sealed containers are critical for the prevention of gas or vapor leakage and protection from fire or sunlight.

Flammable substances are classified into four types on the basis of the definitions in Table 5-11, and any substance that is not a special flammable substance is referred to as a regular flammable substance.

(1) Special flammable substances

Diethyl ether, carbon disulfide, acetaldehyde, pentane, isopentane, propylene oxide, divinylether, and nickel carbonyl.

Handling precautions:

- 1) As these substances possess low ignition points and ignite with relative ease, extinguish any flames and turn off electric heaters and stoves in the vicinity of these substances.
- 2) Considering that these substances exhibit low boiling points and a wide explosion limit, ensure appropriate ventilation and prevent any accumulation of these substances.
- 3) Upon ignition, these substances spread explosively and are difficult to extinguish. Therefore, these substances should be stored away from other flammable substances.
- 4) Wear gas mask and rubber gloves when handling toxic and irritating substances and handle under proper ventilation.

Likely occurrences:

- 1) Special flammable substances have low ignition points; thus, they will ignite during handling if there is flame in the vicinity.
- 2) Ether readily transforms into peroxides and explodes if no residual liquid is formed after distillation.
- 3) When a flask filled with ether solution is placed in a refrigerator, the ether vapor generally leaks (the stored flasks often break); this vapor is ignited by the refrigerator switches and subsequently explodes; thus, utilize explosion-proof refrigerators.

(2) Regular flammable substances

a. Highly flammable substances (ignition point: 20 °C or less)

Hydrogen carbides: Hydrogen carbides possessing a carbon number of up to 8, such as petroleum ether, gasoline, petroleum benzene, ligroin, dimethylbutane, hexene, heptane, cyclopentane, methylcyclopentane, cyclohexane, cyclohexene, octane, benzene, toluene, and ethyl benzene (except special flammable substances).

Esters: Formic acid esters (up to butyl groups), acetate esters (up to propyl and including vinyl groups), methyl and ethyl propionate, methyl and ethyl acrylate and methacrylate, amyl nitrite, carbonic acid methyl, and boric acid methyl.

Alcohols: Up to propyl groups.

Ethers: Propylether, methylal, dioxane, furan, methylfuran, and tetrahydrofuran.

Aldehydes: Propionaldehyde, acrolein, crotonaldehyde, butylaldehyde, and paraaldehyde.

Ketones: Acetone, methyl ethyl ketone, methylvinylketone, and methylpropylketone.

Amines: Diethyl amine, triethylamine, propylamine, arylamine, butylamine, amylamine, pyridine, piperidine, and methylmorpholine.

Halides: Aryl chloride, aryl bromide, butyl chloride, butyl bromide, amyl chloride, vinylidene chloride, dichloroethane, chloropropane, dichloropropane, and chloro benzene.

Acid chlorides: Acetyl chloride and propionyl chloride.

Mercaptans: Ethylmercaptan, butylmercaptan, thiophene, and tetrahydrothiophene.

b. Moderately flammable substances (ignition point: 21–70 °C)

Hydrocarbons:	Kerosene, light oil, turpentine oil, cumene, cymene, decane, dicyclopentadiene, dipentene, styrene, methylstyrene, propyl benzene, and diethyl benzene.
Esters:	Butyl acetate, amyl acetate, butyl propionate, ethyl crotonate, ethyl acetate, methyl chloroacetate, ethyl bromoacetate, methyl lactate, ethyl lactate, and diethyl carbonate.
Alcohols:	Butanol, amyl alcohol, hexyl alcohol, methacryl alcohol, cyclohexanol, cellosolve, and diacetone alcohol.
Ethers:	Butylether, amylether, and anisole.
Aldehydes:	Furfural and benzaldehyde.
Ketones:	Methylbutylketone, methylamylketone, diethyl ketone, and dipropylketone.
Amines:	Hexylamine, cyclohexylamine, tripropylamine, ethylenediamine, propylenediamine, diethyl ethylenediamine, picoline, methylpicoline, and hydrazone.
Halides:	chlorobenzene, bromobenzene, chlorophenol, epichlorohydrin, ethylenechlorohydrin, and propylenechlorohydrin.
Nitrides:	Nitroethane, nitromethane, and nitropropane.

c. Low flammability substances (ignition point: 70 °C and above)

Hydrocarbons:	Lubricants, such as fuel oil, creosote oil, spindle oil, gear oil, and motor oil; high-grade liquid hydrogen carbide, such as transformer oil and tetralin.
Esters:	Octyl acetate, phenyl acetate, methyl and ethyl benzoate, ethyl oxalate, ethyl maleate, butyl phthalate, and octyl phthalate.
Alcohols:	Octanol, benzyl alcohol, aldol, furfuryl alcohol, tetrahydrofurfuryl alcohol, ethyleneglycol, diethyleneglycol, propyleneglycol, glycerine, and ethylene cyanohydrin.
Ethers:	Diethylene glycol dimethyl and ethyl ether.
Amines:	Tributylamine, ethanolamine, aniline, <i>N</i> -mono and disubstituted aniline, toluidine, and phenylhydrazine.
Chlorides:	Benzyl chloride.
Carbonic acids:	Acetate and anhydrous propionic acid.
Acid chlorides:	Benzoyl chloride.
Nitrides:	Liquid monosubstitution of nitrobenzene and nitroxyleno.

Other:  $\gamma$ -butyrolactone, styrene oxide and dimethylsulfoxide.

Animal and vegetable oils: Soybean oil, sesame oil, coconut oil, sardine oil, flaxseed oil, and whale oil.

Handling precautions:

- 1) High flammability substances are not as flammable as special flammable substances; nevertheless, these substances are still highly flammable and are easily ignited by sparks from switches or static electricity as well as red-hot materials, such as electric heaters or burning cigarettes. Thus, fire in the vicinity should be avoided, and these substances should never be heated with a direct flame.
- 2) Acetone, petroleum ether, hexane, benzene, methanol, ethanol, ethyl acetate, and tetrahydrofuran are often used as solvents. As these chemicals possess a high vapor pressure and are highly flammable, they should be handled with necessary caution.
- 3) High flammability substances have considerably high vapor pressure and vapor density and consequently accumulate with great ease; hence, appropriate ventilation should be maintained.
- 4) Moderately flammable substances are easily ignited when heated; therefore, appropriate care should be ensured to contain the vapor when heated in open containers.

Likely occurrences:

- 1) These substances boil explosively and ignite owing to heating and the inadvertent addition of zeolite during distillation; this is a frequent occurrence in laboratories, and the zeolite should be added after refrigeration.
- 2) When flasks are rinsed with acetone and then placed in a dryer for drying, acetone in the flask will vaporize and may explode.

(3) Organic solvents

Organic solvents are frequently used in laboratories in large quantities. Because these substances can be either special flammable substances or high flammability substances, their management and storage is governed by the Fire Services Act and fire prevention ordinances. In addition, necessary precautions should be exercised while handling these substances to prevent organic solvent poisoning and maintain hygienic conditions.

Handling precautions:

- 1) The substance amounts that can be stored at each laboratory are governed by the Fire Services Act and fire prevention ordinances; therefore, the minimum amounts needed are stored within laboratories. When purchased in petroleum barrels, these substances should always be stored in a hazardous material warehouse, and the required amounts should be transported to laboratories only when these substances are needed.

- 2) Special flammable substances and high flammability substances, which exhibit high evaporation points and low ignition points, are handled by strict observing the relevant warnings concerning potential accidents.
- 3) As these substances are critically tied to the biological and chemical oxygen demand in water bodies, which are matters of concern for the local regulation of water and prevention of its pollution, the liquid waste should be treated in accordance with the rules and instructions specified by the university.
- 4) In terms of hygiene, although acute toxicity is not necessarily strong enough to create a negative impact in terms of hygiene, in terms of chronic toxicity, these substances should be handled carefully (refer to Section 4, 1.5).

#### 4 Acids

These substances consist of inorganic strong acids (sulfuric acid, hydrochloric acid, nitric acid, and hydrofluoric acid), organic strong acids (trichloroacetic acid, trifluoroacetic acid, sulfonic acid, and picric acid), and weak acids (phosphoric acid, boric acid, and organic carboxylic acid).

Fuming nitric acid (concentrated nitric acid containing  $\text{NO}_2$ ): Exhibits considerably strong oxidizability and ignites and oxidizes phosphine ( $\text{PH}_3$ ), hydrogen sulfide ( $\text{H}_2\text{S}$ ), and hydrogen iodide ( $\text{HI}$ ).

An oxidant and nitrating agent. The nitrogen dioxide ( $\text{NO}_2$ ) gas generated is extremely toxic.

Fuming sulfuric acid ( $\text{SO}_3\text{-H}_2\text{SO}_4$ ): Reacts violently with water to yield sulfuric acid (accompanied by significant heat generation). Acts as a strong oxidant, sulfonating agent, and skin irritant.

Chlorosulfonic acid ( $\text{HSO}_3\text{Cl}$ ): A sulfonating agent, which reacts violently with water to generate sulfuric acid and hydrochloric acid and irritates the skin.

Anhydrous sulfuric acid (sulfur trioxide;  $\text{SO}_3$ ): Reacts violently with water to yield sulfuric acid (accompanied by significant heat generation). Acts as a strong oxidant, sulfonating agent, and skin irritant.

Concentrated nitric acid (commercially available;  $\text{HNO}_3$  content of 62–70%): Exhibits strong oxidizability. Used to manufacture nitric acid salts and as a nitrating agent. Harms the trachea when inhaled, resulting in pneumonia-like symptoms. Additionally, this substance harms the skin mucous membrane.

Concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ): Exhibits an extremely high heat of dilution; when water is added to concentrated sulfuric acid, it generates heat and explodes. In addition, it reacts with charcoal to produce  $\text{CO}_2$ , acts as a dehydrating agent, and exhibits oxidation action at high temperatures. It is used to manufacture sulfuric acid salts and sulfonic acid and harms the skin.

Anhydrous chromic acid (chromium trioxide:  $\text{CrO}_3$ ): Dissolves in water to yield chromic acid. A Strong oxidant, which exhibits severe toxicity and irritates the kidneys.

Perchlorate ( $\text{HClO}_4$ ): A fuming liquid (anhydride). It is unstable and decomposes when left to stand; explodes when heated. Exhibits strong oxidizability. In addition to monohydrate, dihydrate and trihydrate forms exist, but the commercially available product is a 60% or 70% aqueous solution.

Thionyl chloride ( $\text{SOCl}_2$ ): Reacts with water to produce sulfurous acid gas (sulfur dioxide;  $\text{SO}_2$ ) and hydrogen chloride ( $\text{HCl}$ ). It is used in the manufacture of acid chloride from carboxylic acid and sulfonic acid.

Sulfuryl chloride ( $\text{SO}_2\text{Cl}_2$ ): Decomposes into sulfuric acid and hydrochloric acid after reacting with water.

Handling precautions:

- 1) When the above-mentioned substances are mixed with the chemicals specified in the Fire Services Act hazardous material Classes 1–5 chemicals, these acids oxidize, dehydrate, and react, and the reaction generates heat, ignition, explosions, product decomposition, and explosions, thus igniting and exploding the generated gas.
- 2) Use special fire retardants and not water to extinguish fire in places where the above-mentioned acids are stored.
- 3) Accidents in laboratories and research centers involving the above-mentioned acids often result in chemical burns to the skin, mouth, and eyes. These are described in detail along with the relevant measures in Section 3 concerning acids and alkalis.

## 5 Mixed hazardous materials

In general, when two or more substances are mixed together, rapid boiling, scattering, ignition, or explosions may occur owing to the heat generated by the heat of mixing or chemical reaction from diffusion or dissolution. These substances are referred to as mixed hazardous materials. Physical examples include the addition of water to concentrated sulfuric acid, addition of small amounts of water to large amounts of solid caustic soda, and mixing of high-temperature liquids and low-boiling point substances. When classifying On the basis of cause of ignition or explosion, these materials are classified into ① those materials that burn or explode when heat is generated via rapid decomposition or reactions, ② those materials that generate explosive compounds, and ③ those materials that decompose and explode when mixed with air or oxygen. The combination examples listed in Table 5-12 represent mixed hazardous materials. Table 5-13 presents the mixing risks according to the Fire Services Act. Table 5-13 should be referenced for the storage or transportation of chemicals, liquid waste collection from the laboratory, or solid waste accumulation.

Table 5-12 Chemical combinations with explosion hazard when mixed (A+B)

Chemicals A	Chemicals B	Chemicals A	Chemicals B
Alkali metals, powdered aluminum, or magnesium.	Carbon tetrachloride, carbon disulfide, and halogen (reaction).	Iodine (violent heat generation and product decomposition).	Acetylene, ammonia (in solution or anhydrous form), and hydrogen.
Potassium, sodium (reaction).	Carbon tetrachloride, carbon dioxide, and water.	Fluorine (same as above, especially large heat generation owing to large binding energy).	Significantly high reactivity to all compounds.
Copper (acetylide generation and decomposition reaction).	Acetylene and hydrogen peroxide.		
Silver (acetylide generation and decomposition reaction and silver fulminate and silver azide generation).	Acetylene, oxalic acid, tartaric acid, fulminic acid, and ammonium compounds.	Hydrogen peroxide (rapid decomposition reaction).	Copper, chrome, iron, or salts thereof, alcohol, acetone, organic substances, aniline, flammable material, flammable liquid, and nitromethane.
Mercury (acetylide, fulminic acid mercury and azide generation).	Acetylene, fulminic acid, and ammonia.	Ammonia (anhydrous) (mercury and silver generation, violent heat generation reaction, and product decomposition).	Mercury (e.g., monometer mercury) chlorine, calcium hypochlorite, iodine, bromine, anhydrous hydrofluoric acid, and silver compounds.
Chlorine (violent heat generation reaction and product decomposition).	Ammonia, acetylene, butadiene, butane, methane, propane (other petroleum gas), hydrogen, sodium, carbide, turpentine oil, benzene, and finely powdered metals.	Chromic acid (oxidation reaction and oxygen generation).	Acetate, naphthalene, camphor, glycerine, turpentine oil, alcohols, and common oxidizers.
		Potassium permanganate (rapid oxidation reaction).	Ethanol or methanol, glacial acetic acid, anhydrous acetate, benzaldehyde, carbon disulfide, glycerine, ethylene, glycol, ethyl acetate, methyl acetate, and furfural.
Anhydrous hydrofluoric acid (violent heat generation reaction)	Ammonia (water-containing or anhydrous form).		



Nitric acid (concentrated) (oxidation reaction, heat generation)	Acetate, aniline, chromic acid, cyanide acid, hydrogen sulfide, flammable liquid, flammable gas		
Sulfuric acid (free of chloric acid; permanganic acid generation and decomposition and oxidation reaction thereof).	Potassium chlorate, potassium perchlorate, potassium permanganate, or permanganic acid salts of light metals such as sodium, potassium, or lithium.	Hydrogen carbides such as butane, propane, benzene, gasoline, and turpentine oil.	Fluorine, bromine, chromic acid, and sodium peroxide (violent heat generation reaction, oxidation reaction and peroxide generation).
		Acetylene (violent heat generation reaction, product decomposition and acetylide generation)	Chlorine, bromine, copper, fluorine, silver, mercury.
Chlorine dioxide (violent heat generation reaction and product decomposition).	Ammonia, methane, phosphine, and hydrogen sulfide.	Aniline (oxidation reaction).	Nitric acid and hydrogen peroxide.
Chlorates (explosives mixed in gunpowder or its high-explosive equivalent)	Ammonium salts, acids, metal powder, sulfur, finely powdered general organic substances, or flammable substances.	Oxalic acid (rapid decomposition).	Silver and mercury.
		Cumene hydroperoxide (rapid decomposition).	Oxygen (organic or inorganic).
Potassium permanganate (rapid oxidation reaction).	Anhydrous acetate, bismuth and alloys thereof, alcohol, paper, and wood.	Flammable liquid (oxidation reaction, peroxide generation, and rapid reaction).	Ammonium nitrate, hydrogen peroxide, nitric acid, sodium peroxide, and halogen.

NOTE: () in table indicates cause.

Table 5-13 Mixing risks according to the Fire Services Act

	I	II	III	IV	V	VI
Class 1 Hazardous materials (I oxidizing solid)		×	×	×	×	○ <sup>b</sup>
Class 2 Hazardous materials (II flammable solid)	×		×	○	○ <sup>a</sup>	×
Class 3 Hazardous materials (III spontaneous combustible • water-prohibitive substance)	×	×		○ <sup>b</sup>	×	×
Class 4 Hazardous materials (IV flammable liquid)	×	○	○ <sup>b</sup>		○ <sup>b</sup>	×
Class 5 Hazardous materials (V self-reactive substances)	×	○	×	○ <sup>b</sup>		×
Class 6 Hazardous materials (VI liquid oxide)	○ <sup>b</sup>	×	×	×	×	

NOTE: × is mixing prohibited. ○ is mixable.

○ is mixable, but

a: Mixing risk should be considered.

b: Mixing risk should be considered depending on the situation.

#### Mixture precautions:

- 1) Do not inadvertently mix inorganic and organic compounds. In addition, when mixing, always be careful with chemical combinations that represent explosion hazards.
- 2) Spontaneous pyrophoric substances, oxidizers, and water-prohibitive substances should never be inadvertently mixed with other substances.
- 3) When Fire Services Act Class 6 strong acids are mixed together with Classes 1, 2, 3, and 5 chemicals, extreme caution should be exercised owing to the heat of neutralization and generation of hydrogen halides.
- 4) Phosphorus trichloride (PCl<sub>3</sub>), phosphorus pentachloride (PCl<sub>5</sub>), thionyl chloride (SOCl<sub>2</sub>), titanium chloride (IV) (TiCl<sub>4</sub>), silicon tetrachloride (SiCl<sub>4</sub>), and acid chloride (RCOCl) (similar outcomes with Br and I as that of Cl), which are not classified as water-prohibitive substances under the Fire Services Act, react violently with water, alcohol, and amines and generate hydrogen halides; therefore, necessary caution should be taken when handling these substances.
- 5) Fire Services Act Class 4 compounds include liquid compounds that exhibit various properties (e.g., amines, carboxylic acid, and acid chloride), and thus require careful handling; only those substances that do not react or neutralize should be mixed.
- 6) The risks associated with mixing these compounds are significant and require attention; as the reactions are not always fast, fire or explosions may occur even when the liquid laboratory waste is stored separately, during its transit to a temporary storage facility, or during storage. In addition, these compounds may cause fire or explosion in solid waste storage locations. Precautions should be taken for the collection, storage, and preservation of waste and liquids used in experiments.

## Section 3 Acids and alkalis

Acids and alkalis are typically used in laboratories. These chemicals range widely from inorganic and organic strong acids and strong alkalis to weak acids and weak alkalis. The chemical types that tend to result in accidents have been described in this section.

### 1 Acids

Sulfuric, hydrochloric, nitric, and hydrofluoric acids are inorganic strong acids, whereas trichloroacetic, trifluoroacetic, sulfonic, and picric acids are organic strong acids. Additionally, phosphoric, boric, and carbonic acids are inorganic weak acids, and various organic carboxylic acids are organic weak acids.

The acids with a high risk of associated accidents in laboratories are inorganic acids, such as sulfuric, hydrochloric, and nitric acids with a high concentration and hydrofluoric acids, which exhibit special action. Handling precautions:

- 1) Sulfuric acid (fuming sulfuric and concentrated sulfuric acids, hereinafter referred to as sulfuric acid), nitric acid (fuming nitric and concentrated nitric acids, hereinafter referred to as nitric acid), and concentrated hydrochloric acid are strongly acidic mineral acids, which may cause chemical burns or vision loss upon contact with the skin or eyes. In addition, contact with an explosively decomposing substance may result in an explosion or ignition.
- 2) Sulfuric, hydrochloric, nitric, hydrofluoric, chlorosulfuric, trichloroacetic, and trifluoroacetic acids are highly corrosive substances and should be immediately rinsed off upon contact with the skin. Hydrofluoric acid is particularly dangerous in this regard; thus, rubber gloves should be worn when handling this acid.
- 3) As nitric, hydrochloric, anhydrous, and fuming sulfuric, and hydrofluoric acids release toxic gas, proper care should be exercised to avoid inhalation or contact with the skin. Because hydrofluoric acid, in particular, can cause respiratory disorders or injure the eyes, a gas mask should be worn when handling this acid.
- 4) Nitric acid oxidizes and sulfuric acid dehydrates; these acids generate a large amount of heat during their respective processes, thus generating heat or undergoing ignition when mixed with organic substances.
- 5) Sulfuric acid generates considerable heat upon dilution, and other acids also exhibit a large heat of neutralization when neutralized with concentrated alkali. Refer to the section concerning the handling of sulfuric acid. For the other acids, neutralize the individual dilute solutions, and add other concentrated solutions to dilute the solution in small amounts while mixing thoroughly.

#### (1) Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, including anhydrous sulfuric and fuming sulfuric acids)

##### a. Hazards

Sulfuric acid does not self-explode or self-ignite; nevertheless, note the properties described in the

segment labeled "Handling precautions" in entries 1), 2), and 5).

b. Corrosive and physiological effects

Sulfuric acid reacts with various metals, often generates hydrogen gas, and dehydrates organic substances; occasionally, the generated heat may result in ignition. Biocorrosion reactions to concentrated sulfuric acid and hot sulfuric acid include severe tissue damage, chemical burns, and vision loss upon contact with the eyes. Inhalation of large quantities of the vapor from heated sulfuric acid or fuming sulfuric acid causes damage to lung tissue.

c. Precautions for use

- 1) May ignite or explode when in contact or mixed with oxidants, explosively decomposing substances, metal powders, or organic substances; thus, handle this acid at a safe distance from these triggering substances.
- 2) As sulphuric acid may cause chemical burns, avoid contact with any part of the body.
- 3) Sulphuric acid possesses a large specific gravity. Thus, when this acid is placed in a large glass beaker, the beaker may break if it is held from the top or edges and should be supported from the bottom with both hands to avoid breakage.
- 4) When diluting anhydrous sulfuric acid ( $\text{SO}_3$ ) or fuming sulfuric acid, utilize sulfuric acid that is as concentrated as possible.
- 5) Rinse out empty bottles after use and store them in a designated place.

d. Measures for spillage

Sulphuric acid corrodes concrete floors and metals and carbonizes organic substances. Any spilled acid that is flowing should be rinsed and diluted with large quantities of water. Subsequently, wipe off the diluted acid while wearing rubber gloves. Alternatively, dilute the acid with water, neutralize it with baking soda or lime, and subsequently wipe it off the surface.

- e. When concentrated sulfuric acid clings to clothes, immediately rinse with large quantities of water, neutralize the acid with diluted ammonia water or 1–2% baking soda (or sodium carbonate), and thoroughly rinse with water. As dilute sulfuric acid will concentrate over time and damage the fabric, wash the clothes with neutralizing water.

Likely occurrences:

- 1) Inhalation of dilute sulfuric acid into the mouth may occur with relative ease when drawing from a pipette.
- 2) During the preparation of dilute sulfuric acid, the addition of water to concentrated sulfuric acid may generate heat and cause the acid to splash into the eyes. Moreover, rapid heating will break the beaker, resulting in the spillage of sulfuric acid.
- 3) During measurements for the melting point of an organic substance, the measuring tube containing hot concentrated sulfuric acid may break, and the resultant spill may burn the hands or face.
- 4) If rags soaked in concentrated sulfuric acid are disposed of with rags soaked in waste oil, ignition of this acid may occur.

(2) Hydrochloric acid (HCl, commercial concentrations ranging from 35% to 38%)

a. Hazards

Hydrochloric acid presents minimal hazard; nevertheless, note the properties listed in the segment labeled “Handling precautions” in entries 2) and 3). In other words, hydrochloric acid reacts with various metals and generates hydrogen.

b. Corrosive and physiological effects

Hydrochloric acid is damaging to most metals, but not to plastics. Compared to sulfuric acid, contact with the skin and mucous membranes causes less inflammation. The greater risk is posed by the inhalation of HCl gas or mist generated by hydrochloric acid. For hydrochloric acid gas, the tolerance concentration is 5 ppm.

c. Precautions for use

Because the internal pressure of capped bottles is considerably high, resulting in the contents to spray outward, these bottles should be opened with the bottle opening facing away from users and at a safe distance from their faces. Note that hydrochloric acid is highly corrosive, and hydrogen chloride gas and mist are toxic.

d. Measures for leakage

Although their chemical reactivities differ moderately, the measures involved are identical to those for sulfuric acid.

e. When it clings to clothes

Observe the measures stated for sulfuric acid.

Likely occurrences:

When a new bottle of hydrochloric acid is opened during summer, gas may spray out forcefully owing to the high internal pressure and cover the body.

(3) Nitric acid (HNO<sub>3</sub>, including fuming nitric acid)

a. Hazards

Nitric acid alone is not explosive and does not burn or spontaneously ignite; however, unlike sulfuric or hydrochloric acid, it is an oxidizing acid. In addition to the properties listed in “Handling precautions” in entries 1), 2), 3), and 4), its oxidation reaction to hydrogen sulfide, carbon disulfide, acetylene, hydrazines, or amines is violent and may ignite or explode if mixed. In addition, contact with many organic substances, including alcohols, glycols, glycerines, oxygen or sulfur-containing compounds, wood fragments, paper, paper scraps, or rags generates ester bonds or unstable compounds and may result in explosion or spontaneous ignition. In addition, nitric acid reacts with most metals.

b. Corrosive and physiological effects

Nitric acid is corrosive and exhibits oxidation action. It irritates the skin and mucous membranes upon contact, leaving chemical burns of yellowish-brown color, and it may cause damage or vision

loss upon contact with the eyes. Owing to its high acidity, oral consumption will result in corrosion of the stomach tissue. Concentrated nitric and fuming nitric acids generate nitrogen oxide gas and damage the respiratory organs upon inhalation. The tolerable concentration for nitric acid is 10 ppm.

c. Nitrogen oxide gas damage

Nitrogen dioxide ( $\text{NO}_2$ ; reddish-brown color) and dinitrogen trioxide ( $\text{N}_2\text{O}_3$ ; dark blue color) are highly toxic compounds. Upon inhalation of 5 ppm of gas for 8 h, symptoms of pulmonary edema will inevitably appear within the following 5–48 h. Concentrations of 500–1000 ppm will have fatal consequences if the gas is inhaled all at once within a short time.

d. Precautions for use

Nitric acid is a Fire Services Act Class 6 hazardous material. It generates toxic  $\text{NO}_x$  gas and exhibits oxidizing properties; therefore, entries 1), 2), and 5) in the precautions listed for the usage of sulfuric acid and those for the usage of hydrochloric acid should be considered.

e. Measures for spillage

Although the chemical reactivity of nitric acid differs moderately from that of sulfuric and hydrochloric acid, measures involved for spillage of nitric acid are similar to those for these other acids; hence, the initial dilution of the acid with water is essential. In particular, nitrogen oxide is harmful and should never be inhaled. Upon immediate neutralization with soda ash or lime, a large quantity of nitrogen oxide gas is generated owing to the heat of neutralization.

f. When it clings to clothes

In a manner similar to that for the removal of sulfuric and hydrochloric acids clinging to clothes, immediately rinse with large quantities of water, and neutralize with 2% sodium carbonate water (or sodium carbonate water solution) or lime. After neutralization, thoroughly rinse further with water. Cotton and rayons, in particular, will generate nitrocellulose upon contact with concentrated nitric acid and thus are at risk of burning. Therefore, these fabrics should not be left untreated.

g. Hygiene precautions

Sites wherein nitrogen oxide gas is generated should be well ventilated. If any gas is generated, immediately vacate the room, and do not enter until the gas has fully dissipated.

Likely occurrences:

Inadvertent spillage of concentrated nitric acid will result in yellowing of the skin followed by burning.

(4) Hydrofluoric acid (HF, regular commercial concentration ranging from 40% to 50%)

Precautions: Because certain glass marking, patterning, matting, and metal surface treatment agents contain hydrofluoric acid, the presence of hydrogen fluoride in these agents should be determined before handling them.

a. Hazards and toxicity

Hydrofluoric acid can dissolve most metals except for gold and platinum (lead is used for

containers or linings because fluorides are poorly soluble in water). It corrodes silicates such as silicon dioxide, pottery, porcelain, and glass and produces volatile silicon tetrafluoride.

b. Corrosive and physiological effects

Hydrofluoric acid is employed for etching metals, silicate, enamel, and galvanized iron. Owing to its powerful action, contact with this acid will result in harsh effects on the human body. Contact with the skin causes harsh irritation and chemical burn as well as tissue penetration of tissue, the effects of which are much worse compared to the other acids. The tolerable concentration for hydrofluoric acid is 3 ppm. Upon contact with the eyes, it causes intense pain in the eyes and eyelids, resulting in long-term or permanently impaired vision or complete loss of vision. When it enters the respiratory organs, this acid causes harsh inflammation or hyperemia in the airway or lungs, which in serious cases leads to death. Upon ingestion, this acid causes gangrene in the esophagus and stomach, vomiting, diarrhea, and disruption of the circulatory system, ultimately leading to death.

c. Protection and prevention

Hydrofluoric acid is highly toxic and has a harsh corrosive effect on living bodies. Consequently, rubber gloves should always be used when handling this acid, and the use of protective masks is also recommended. In addition, to avoid any contact with its vapor mist, handle this acid under appropriate ventilation. Alkaline rinsing of the exhaust gas should be performed, and the hydrogen fluoride gas should never be directly released into the atmosphere. In addition, because the contact of this acid with silicate generates strongly toxic hydrogen silicofluoride gas, necessary caution should be exercised while analyzing the glass etching and silicate.

d. Measure for spillage

Hydrofluoric acid is toxic, and its physiological effects are severe. Thus, complete precautions should be taken when a spillage occurs on the floor or in other areas. Dilute the spilled acid with water, and add carbonic acid soda or a solution thereof in small drops to neutralize it into sodium fluoride (NaF), which does not exhibit corrosive action. Furthermore, as hydrofluoric acid reacts with glass and similar substances to generate hydrogen silicofluoride gas, so precautions should be taken.

e. When it clings to clothes

Immediately remove the clothes, and rinse them with large quantities of water. Thereafter, neutralize them with 2% sodium bicarbonate (sodium bicarbonate aqueous solution); after neutralization, thoroughly rinse further with water.

## 2 Alkalis

Strong alkaline sodium hydroxide (caustic soda), potassium hydroxide (caustic potash), and weak alkaline aqueous ammonia are frequently used in research centers and cause accidents.

Handling precautions:

- 1) Concentrated and hot sodium hydroxide solution is an extremely corrosive chemical, and it particularly decomposes proteins and can penetrate deep into tissue. Therefore, avoid any alkali contact with the skin and clothes.
- 2) Concentrated or hot ammonia water exhibits irritating action, which is weaker than that of sodium hydroxide. Nevertheless, it should be handled cautiously because it generates toxic ammonia gas; the tolerable concentration is 100 ppm.

(1) Sodium hydroxide (caustic soda; NaOH) and potassium hydroxide (caustic potash; KOH)

a. Corrosive and physiological effects

Their aqueous solutions can harshly corrode various metals and generate hydrogen. They penetrate bodies, decompose proteins, and ultimately destroy the tissue. Their corrosive action is particularly pronounced in a molten state. Upon contact of their aqueous solutions with the eyes, vision will decrease or vision loss will occur. Upon ingestion, they cause inflammation of the esophagus and gastric wall and occasionally cause gastric perforations, which may lead to death.

b. Precautions when melting

Melting of solid sodium hydroxide should be carefully conducted; because of the considerable heat generated, its temperature may rise considerably above the boiling point, which may cause it to splash and scatter. To avoid such a mishap, melt the sodium hydroxide while mixing in small quantities of water.

c. Measures for spillage

Rise with water. After the spilled alkali has been diluted, neutralize it with dilute acetic acid, and wipe it off the surface.

d. When it clings to clothes

Immediately rinse the clothes with large quantities of water. Subsequently, neutralize them with dilute acetic acid (2%), and rinse them further with water. Animal fibers such as wool and silk are more prone to corrosion from these alkalis than plant fibers.

(2) Ammonia water (NH<sub>3</sub> aq, aqueous solution with a regular commercial concentration from 25% to 28%)

a. Corrosive and physiological effects

Ammonia water corrodes copper, copper alloys, and aluminum alloys. Ammonia water demonstrates localized irritating action upon contact with the body, but it poses no particular problems unless it gets into the eyes or is ingested. Precautions must be taken to avoid inhalation of the generated ammonia gas; the tolerable concentration is 100 ppm.

b. Precautions for use

Sealed bottles should be uncapped carefully; the internal pressure of the container rises for high ambient temperatures, resulting in the contents to spray out. Thus, while uncapping the containers,



avoid positioning the case right above the cap, and open with the bottle opening facing away from the user.

c. When it spills and clings to clothes

Rinsing with a large quantity of water will remove the ammonia sufficiently.

Likely occurrences:

- 1) When the bottle is opened during summertime, the contents may spray out and cause difficulty in breathing if the spray is received directly upon the face.
- 2) Incomplete closing of the valve of an ammonia cylinder may result in gas leakage, which will necessitate evacuation of the premises.
- 3) The welds of a handmade container wrapped in cloth and filled with ammonia gas may rupture during transport, resulting in ammonia leakage, which causes frostbite and respiratory disorders.
- 4) Direct inhalation of the reaction products of dissolved unreacted ammonia may cause fainting.

## Section 4 Toxic and harmful chemicals

Generally, chemicals used in laboratories and research centers are toxic and harmful in nature. These chemicals include deadly poisons, such as cyanide compounds and toxic gas, and widely used chemicals such as benzene and toluene. Although these chemicals may not exhibit considerably acute toxicity, they should be handled carefully considering their chronic toxicity. First, the chemicals used in experiments and generated by reactions should be thoroughly studied in terms of their toxicity, potential for harm, strength, and tolerable concentrations. For toxic or harmful chemicals, their invasive oral or dermal toxicity should be identified. In addition, highly toxic chemicals should be investigated to ascertain alternative methods that do not involve their usage. In cases where their usage cannot be avoided, experimental methods should be determined to minimize their quantities.

Proper caution should be exercised in activities concerning toxic or harmful chemicals; the supervising instructors and bystanders are to be fully briefed, and any accidents should be addressed completely. In particular, improper handling will cause harm not only to the user but also to the bystanders. Additionally, thorough detoxification of the generated exhaust and waste should be incorporated into experimental protocols.

The usage of toxic chemicals is a matter of concern; any misuse, including improper handling and improper management of these substances, may have severe repercussions and even result in loss of life. Consequently, **prevention of theft or loss and proper storage and management of toxic chemicals are essential to the safe usage of these chemicals.** As detailed in part 2 of this section, methods for the storage and management of poisonous and deleterious substances are set forth by law. For safe usage, this institution has enacted the rules for the management of poisonous and deleterious substances specified by Nagaoka University of Technology. Toxic chemicals are to be stored and managed in accordance with these laws and rules.

The hazardous substance classifications (refer to part 2 of this section for further information on poisonous substances and deleterious substances as set forth by law) and the potential for physical harm of toxic chemicals are listed in Tables 5-14 and 5-15, respectively.

Table 5-14 Hazardous substance classifications

Classification	Characteristics	Typical substances
Toxic gas	Gas with tolerable concentration * of 200 mg/m <sup>3</sup> or less.	Arsenic, fluorine, phosgene, and hydrogen cyanide.
Poisonous substances	Lethal oral dose of 30 mg or less for 1 kg of body weight.	Arsenous acid, potassium cyanide, yellow phosphorus, nickel carbonyl, and tetraalkyl lead (specified toxic substance).
Deleterious substances	Lethal oral dose of 30–300 mg for 1 kg of body weight.	Nitric acid aniline, chloropicrin, dimethyl sulfate, and methanol.

NOTE 1) Indicated in terms of the lethal oral dose or minimum lethal dose injected subcutaneously in the case of poisonous and deleterious drugs (specified drugs: those identified by laws concerning the quality, efficacy, and safety of drugs and medical devices; other drugs and quasi-drugs: as set forth in the Poisonous and Deleterious Substances Control Act) and with reference to the tolerable concentration or lethal concentration time for toxic gases, vapors, fumes, or dust.

2) \* The minimum concentration that triggers acute or chronic symptoms, which appear after a normal workday; it may not necessarily be proportional to the hourly lethal concentration exposure.

Table 5-15 Physical harm from hazardous substances

Type	Typical substances
a Skin disorders	Skin cornification: Arsenic, cobalt, and dilute alkali solutions. Skin discoloration: Picric acid, silver nitrate, and iodine. Dyschromatosis: Tar, pitch, and arsenic. Acute dermatitis and eczema: Acids, alkalis, chlorodinitrobenzene, formalin, tar, and pitch. Ulcers: Chromium, nickel, acids, and alkalis. Hair and sebaceous glands lesions: Mineral oil, tar, and chloronaphthalene. Hair lesions: Thallium, manganese, etc. Nail plate and peripheral lesions: Selenium, thallium, and fluorine.
b Mucous membrane disorders	Mainly affects the upper respiratory tract: Aldehyde, alkali dust and mist, ammonia, chromic acid, ethylene oxide, hydrogen chloride, hydrogen fluoride, zinc sulfate gas, and anhydrous sulfuric acid. Affects the upper respiratory tract and lung tissue: Bromine, chlorine, chlorine oxide, cyanogen bromide, cyanogen chloride, dimethyl sulfate, fluorine, and iodine. Affects the end airway and alveoli: Arsenic trichloride, nitrogen peroxide, and phosgene.
c Asphyxia	Simple asphyxia: Carbonic acid gas, ethane, helium, hydrogen, methane, nitrogen, and nitrous oxide. Chemical asphyxia: Carbon monoxide, cyanide, hydrogen cyanide, nitril, aromatic nitro compounds (e.g., nitrobenzene and dinitrobenzene), aromatic amines compounds (e.g., aniline and methylaniline), and hydrogen sulfide.
d Anesthesia	Several organic solvents and fat-soluble solids demonstrate anesthetic action, but differ in the degree of action.
e Neurological disorders	Carbon dioxide, halogenated hydrocarbons, methanol, thiophene, tetraethyl lead, manganese, and mercury.
f Hepatic and renal disorders	Carbon tetrachloride, ethane tetrachloride, hexachloronaphthalene, trinitrotoluene, and dioxane. Uranium and cadmium affect the kidneys in particular.
g Hematological disorders	Benzene, lead, radioactive substances, phosphine, and arsenic.
h Hard tissue disorders	Acid mist, yellow phosphorus, and fluorine.
i Pulmonary disorders	Alveoli irritants (pulmonary edema and pneumonia), slightly soluble dust (pneumoconiosis), free silicic acid (silicosis), asbestos (asbestosis), talc (talcosis), agalmatolite (pyrophyllitosis), aluminum (aluminosis pulmonum), coal powder (anthracosis), graphite (graphitosis), welding dust (pneumosiderosis), and beryllium (pulmonary berylliosis).

j	Cancer	Bladder cancer: $\beta$ -Naphthylamine, benzidine, 4-aminobiphenyl, auramine, and magenta. Skin cancer: Coal tar, pitch, shale oil, soot, and carbon black. Lung cancer: Asbestos, chromate, nickel, coal tar, pitch, and radioactive dust. Nasal and paranasal cancer: Nickel. Leukemia: Radioactive substances and benzene.
k	Other	Allergies: Metal oxides and fumes. Circulatory function disorders: Nitroglycol and nitroglycerine.
l	Radioactive	Radioactive ore, radium, uranium, or plutonium salts, and radioactive argon.

## 1 Toxicity, toxicity measures, and anti-pollution measures

### (1) Toxicity measures

Individual toxicities and measures are described in Section 1.1; experiments involving toxic substances exhibit minimal commonalities that are of notable concern.

- a. Prior to their usage, fully study the toxicity of the chemicals that are utilized and generated in the experiments, involved measures, and experimental methods. Measures for the exhaust of chemicals, washing the body and the eyes, and prompt notification in the event of an accident should be considered.
- b. Avoid inhaling the vapor, fumes, and dust from lethal substances. Wear gas masks and dust masks as required.
- c. Wear rubber gloves and protective masks when handling skin-irritating substances, especially those capable of chemical burns.
- d. Exercise careful conduct when handling skin-penetrating toxic chemicals should be handled with extreme care. In addition, wear rubber gloves as needed.
- e. For the measurement of toxic liquid chemicals and toxic chemical solutions, employ a pipette for poisonous chemicals or rubber-stoppered volumetric pipette for poisonous substances, and do not use the mouth to suck.
- f. In case of any existing chemical allergies, consult a doctor and convey the specifics of the concerned chemical.

### (2) Anti-pollution measures

Hazardous or harmful substances that escape untreated through waste or exhaust act as pollutants. Therefore, strict compliance to these anti-pollution measures is necessary.

- a. Several toxic gases, including those yet to be fully investigated, have been identified as air pollutants. Therefore, depending on the gas type, these gases can either be absorbed via appropriate absorbents or detoxified through oxidation or burning.
- b. Odorless substances can be utilized to absorb alkalis and detoxify them through oxidation; this measure is in line with the Offensive Odor Control Law.

- c. The handling rules specified by this university for elements and compounds identified as harmful water-polluting substances along with those for water-soluble salts and laboratory waste thereof are to be strictly observed.
- d. The elements and compounds mentioned above that are water-insoluble solids, especially in small quantities, are transformed into water-soluble salts (e.g., chlorides, sulfuric acid salts, or nitric acid salts) transformed into aqueous solutions and are finally transported for processing to a temporary storage facility for laboratory waste. Large quantities are handled according to the “Laboratory waste processing guide.”
- e. In case of spillage of water-polluting harmful substances on a desk or the floor, collect as much of the substances as possible; handle the water-soluble substances according to the methods detailed in measure “c” of this section. For insoluble substances, handle the chemicals according to the methods presented in measure “d” of this section by transforming them into a soluble salt and rendering into a solution.
- f. The handling of water-soluble salts of elements, which are not harmful water-polluting substances, and liquid waste containing these substances are governed by the “Laboratory waste processing guide.”
- g. Small quantities of the above-mentioned water-soluble solids are transformed into soluble salts, such as chlorides, sulfuric acid salts, or nitric acid salts, and delivered to the same facility as that for the aqueous solution; large quantities are to be handled according to methods specified in measure “d” of this section.
- h. In the interest of safety of laboratory waste handlers, water prohibitive, flammable, and skin-penetrating organometallic compounds, which are poisonous and lethal in nature, should never be included in the general waste. However, this limitation does not apply to those compounds that have been detoxified with organic phosphorus compounds or organic lead compounds and sufficiently diluted according to the measures specified in the “Laboratory waste processing guide.”

## 1.1 Toxic gas and vapor

The following toxic gasses are often handled in laboratories and research centers:

◇ Tolerable toxic gas concentrations

- 1.0 mg/m<sup>3</sup> or less: Arsenic, phosphine, fluorine, bromine, ozone, phosgene, chlorine, acrolein, and diazomethane.
- 10 mg/m<sup>3</sup> or less: Zinc sulfate gas, hydrogen fluoride, hydrogen chloride, formaldehyde, hydrogen cyanide, and ketene.
- 50 mg/m<sup>3</sup> or less: Carbon monoxide, ethylene oxide, methyl bromide, ammonia, and nitrogen oxide.

100 mg/m<sup>3</sup> or less: Methyl chloride.

◇ Tolerable toxic vapor concentrations

0.1 mg/m<sup>3</sup> or less: Organic mercury compounds and mercury.

1.0 mg/m<sup>3</sup> or less: Nickel carbonyl, hydrazone, and acrolein.

10 mg/m<sup>3</sup> or less: Carbon disulfide.

Acute poisoning is a commonly observed phenomenon owing to the large number of existing lethal and poisonous gases; thus, precautions should be strictly observed to avoid such harmful instances.

(1) Toxicity, anti-pollution measures

- a. Experiments using highly toxic gases or chemicals should be conducted using a local exhaust ventilation system and wearing a dedicated (or compliant) gas mask. In addition, ensure satisfactory air flow in the room, occasionally check the gas concentration using a detector, and explore exposure countermeasures in case of accidental gas-mask removal. The detection of gas leaks for highly irritating gases is not a challenging task. However, special precautions should be taken with non-irritants such as hydrogen cyanide, carbon monoxide, nickel carbonyl, mercury, and toxic mercury. Occasionally, experiments are conducted with a canary possessing low resistance to these gases placed in the room.
- b. Considering the risk of acute poisoning, never perform the experiments alone.
- c. Toxic gas and vapor are pollutants, and the reaction resulting capture or oxidation with appropriate absorbents, may result in detoxification or combustion. Incinerate the gases, which may burn on a burner, by using N<sub>2</sub> as the carrier gas.

NOTE: Improper use of the gas mask is extremely dangerous. A specialized or appropriate gas mask (refer to Table 5-16) should be adopted, i.e., the gas mask should have sufficient absorbent capability.

Likely occurrences:

- 1) In cylinders containing corrosive gases such as chlorine. In particular, the valve may rot; in such cases, forcibly opening the cylinder may result in loss of control over the gas release. When the cylinder has a valve that does not open, have it handled by an expert.
- 2) When dealing with toxic gas or vapor, acute poisoning may occur owing to any unidentified gas leakages.
- 3) When dealing with toxic gas or vapor, acute poisoning may occur even after wearing a gas mask. If the gas mask absorbent material has expired, the gas may not be completely absorbed at high concentrations.
- 4) Experiments dealing with chlorine, nitrogen oxides, hydrogen sulfide, or zinc sulfate gas may cause sickness and nausea.

Table 5-16 Gas mask cannisters and corresponding gasses

Gas mask cannister type	Gas type	Gas mask cannister color	Carbon tetrachloride	Benzene	Chloropicrin	Methyl bromide	Tetraalkyl lead	Carbon disulfide	Methyl ethyl ketone	Acrylonitrile	Trichloroethylene	Parathion	Hydrogen chloride	Phosgene	Hydrogen fluoride	Chlorine	Nitrogen oxide	Nitrogen sulfide	Zinc sulfate gas	Hydrogen cyanide	Carbon monoxide	Ammonia	Lead/Zinc	
			⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙
Organic gas	Black	Black	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	△	△	×	△	×	△	×	×	×	×	×	△
Regular gas			△	△	△	×	○	○	△	○	○	△	⊙	⊙	×	△	△	△	×	×	×	×	×	△
Smoke	White/Black	White/Black	△	△	△	×	△	△	△	△	△	△	○	○	×	△	△	△	×	×	×	×	×	⊙
Acidic gas	Grey	Grey	×	×	×	×	×	×	×	×	×	×	×	×	⊙	⊙	○	△	△	×	×	×	×	×
Zinc sulfate gas	Orange	Orange	×	×	×	×	×	×	×	×	×	×	△	×	○	○	⊙	△	⊙	×	×	×	×	×
Hydrogen sulfide	Yellow	Yellow	×	×	×	×	×	×	×	△	×	×	○	○	○	○	△	⊙	○	×	×	×	×	×
Hydrocyanic acid gas	Blue	Blue	×	×	×	×	×	×	×	△	×	×	○	○	△	○	△	○	○	⊙	×	×	×	×
Ammonia	Green	Green	×	×	×	×	×	×	×	×	×	×	×	×	×	△	×	△	×	×	×	×	⊙	×
Carbon monoxide	Red	Red	×	×	×	×	×	×	×	×	×	×	△	△	△	△	△	△	△	×	⊙	×	×	×
Firefighting	White/Red	White/Red	△	△	×	×	×	×	×	×	×	×	△	△	△	△	△	△	△	×	△	×	×	×

NOTE: ⊙○: Appropriate △: Should be avoided ×: Unusable

## 1.2 Mercury and mercury compounds

Warnings: Deadly poison, severely poisonous in nature.

### ◇ Inorganic compounds

Poisonous: Liquid (Hg), solid Hg (ClO<sub>4</sub>)<sub>2</sub>, HgO, Hg (CN)<sub>2</sub>, HgCl<sub>2</sub>, Hg<sub>2</sub>Br<sub>2</sub>, HgBr<sub>2</sub>, HgI<sub>2</sub>, Hg (NO<sub>2</sub>)<sub>2</sub>, Hg (NO<sub>3</sub>)<sub>2</sub>, Hg (SCN)<sub>2</sub>, Hg<sub>2</sub>SO<sub>4</sub>, and HgSO<sub>4</sub>.

Deleterious: Hg<sub>2</sub>Cl<sub>2</sub>.

Unspecified: Hg<sub>2</sub>I<sub>2</sub> and HgS.

### ◇ Organic mercury compounds

Deadly: Liquid (CH<sub>3</sub>)<sub>2</sub>Hg, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Hg, other low-grade dialkyl mercury compounds, solid CH<sub>3</sub>HgCl, C<sub>2</sub>H<sub>5</sub>HgCl, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Hg, CH<sub>3</sub>HgOCOCH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>HgCl, C<sub>6</sub>H<sub>5</sub>HgOCOCH<sub>3</sub>, mercurphen, afridol, methylaryl, and mercurochrome.

Except for a few compounds that are poorly soluble in water, several inorganic mercury compounds are poisonous. Owing to the residual toxicity of organic mercury compounds, their commercial production manufacture has been discontinued, and a few such compounds are currently allowed for use.

Mercury and its compounds are generally poisonous water pollutants; these pollutants demand utmost attention owing to their low regulation value. Measures for handling materials containing mercury and compounds thereof, including laboratory waste, thermometers, mercury manometers and batteries, and fluorescent lights, should be rigorously adhered to.

In addition, purchases, usage logs, and inventory balances related to mercury and its compounds should be regularly checked.

(1) Mercury and mercury compound poisoning

Mercury poisoning symptoms (upon inhalation of mercury vapor or ingestion of mercury)

- a. Acute:
  - Intraoral inflammation (teeth and throat pain).
  - Respiratory and cardiovascular disorders (chest tightness).
  - Kidney disorders (impaired urination).
- b. Chronic:
  - General fatigue.
  - Bleeding gums.
  - Psychiatric symptoms include irritation, impatience, anxiety, and nervousness resulting from inorganic mercury exposure.
  - Neurological symptoms such as hand tremors caused by inorganic mercury exposure).

(2) Toxicity and hazard measures

- a. Mercury vapor is a deadly poison (tolerable concentration of 0.1 mg/m<sup>3</sup>). The vapor pressure for a range of ambient temperatures, as shown in Table 5-17, is 100–200 times that of the tolerable concentration. Thus, ensure proper ventilation and seal the mercury containers and mercury waste reservoirs after drowning the mercury in water.
- b. Inorganic mercury compounds generally decompose when heated at relatively low temperatures, generating free mercury vapor; thus, heat these compounds with extreme caution.

c. As organic mercury compounds include further deadly poisons (tolerable concentration of 0.01 mg/m<sup>3</sup>) and penetrate the skin, liquids and high-pressure vapor should be handled in well-ventilated sites with rubber gloves and gas masks if needed.

Table 5-17 Mercury vapor pressure

Temperature (°C)	Mercury vapor pressure (mmHg)	Mercury air saturation (mg/m <sup>3</sup> )
10	0,00049	5.5
15	0,00077	8.6
20	0,00120	13.2
25	0,00184	19.6
30	0,00278	29.6
35	0,00414	43.4

d. Always use a bulb pipette designed for poisonous substances for measuring mercury compound solutions, and ensure that no substances are inhaled through the mouth.



- e. Mercury has a high specific gravity of 13.55; thus, small quantities of mercury are considerably heavy. In addition, as mercury is a deadly poison in its vapor form, it should be sealed in a polyethylene container and then stored in another polyethylene container or glass bottle.
- f. During instances of mercury spillage onto the desk or floor, suck up the large mercury beads with a mercury dropper, and use a feather brush or whiskbroom to sweep it up together along with the dust onto a piece of paper. Thereafter, rinse out a large beaker with water, and only place the mercury inside the beaker. If some mercury falls into dents or gaps, collect it with a syringe or as an amalgam by using an acid surface-treated copper wire or copper plate. Use a large beaker or vat to prevent the mercury from flowing into drains.
- g. If mercury compounds spill out onto the desk or floor, immediately collect them if they are in solid form or wipe up the compounds with a cleaning rag if they are in an aqueous solution. Subsequently, prepare an aqueous solution and follow the processes specified in the “Laboratory waste processing guide.”
- h. Mercury compounds include explosive substances (e.g., mercury fulminate acetylides, and azides; refer to Section 2, 2. (2) Explosively decomposing chemicals (see page 98)); thus, take precautions to prevent their evolution.

### (3) Anti-pollution measures

- a. Metallic mercury forms an amalgam with the lead in drainage pipes and several other metals, leading to a buildup of sludge in onsite drainage ditches. Furthermore, if this sludge is released, it (i.e., its surface) is oxidized by oxidants, forming an oxide solution, which is then dissolved into acidic drainage, partially transforming into organic mercury. Consequently, spilled mercury should never be disposed of in the sink.
- b. Approximately 1 g of mercury is used in mercury thermometers. For spillage occurring from damaged thermometers, collect the mercury as detailed in Section 1.2(2)f, and finally store it in a mercury waste reservoir. Mercury waste generated from relay units should be handled in the same manner as that for damaged thermometers.
- c. Mercury compounds react with reducing substances in wastewater ditches to yield mercury metal, which behaves as described in measure “a.” mentioned above. Therefore, not only liquid waste containing mercury but also containers and sediments should be iteratively collected up to five times and transported to a temporary storage facility for laboratory waste.
- d. If mercury compounds are spilled onto the desk or floor, treat them by following the methods described in Section 1.2(2)g.
- e. Organic mercury compounds are oxidized and rendered inorganic via the methods mentioned below, transformed into their aqueous form, and handled as detailed in measure “c.”; 60 mL

concentrated nitric acid and 20 mL permanganate aqueous solution (6%) are added to 1 L liquid waste (Hg concentration of 0.025 mg/m<sup>3</sup> or less) and heated to reflux for two hours. When the potassium permanganate has lost its color, reduce the liquid temperature to a value of 60 °C or less, add further 20 mL potassium permanganate aqueous solution. and finally reheat the solution.

- f. Transport any materials that may generate mercury pollution, such as unusable mercury batteries, mercury lamps, or fluorescent lights, to locations designated by the university.
- g. When spillage of organic mercury compounds occurs in a well-ventilated place, soak the compounds in diatomaceous earth or polishing sand, and place in a flask along with water to obtain sulfuric acidity. Subsequently, add potassium permanganate aqueous solution in small quantities to yield mercury sulfate oxide; handle the filtrate together with the cleaning solution as described in measure “c.” Always wear rubber gloves when handling these compounds.

Likely occurrences:

- 1) When mercury is accidentally spilled on a red-hot plate, a risk of absorption of large quantities of mercury vapor occurs, which may lead to fatal acute toxicity.
- 2) Regardless of exposure to tolerable concentrations, sustained exposure and inhalation of mercury vapor over extended periods may result in mercury poisoning.

### 1.3 Cyanide compounds

Cyanide compounds are high in toxicity and have been identified as pollutants.

◇Poisonous: Potassium cyanide (KCN), sodium cyanide (NaCN), hydrogen cyanide (HCN), cadmium cyanide [Cd(CN)<sub>2</sub>], silver cyanide (AgCN), gold cyanide (AuCN), copper cyanide [CuCN (I), Cu(CN)<sub>2</sub> (II)], gold (I) potassium cyanide [KAu(CN)<sub>2</sub>], gold (II) potassium cyanide [KAu(CN)<sub>4</sub>], nickel cyanide [Ni(CN)<sub>2</sub>], and nickel potassium cyanide [Ni (CN)<sub>2</sub> · 2KCN].

◇Unspecified: Ferrocyanide salt and complex salts thereof: Na<sub>4</sub> [Fe (CN)<sub>6</sub>], K<sub>4</sub> [Fe (CN)<sub>6</sub>], and complex salts thereof.

Ferricyanide salt and complex salts thereof: Na<sub>3</sub> [Fe (CN)<sub>6</sub>], K<sub>3</sub> [Fe (CN)<sub>6</sub>], and complex salts thereof.

(1) Toxicity measures

- a. Potassium cyanide (KCN) and sodium cyanide (NaCN) are toxic chemicals and should be stored in a prescribed location with safety considerations.
- b. Hydrogen cyanide (HCN) is a toxic gas; thus, it should be properly handled.
- c. While sampling a solution, observe the guidelines in Section 1.(1)e, and utilize a poisonous chemical pipette or rubber-stoppered bulb pipette for poisonous substances to avoid accidental inhalation through the mouth.

- d. In case of accidental ingestion, consume a large quantity of water, and insert finger into throat to induce vomiting; repeat this step three times and received treatment from the doctor immediately.

(2) Anti-pollution measures

- a. Hydrogen cyanide and dicyanogen have been identified as air-polluting substances and thus should be released only after detoxification via alkali absorption and oxidation.
- b. Cyanide compounds containing heavy metals (e.g., yellow potash, red potash, and ferrocyanide metal complex salts) are transported to temporary storage facilities for laboratory waste. In particular, other cyanide compounds are broken down into their constituents. However, if experienced faculty members are unavailable or no safe facilities for decomposition are present, these compounds are to be transported to a temporary storage facility. Nevertheless, the disposal of these compounds is regulated by the “Laboratory waste processing guide.”
- c. If these chemicals are spilled onto the desk or floor, store them according to methods described in Section 1.(2)e, and treat as detailed in measure “b” of this section.

#### **1.4 Other inorganic toxic and harmful substances**

Many of the chemical substances infrequently used at this university are toxic and require environmental protection precautions. These chemicals chiefly consist of cadmium compounds, lead and lead compounds, chromium compounds, arsenic, antimony, bismuth compounds, and phosphorus compounds thereof. The inorganic chemicals are summarized in Table 5-18. In cases wherein these toxic and harmful substances must be dealt with, carefully read the details concerning the appropriate materials and receive detailed instructions from the instructor.

Table 5-18 Physical effects of inorganic toxic and harmful chemicals

Effects Chemicals	Direct effects	Chronic effects
Cyanide compounds	<p>Cyanides affect body tissues, causing asphyxia and death.</p> <p>Poisoning symptoms usually appear within several seconds to minutes, causing headaches, dizziness, disturbance of consciousness, spasms, hypothermia, and death.</p> <p>Small quantities may cause dizziness, headaches, tinnitus, vomiting, elevated breathing, elevated pulse, further disturbance of consciousness, spasms, and death.</p> <p>The fatal dosage for KCN ranges from 150 to 300 mg.</p>	<p>Consumption in small doses over an extended period causes chronic poisoning.</p> <p>Symptoms include headaches, nausea, and tightness in the chest and abdomen.</p>
Alkyl mercury	<p>Consumption in small doses causes nausea, vomiting, stomach aches, diarrhea, stomatitis, and hand tremors.</p>	<p>Memory loss, loss of concentration, headaches, insomnia, impaired taste and smell, neuralgia, and overall central nervous system disorders such as neurological weakness (causes of Minamata disease) when consumed for a considerable period.</p>
Total mercury	<p>Consumption of large doses results in teeth rot and bloody stool (i.e., signs of inorganic mercury poisoning).</p>	
Organic phosphorus	<p>Mild: General fatigue, headaches, dizziness, excessive sweating, nausea, and vomiting.</p> <p>Moderate: Abnormal crying, miosis, muscle atrophy, speech impairment, and vision loss.</p> <p>Severe: Impaired consciousness, general spasms, incontinence, and death.</p>	
Cadmium	<p>Blocks the reabsorption of renal urinary cells and causes loss of calcium and calcium imbalance in the body followed by osteomalacia. Bone changes owing to pregnancy, lactation, menopause, and aging as well as calcium and protein deficiencies; may trigger further bone changes (as evident in Itai-itai disease).</p>	
Lead	<p>A large dose of lead in the body causes acute toxicity, stomachache, vomiting, diarrhea, and urinary retention; severe gastroenteritis and consequent shock may cause death.</p>	<p>Prolonged introduction of small doses of lead to the human body causes loss of appetite, constipation, general fatigue, anemia, arthritis, stomachache, limb paralysis, visual impairment, spasms, and coma. Accumulation of lead in the body is characterized by a daily consumption of 0.5 mg or more.</p>

Chromium (hexavalent)	<p>Large doses of chromium cause vomiting, urinary retention, shock spasms, coma, and uremia, eventually leading to death.</p> <p>Contact with the skin causes dermatitis, edema, and ulcers. For concentrations of 100 ppm or more, the effects on the skin are noticeable.</p> <p>If more than 0.1 ppm chromium is consumed orally, symptoms such as nausea are observed.</p> <p>The lethal dose is approximately 5 g.</p>	
Arsenic	<p>Large doses of arsenic causes acute toxicity. Common symptoms include illness, nausea, diarrhea, dehydration, stomachaches, noxious exhalations, incontinence, thirst, and decreased urine output within 1 hour of ingestion.</p> <p>At higher doses, death occurs owing to severe gastroenteritis symptoms, bloody stool, hypothermia, hypotension, spasms, coma, and circulatory disorders.</p> <p>The lethal dose is approximately 120 mg, but a dose of 20 mg can be dangerous as well.</p>	<p>Consumption of small doses over a long time causes tactile disorders in the hands and feet, bronze coloring of the skin, edema, and cornification on the palms and soles of feet.</p> <p>Arsenic may cause nausea, vomiting, stomachache, lacrimation, hepatomegaly and hepatitis, leading to death from cardiovascular disorders. The chronic toxicity dose in tap water approximately ranges from 0.2 to 0.4 ppm.</p>

## 1.5 Organic toxic and harmful substances

Commercially available organic chemicals that are designated as poisonous or deleterious substances are listed in Table 5-19. These substances include toluene ( $C_6H_5CH_3$ ), methanol ( $CH_3OH$ ), chloroform ( $CHCl_3$ ), methyl iodide ( $CH_3I$ ), acetonitrile ( $CH_3CN$ ), acrylonitrile ( $CH_2=CHCN$ ), and carbon tetrachloride ( $CCl_4$ ), which are frequently handled on a regular basis.

In general, solid organic compounds are measured by weight. In the case of liquids, if they are specified by weight, the volume is calculated from the difference before and after weighing or calculated from the specific gravity. If specified by volume, they are measured with a graduated cylinder, rubber-stoppered graduated pipette, or syringe.

In addition, as reactions are performed in sealed reaction vessels and under reflex conditions, the toxicity of the chemicals used for raw materials do not pose any significant challenges. For a highly toxic products, the extraction, concentration, distillation, and crystallization are extremely time-consuming processes; thus, caution should be taken to prevent inhalation of vapors or contact with the skin. In other words, proper care should be exercised for toxic substances that emanate deadly vapors such as mercury or organic mercury or penetrate the skin such as tetraethyl lead, phosphorus pesticides, and dimethyl sulfate.

In particular, if the waste does not consist of any mercury compounds, an appropriate medium should be employed for transformation into liquid waste, and this waste should be transport to a temporary storage facility for laboratory waste. The following precautions should be observed to ensure the health and safety of the staff present:

- a. Substances listed in Section 2, 1. (2) Spontaneous pyrophoric substances and Section 2, 1. (4) Water prohibitive substances should be treated at their source (certain compounds such as aluminum compounds cause severe chemical burns). Prior to treatment, the substances should be brought in according to the instructions from the faculty and staff to identify their names.
- b. Skin-penetrating poisonous and deleterious substances such as tetraethyl lead, tetramethyl lead, dimethyl sulfate, and phosphorus pesticides should be treated as much as possible at the source. If these compounds are to be transported for treatment, they are first diluted with inactive solvents as described in measure "c" mentioned below, the compound types are subsequently contained, and their concentrations and amounts are finally identified.
- c. The general dilution standard with regular solvents (solvents not specified for poisonous and deleterious substances) is 1% for poisonous substances and 10% or less for regular deleterious substances. Thus, vapor pressure is approximately one-tenth of that normally observed for relatively low boiling point compounds.
- d. Irritating noxious chemicals are diluted as needed prior to transportation for treatment.
- e. If there is no suitable solvent and oxides and hydroxides are harmful in nature, treat the chemicals with mineral acid after burning or oxidative decomposition and subsequently transport as a salt solution.
- f. Platinum, gold, and silver present in the solutions are either reduced with an appropriate reducing agent such as formalin or recovered in metal form via ion exchange
- g. For mercury compounds, see Section 4, 1.(2).
- h. For treatment of organic peroxides, see Section 2, 1.(1).

Table 5-19 Main organic solvents and toxicity

Organic solvent name		Main harmful actions					Notes	
		Liver	Kidneys	Hematopoietic organ	Neurological			Skin mucous membrane
					Anesthesia	Other		
Carbonization hydrogen	Petroleum ether				△		△	Be careful of mixed benzenes.
	Petroleum benzine				△		△	"
	• n-Hexane				△		△	
	Cyclohexane				○		○	
	• Benzene	△	△	⊙	○	○	○	May result in reduced white blood cells, red blood cells, thrombocytopenia, or addiction.
	• Toluene	△	△	○	○	○	○	Mixed benzenes may cause addiction.
Alcohol	• Methanol	△	△		⊙	○	△	Vision loss from neurological disorders or formaldehyde generated in vivo.
	Ethanol	△	△		○		△	
	cyclohexanol	△						
Ether	Ether	△	△		⊙	○	△	May cause addiction.
	Tetrahydrofuran	△	△		○		⊙	
	• Dioxane	○	○		△		△	
Ketone	Acetone				○		△	
	Methyl ethyl ketone				○		△	
	• Furfural				○			
Chlorinated hydrocarbons	Methylene dichloride	△			⊙		○	
	• Chloroform	⊙	○		⊙		△	
	• Carbon tetrachloride	⊙	○		⊙		△	
	Ethylene trichloride (trichloroethylene)	△	△		⊙	○	△	Cases of peripheral neurological abnormalities, multiple mental illnesses, and addiction.
	Chlorobenzene	△	△	△	○		△	
Ester	Methyl acetate				○	○	△	Ophthalmic nerve disorders and risk of vision loss.
	Ethyl acetate				○		△	
Other	Pyridine	○	○		○	○	△	Central nervous system dyskinesia.
	• Dimethylformamide	⊙	△				⊙	
	Dimethyl sulfoxide						○	A solution of poisonous substances is dangerous as it penetrates skin and mucous membranes.
	• Carbon disulfide	○	○		⊙	⊙	△	Psychiatric schizophrenia-like symptoms and multiple neurological disorders.

NOTE 1) Toxicity strength shown in order of ⊙ > ○ > △.

2) Organic solvents with ● to the left of their names are those substances for which contact with the skin may result in the amount absorbed percutaneously reaching a degree that cannot be ignored in terms of health effects on the whole body or the absorption amount, as listed in Table I-1 of the recommendations for tolerable concentrations by the Japan Society for Occupational Health (2022, Industrial Hygiene Journal, 2022,64,253-285, <https://www.sanei.or.jp/files/topics/oels/oel.pdf>).

## 2 Storage and management of poisonous and deleterious substances

Because hazardous substances may be fatal to humans, precautions must be fully taken to prevent abuse or improper handling. Accordingly, the “Poisonous and Deleterious Substances Control Act” (hereinafter referred to as “the Act”) was enacted, and toxic substances should be properly managed in accordance with the specified regulations. In “the Act”, toxic substances are listed as poisonous substances (those listed in Table 1 of “the Act” other than drugs and quasi-drugs), deleterious substances (those listed in Table 2 of “the Act” other than drugs and quasi-drugs), and specified toxic substances (those listed in Table 3 of “the Act”). Poisonous substances are more toxic than deleterious substances; however, as mentioned below, storage protocols for both these types of substances are similar, except for labelling.

A list of these poisonous and deleterious substances and related information can be obtained from the following websites:

<http://www.nihs.go.jp>

(Ministry of Health, Labour & Welfare, National Institute of Health Sciences website)

<http://www.nihs.go.jp/law/dokugeki/dokugeki.html>

(Poisonous and Deleterious Substances Control Act, Poisonous and Deleterious Substances Database)

The poisonous and deleterious substances that are frequently used in laboratories are listed in Tables 5-20 and 5-21, respectively. In addition, because these poisonous and deleterious substances are listed on chemical containers and reagent catalogs (in the case of Japanese reagent companies), they can be easily distinguished from general chemicals.

Poisonous and deleterious substances set forth in “the Act” also account for social circumstances, chemical distribution, and other factors; thus, “the Act” fails to encompass all toxic substances. For example, toluene is specified, but not benzene. In addition, as methyl chloride and ethyl chloride are deleterious substances, propyl chloride and butyl chloride may be considered similar to deleterious substances. In other words, even if a compound has not been specified as a poisonous or deleterious substance, if it shares similar properties, it should be handled as a highly toxic substance.

The rules for the management of poisonous and deleterious substances at Nagaoka University of Technology have been enacted in accordance with the “the Act.” Poisonous and deleterious substances set forth by “the Act” and other chemicals set forth by the university president should be stored and managed in accordance with these rules. The gist of these rules is outlined below:



1. When purchasing, using, and disposing toxic and deleterious substances, immediately log them into the management system for lab chemicals (IASO) after purchase, and use these substances while managing the amounts through the weight management system; after its usage, perform empty bin treatment and waste procedures, and cancel the registration via the chemical management support system (Section 1.1).
2. Toxic and deleterious substances are securely stored in special lockers separate from those for general chemicals made of metal or similar material with safety measures in place to prevent spillage in the event of earthquakes. Warehouses and containers are labeled “non-medical” and “poisonous substances” in white letters on a red background for poisonous substances and “deleterious substances” in red letters on a white background for deleterious substances.
3. If there is any theft or loss of toxic or deleterious substances, immediately report such instances to managers (e.g., supervising faculty) responsible for poisonous or other substances.
4. Fully detoxify the waste and subsequently treat it according to the rules for waste treatment. For example, because toxicity may have serious effects even in small amounts, adhere to the directions provided by the supervising faculty.

In addition, the following substances should be securely managed according to other laws irrespective of their poisonous or deleterious nature.

Hazardous substances: Potassium chlorate and sodium chlorate.

Narcotics: Morphine, opium, codeine, heroin (diacetylmorphine), cocaine, marijuana, hashish, and lysergic acid diethylamide.

Stimulants: Phenylamino propane hydrochloride, phenylmethylaminopropane hydrochloride, ephedrine hydrochloride, adrenaline, amphetamines, Benzedrine, Dexedrine, Dexamyl, Mezadrine, methamphetamine, and Biphphetamine.

Poisonous and deleterious substances are generally described as hazardous substances in the Fire Services Act, but they simultaneously exhibit toxic properties. Consequently, during storage, precautions must be taken against explosions or fire by considering the designated quantities and mixing prevention rules described in Sections 1 and 2. In addition, if toxic and deleterious substances are radioactive, they should be handled as described in Chapter 8.

Table 5-20 "Poisonous substances" specified in “the Act” used with relative frequency in laboratories

- 
- \* Aryl-alcohol
  - \* Phosphoryl chloride
  - \* Yellow phosphorus
  - \* Curare
  - \* Phosphorus pentachloride, phosphorus trichloride, and phosphorus trifluoride
  - \* Boron trichloride and boron trifluoride
  - \* Diacetoxypipene
  - \* Tetraalkyl lead (specified toxic substance)

- \* Inorganic cyanide, hydrogen cyanide, and sodium cyanide
- \* Dinitrocresol and dinitrocresol salts
- \* Sulfur tetrafluoride
- \* Diborane
- \* Mercury and mercury compounds
- \* Strychnine
- \* Selenium and selenium compounds
- \* Nicotine and nicotine salts
- \* Nickel carbonyl
- \* Arsenic and arsenic compounds
- \* Hydrogen fluoride
- \* Phosgene
- \* Methyl phosphonic dichloride
- \* Methyl mercaptan
- \* Monofluoroacetic acid, monofluoroacetic acid salts, and monofluoroacetic acid amide (specified toxic substance)
- \* Aluminum phosphide/accelerant (specified toxic substance)
- \* Hydrogen phosphide
- \* Phosphorus sulfide
- \* Thiosemicarbazide

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Because there are several other substances classified as pesticides, caution is necessary.

Parathion, methyl parathion, scharadan, methyl dimeton, and tetraethyl pyrophosphate are specified toxic substances.

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Table 5-21 "Deleterious substances" specified in "the Act" used with relative frequency in laboratories

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- \* Ammonia
- \* Hydroxylamine and salts thereof
- \* Chlorine, bromine, and iodine
- \* Hydrogen chloride, hydrogen bromide, and hydrogen iodide
- \* Hydrogen peroxide, sodium peroxide, and urea peroxide
- \* Potassium, sodium and sodium-potassium alloy
- \* Hydrofluorosilicic acid and silicofluoride salt
- \* Fluoroboric acid and salts thereof
- \* Sodium cyanate
- \* Sulfuric acid, fuming sulfuric acid, and nitric acid
- \* Sodium hydroxide and potassium hydroxide
- \* Inorganic zinc salts
- \* Inorganic gold salts
- \* Inorganic silver salts
- \* Inorganic tin salts
- \* Inorganic copper salts
- \* Dichromic acid, chromic anhydride, and chromic acid salts
- \* Sodium nitrate, thallium acetate, and thallium sulfate
- \* Antimony compounds
- \* Cadmium compounds
- \* Barium compounds (except barium sulfate)
- \* Lead compounds
- \* Soluble uranium compounds
- \* Chlorates
- \* Sodium chlorite

- \* Nitrites
- \* Trichlorosilane
- \* Ammonium hydrogen difluoride
- \* Vanadium pentoxide
- \* Zinc phosphide
- \* Methyl nitrite
- \* Dimethyl sulfate
- \* Thionyl chloride
- \* Triaryl tin hydroxide, trialkyl tin hydroxide, and salts and anhydrides thereof
- \* Acrylonitrile, acrylamide, acrylic acid, and methacrylic acid
- \* Acrolein
- \* Aniline, aniline salts, *N*-alkyl aniline, and 2-chloro aniline
- \* Ethylene oxide
- \* Epichlorohydrin, and ethylene chlorohydrin
- \* Formic acid (90% or more)
- \* Oxalic acid
- \* Formaldehyde
- \* Methanol, toluene, xylene, ethyl acetate, methyl ethyl ketone, and carbon disulfide
- \* Methyl chloride, ethyl chloride, chloroform, and carbon tetrachloride
- \* Methyl bromide, ethyl bromide, dichlorobutane, 1,2-dibromoethane, dibromo chloropropane, and 1-chloro-1,2-dibromoethane
- \* Methyl iodide
- \* Dichloroacetate, trichloroacetic acid, monochloroacetate, and sodium chloroacetate
- \* Monofluoroaceto-*p*-bromoanilide and monofluoroaceto-*p*-bromobenzyl amide
- \* Chloroacetyl chloride
- \* Methylamine (40% or more), dimethylamine, and cyclohexylamine
- \* 2-aminoethanol
- \* Phenol, cresol, and  $\beta$ -naphthol
- \* Nitrobenzene and 2,4-dinitrotoluene
- \* Dichlorodinitromethane and tetrachloronitroethane
- \* Toluidine, *N*-alkyl toluidine, and toluidine salts
- \* Quinoline
- \* Picric acid and salts thereof
- \* Chloropicrin
- \* Organocyno compound (except long-chain nitrile compounds: *m*- phthalonitrile and *p*-phthalonitrile)
- \* Trifluoromethanesulfonic acid
- \* Hydrazone monohydrate and hydroxyethyl hydrazine
- \* Chloroprene
- \* Acetylene dicarboxylic acid
- \* Emamectin
- \* Chlorosulfonic acid
- \* 2-chloroethyl trimethylammonium
- \* Di (2-chloroisopropyl) ether
- \* 2,4-dichloro-6-nitrophenol and salts thereof
- \* Cycloheximide
- \* 3,5-dibromo-4-hydroxy-4'-nitroazobenzene
- \* 5-dimethylamino-1,2,3-trithiane and salts thereof
- \* Sulfonal
- \* 2,4,5-trichlorophenoxy acetate and esters thereof

- \* Tributyltrithiophosphate
- \* 2-hydroxy-4-methylthiobutanoic acid
- \* Blasticidin S
- \* Hexamethylenediisocyanate
- \* Heptachlorophenol (PCP) and salts thereof
- \* Methylsulfonal
- \* Zinc methyldithiocarbamate
- \* Dimethyl methyl phosphonate
- \* *N*-methyl-1-naphthyl carbamate
- \* *p*-dimethylaminophenyldiazonium sulfate and salts thereof
- \* Rhodanacetic acid ethyl
- \* Rotenone
- \* Anise

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For other pesticides, proceed with caution for substituent names, such as phosphonate, dithiophosphate, thiophosphoramidate, or imidate for chemicals with such names.