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CHEMICAL LABORATORY

SAFETY AND TECHNIQUES

Mohamed Elzagheid
Chemical Laboratory

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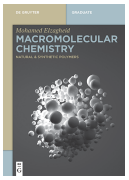

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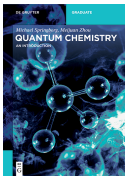

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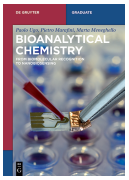

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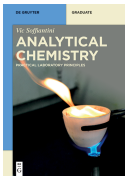

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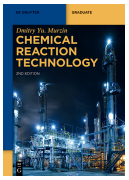

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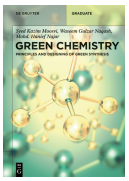

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Chemical Laboratory

Safety and Techniques

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Preface

The first part of this book presents different laboratory safety topics in a concise way starting from general laboratory safety and ending with emergency procedures. In the second part, the book briefly discusses different laboratory techniques.

Topics in this book: The topics presented in this book are based on laboratory techniques and safety in chemical laboratory courses that have been given to industry trainees of different companies and on the Occupational Health and Safety (OHS) and Control of Substances Hazardous to Health (COSHH) Management and Risk Assessment skills that have been developed through work experience for more than 20 years and through online certification courses.

Despite numerous contributions to this important topic, there is still a lack of a concise book that describes both laboratory safety and techniques.

This book can be utilized by both graduate and advanced undergraduate students and not only by chemistry students but also by students who study different science subjects. It can also be utilized by laboratory technicians and laboratory chemists working in academia or industry.

I hope that this book will add useful value to the existing knowledge and readers find the information they are looking for.

Mohamed Ibrahim Elzagheid
Waterloo, Canada
2022

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Contents

Part I: **Chemical Laboratory Safety**

Chapter 1
Introduction

Before starting the discussion of the chemical laboratory safety issues and topics, I wish to bring the attention of technicians, chemists, researchers, and students to the following terms:

1.1 Safety

Safety can be defined as protection or being away from danger, risk, or injury. Laboratory safety is not only the prevention of accidents at work but also a developed system to prevent accidents by proactively identifying possible causes.

1.2 Safety Culture

A behavior-based safety program forms part of a wider safety culture that promotes, regulates, and rewards safety. A safety culture represents an overall approach to managing safety. A good example is the health and safety culture maturity ladder shown in Figure 1.1. The ladder consists of five levels. Starting at level 1 where production is emphasized, people disregard the rules and managers are not visible; at level 2, managers set standards and supervisors follow up to make sure that everyone fully complies with the set rules; at level 3, everyone gets involved including managers and supervisors; at level 4, EHS becomes an integral part of everyday business; at level 5, everyone demonstrates excellent EHS behaviors.

Safety culture is:

- Not a set of rules or procedures. It is an attitude, lifestyle, and habit.
- A practice that is introduced, maintained, encouraged, and practiced by all.

An effective safety culture will also include the following elements:

- High quality, standardized tools, and equipment are provided and used to carry out all tasks and processes.
- Clear, easy-to-understand operating procedures, developed, and followed routinely, without exception.
- Company-wide communication systems for collecting, analyzing, and exchanging safety-related information and incident data.
- A mechanism to encourage ideas for improving safety.
- A comprehensive training program that includes regular refresher training.

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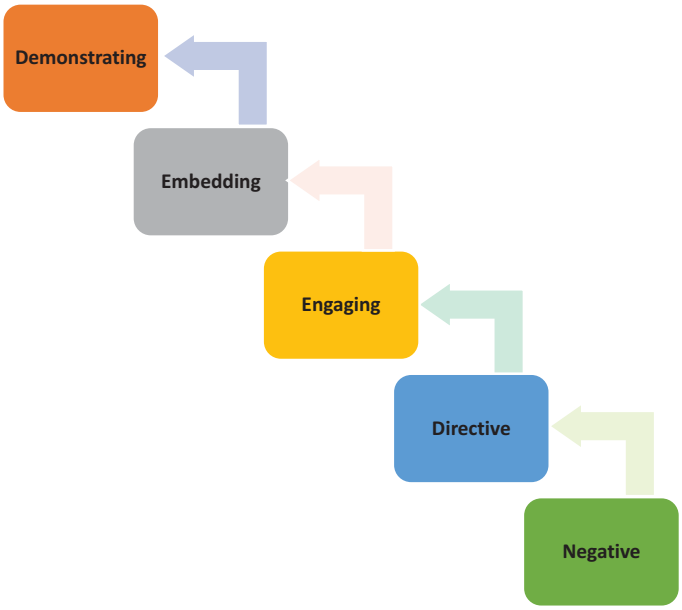

Figure 1.1: Health and safety culture maturity ladder.

1.3 Safety Cycle

In institutions without a safety culture, incidents tend to rise and fall in a safety cycle. An increase in incidents results in management intervention, usually in the form of a greater emphasis on safety and training. This in turn may lead to a decrease in incidents. When the incident rate goes down, the emphasis on safety and training is a success and is reduced. Eventually, incidents increase, and the cycle begins again.

1.4 Hazard

The term "hazard" refers to anything that can cause harm. This could include illness, injury, or physical harm of any kind.

1.5 Incident

An incident is a work-related occurrence by or during which injury, illness, or fatality happened; or injury, illness, or fatality could have happened. This unplanned event could have the potential to lead to an accident.

1.6 Risk

A risk is a likelihood that the hazard will cause actual harm. The level of risk depends on the way the chemicals are used or managed in the laboratory.

1.7 Risk Levels

- Low. Very little chance of injury and, if the injury were to happen, it would be very minor.
- Medium. Some chance of injury and the injury could be quite severe.
- High. A strong chance of injury occurring, and the injury could be severe or very severe.

1.8 Risk Evaluation Matrix

The risk matrix for hazards can range from negligible to severe as shown in Table 1.1. Each severity rating has a clear definition.

- *Severe*. If the risk occurs, it will cause multiple deaths and/or destruction of equipment and resources.
- *Significant*. If the risk occurs, it would cause a large reduction in safety margins, physical distress, or a workload. This will lead to the inaccurate performance of any given task.
- *Moderate*. If the risk occurs, it would cause a major reduction in safety margins and reduction in the ability to cope with adverse operating conditions.
- *Minor*. If the risk is supposed to occur, it would cause a little cost and slight disturbance.
- *Negligible*. Has only a few consequences but no general effect.

Based on Table 1.1, the risk can be assessed as follows:

- ***1–5 Low risk***. Review existing measures.
- ***6–10 Moderate risk***. Improve control measures.
- ***12–16 Significant to high risk***. Consider stopping activity.
- ***20–25 Extreme risk***. Do not proceed and stop everything.

1.9 Accident

An accident is an incident arising from carrying out the work that results in personal injury.

Table 1.1: Risk matrix for hazards.

Risk Probability	Risk Severity				
	5 Severe	4 Significant	3 Moderate	2 Minor	1 Negligible
5 Very Likely	Extreme Risk 25	Extreme Risk 20	High Risk 15	Moderate Risk 10	Low Risk 5
4 Likely	Extreme Risk 20	High Risk 16	High Risk 12	Moderate Risk 8	Low Risk 4
3 Possible	Significant Risk 15	Significant Risk 12	Moderate Risk 9	Moderate Risk 6	Low Risk 3
2 Unlikely	Moderate Risk 10	Moderate Risk 8	Moderate Risk 6	Low Risk 4	Low Risk 2
1 Very Unlikely	Low Risk 5	Low Risk 4	Low Risk 3	Low Risk 2	Low Risk 1

1.10 Dangerous Occurrence

Dangerous occurrence means an occurrence arising from work activities in a chemical laboratory that results in a hazardous situation. It could be a chemical spill, a fire involving any substance, or unintentional explosion.

1.11 Hazardous Substances

A hazardous substance is
- corrosive,
- explosive,
- flammable,
- toxic, and
- easily oxidized.

Or it is a substance that can develop one or more of the above properties when in contact with water or air.

Handling, working with, or transporting hazardous substances may lead to personal illness or injury.

1.12 Chemicals' Routes of Exposure

Chemicals' routes of exposure are:

- Inhalation. Breathing in chemicals, such as formaldehyde or ammonia, are commonly found in cleaners and disinfectants.
- Absorption. Chemicals enter into the eye or mucous membranes such as the nose and mouth, through the skin via open wounds or frequent skin contact with cleaning agents and disinfectants.
- Ingestion. Pesticides, cleaning, and sanitizing solution, or toxic metals such as mercury (used in thermometers) enter the body via contaminated food or hands. This route of exposure may occur if there are poor personal hygiene practices or poor housekeeping.
- Inoculation. Exposure to chemicals such as antineoplastic (cancer) drugs may occur during preparation, administration, or disposal of the drug if a sharp object such as a needle punctures the skin.

1.13 Contributing Factors

There are many factors that contribute to an accident or incident. Among these factors are operating without authority at an unsafe speed, or carrying out unsafe loading, placing, mixing, combining, or failing to use personal protective equipment (PPE).

It can also be due to improper PPE, improper or defective equipment, improper ventilation or lighting, or unsafe dress. In addition, personal factors such as fatigue, defective hearing, or eyesight, or physical or mental impairment can be among the contributing factors.

1.14 Nine Principles of Prevention

The principles of prevention need to be applied by employers to avoid hazards. If hazards cannot be avoided, then a risk assessment must be done in order to reduce it by using measures that protect all workers or by using safer work procedures. Where risk prevention or reduction cannot be achieved, then employers have a duty to put in place appropriate measures for the protection of workers such as training and signage.

The nine principles of prevention are shown in Figure 1.2 and are described as follows:

- Avoidance. The first option you must consider when dealing with risk is to avoid the hazard completely, and so eliminate the risk altogether. If you can, you remove the dangerous item or rearrange things so that the hazard no longer exists.

- Evaluation. When you cannot remove risk, you must evaluate the risk that you cannot avoid. This allows you to analyze the situation and helps you to come up with solutions.
- Risk reduction. After evaluation, you act to reduce the level of risk. This might mean, for example, making sure that there is somebody holding the bottom of a ladder, when in use.
- Adaptation. Getting acquainted with work in a new workplace can be very challenging. Writing down the way of carrying out each task with the least level of risk and having safety procedures and controls that are clearly indicated in the safety statement and keeping them close to the work area will be very helpful.
- Replacement of dangerous items. Dangerous items should be replaced.
- Policy development. A clear policy should be developed and well-enforced. This can greatly reduce the incident rates.
- Training. Training should also be introduced on safe practices. First aid and manual handling training are two areas of training often required.
- Protective equipment. PPE should be the final option considered and be implemented alongside training. When there are no adequate means to eliminate the risks involved in a task, you need to ensure that the staff members or students wear suitable PPE. Employees are obliged to wear PPE when instructed to do so by their employer.

Figure 1.2: The nine principles of prevention.

Chapter 2
General Laboratory Safety

2.1 Personal Health

Technicians, chemists, researchers, and, to some extent, students are exposed to hazardous chemicals through four main routes: inhalation, ingestion, injection, and absorption. This can happen through contact with the eye or skin. The main goal of the laboratory safety procedures and protocols is to minimize contact with chemicals in the lab. Hints to follow are presented in Figure 2.1A–C.

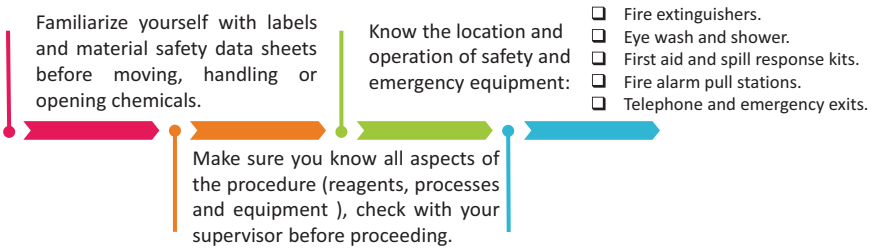

Figure 2.1A: Hints to follow before working in the laboratory.

Figure 2.1B: Hints to follow during working in the laboratory.

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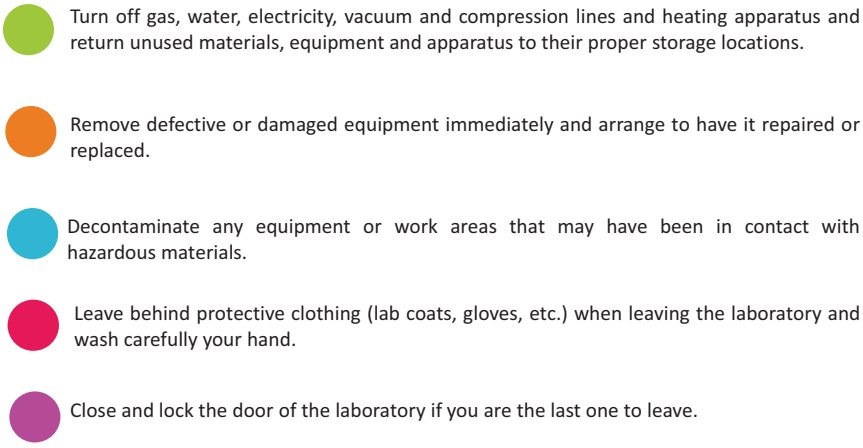

Figure 2.1C: Hints to follow after working in the laboratory.

2.2 Laboratory Housekeeping

Keeping the laboratory clean and well organized is a good way of having a safe hazard-free environment. In order to do so the following practices can be applied:

- Store untouched equipment in a designated area.
- Keep equipment and glassware always clean after each experiment.
- Return chemicals to storage after use.
- Keep the laboratory always tidy.
- Keep all exits all the time unobstructed.
- Clean up any spills immediately.
- Allow easy access to emergency equipment and utility controls.
- Store any personal belongings outside the laboratory.

2.3 Laboratory Dress

Proper choice of clothing helps to minimize chemical exposure.

- Wear a lab coat all the time in the laboratory.
- Wear shoes that protect against any possible spills. Never wear sandals.
- Wear clothing that covers large areas of the skin.
- Avoid wearing loose jewelry or rings that may damage protective gloves.

2.4 Laboratory Misconduct

- Never insert or remove contact lenses that may transfer hazardous chemicals into the eyes.
- Avoid storing, preparing, or consuming food in laboratory facilities and appliances or eating and drinking in the laboratory.
- Avoid horseplay and joking around in the laboratory.

2.5 Laboratory Visitors

A laboratory visitor is anyone who is not assigned to be part of the laboratory and has no duty to handle in the laboratory. Therefore, we should not allow visitors.

If permitted, visitors should be made aware of hazards in the laboratory, and emergency procedures in the event of spill, fire, or alarm, and should be provided with appropriate personal protective equipment as necessary.

2.6 Running Experiments in the Laboratory

Because chemical laboratory experiments are diverse and conducted by different chemists whose skills and backgrounds vary, the lab supervisor should put in place all information related to the level of experiment planning and appropriate documentation for each situation including safety precautions and emergency procedures. Lab supervisor prior approval is required when:

- working with highly toxic chemicals;
- starting a new, unfamiliar experiment or procedure;
- running experiments unattended for a lengthy period of time or overnight;
- running experiments in which there has been an unexpected result or incident;
- working alone or after hours.

2.7 Working Alone and After-Hours Work Practices

Staff working alone and/or working after hours in the laboratory may face risks that are not encountered during regular working hours because in the event of an emergency, assistance may not be readily available; therefore:

- Keep the amount of laboratory work performed alone or after work hours to a minimum and choose low-risk work only if possible.

- Perform new or unfamiliar procedures during regular hours only.
- Ensure that the first aid kit, emergency shower, eyewash, and fire extinguisher are available in the laboratory.
- Have a communication system established so that there is someone for aid in an emergency situation.

Chapter 3
WHMIS in the Laboratory

Workplace **H**azardous **M**aterials **I**nformation **S**ystem is abbreviated as **WHMIS**. It is a knowledge that everyone working in the laboratory should know about the workplace risks associated with hazardous materials. The WHMISC are summarized in Table 3.1.

Table 3.1: The Workplace Hazardous Materials Information System Classes.

Class	**A**	**B**	**C**	**D1**
Interpretation	Compressed gases	Flammable and combustible material	Oxidizing material	Materials causing immediate and serious toxic effects
Class	**D2**	**D3**	**E**	**F**
Interpretation	Materials causing other toxic effects	Biohazardous infectious material	Corrosive material	Dangerously reactive material

The three major components of WHMIS are:
- Worker education
- Labels
- Material safety data sheets (MSDSs)

3.1 Worker Education

WHMIS requires employers of universities, colleges, and companies to educate their new employees working with or is in proximity to controlled products (most of the chemicals used in chemistry or chemical laboratories).

New faculty, staff, and students should be trained before using any controlled products, and periodic refresher training is highly recommended. Training can be done by providing information on WHMIS labeling, MSDSs, and practical advice on implementing and administering WHMIS at the departmental level. Then those designates can deliver training to the staff, students, and faculty in their departments. Such training should cover hazard information for the controlled products used, and lab-specific procedures for safe use, storage, handling, spill clean-up, and disposal.

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3.2 Labeling

Labels are meant to notify users of product hazards and show them the precautions to take while handling chemicals or in case of an emergency. The two major categories of WHMIS labels are supplier labels and worksite labels. These labels and other label types are shown in Figure 3.1. Supplier labels (provided by the manufacturer) are found on the original (supplier) containers of the controlled products. If the original supplier label is found damaged, the replacement label must be provided, either from the supplier or with a worksite label. For the laboratory, a label should be used on samples sent to an outside laboratory for analysis. Whenever possible, these should have a basic supplier label. When chemicals (controlled products) are transferred from original containers to the new ones in the workplace, new worksite labels must be used. If a product will be used only in the laboratory in which it was decanted, it only needs to have a product identifier.

Figure 3.1: Chemical laboratory labeling.

The same product identifier labeling applies to controlled products produced in the laboratory, reaction vessels, mixtures undergoing testing or analysis, and hazardous waste.

However, these simplified labels only apply as long as the controlled product is in the original laboratory. If a decanted product or lab-produced controlled product is transferred elsewhere, then it should have a full worksite label.

3.3 Material Safety Data Sheet (MSDS)

MSDS is a comprehensive document that includes a piece of detailed information on the hazard, control measurement, and emergency information. It provides instruction on the safe use and handling of chemicals. It is also made to ensure that everyone who works with chemicals in any laboratory can do so without any personal harm. It helps in the environmental protection during handling chemical waste. The minimum information required on every MSDS is shown in Figure 3.2.

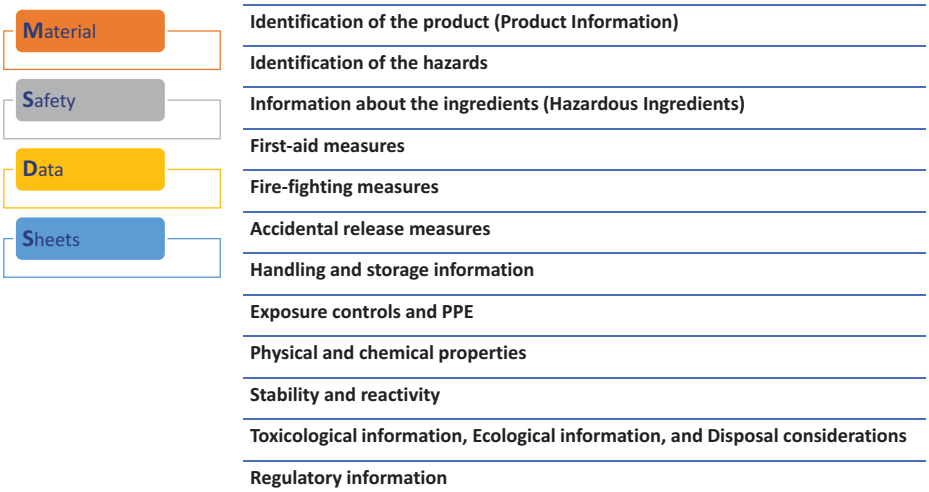

Figure 3.2: Material safety data sheet.

Each hazardous material regulated under WHMIS must have MSDS available with an exception to the chemicals from a laboratory supply house that is labeled with all information required on an MSDS or when the controlled products are produced and kept in the same laboratory. MSDS must be frequently updated, and the current hazard information must be always available. Continuation or discontinuation of hazardous materials used in laboratory should be updated. MSDS should be made available and readily accessible. They can be available in the following forms:

- Paper copies
- Computer-accessed MSDS

If the MSDS is only computer accessed, the following must be ensured:

- The computer must be easily accessible at all times to laboratory personnel.
- Laboratory personnel should know how to access and retrieve the MSDS information.
- Internet links to several MSDS sources should be available especially when the server of primary sources is not available.
- If password and login are required, they must be set up in advance.
- If common laboratory reagents are ordered from different suppliers, a single MSDS from one of these suppliers is acceptable when reagent ingredients are the same, and the product identifier on the label resembles the one on the MSDS and no variations on the hazard information.

Chapter 4
Working with Chemicals

There are four basic principles to consider when working with chemicals in the laboratory. These principles are summarized in Figure 4.1.

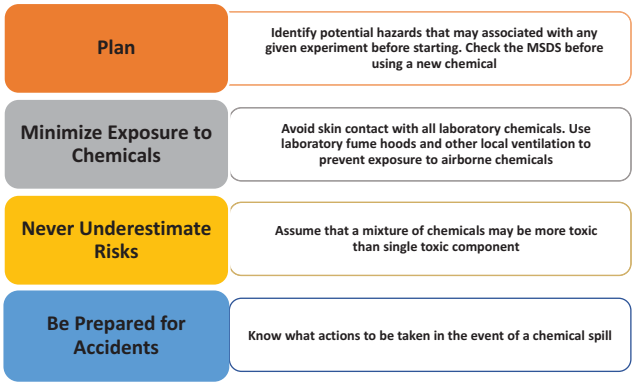

Figure 4.1: The four basic principles to consider when working with chemicals.

4.1 Highly Toxic Chemicals

Highly toxic chemicals are substances with chronic toxic effects such as carcinogens, reproductive or developmental toxins, and mutagens. Information on the potential carcinogenicity, mutagenicity, or reproductive toxicity is generally available on the MSDS. Chemicals with high acute toxicity may be identified using the criteria presented in Table 4.1.

Table 4.1: Criteria for identifying chemicals with high acute toxicity.

Oral *LD_{50} (rats, mg/kg)	<50
Skin contact LD_{50} (rabbits, mg/kg)	<200
Inhalation **LC_{50} (rats, ppm for 1 h)	<200
Inhalation LC_{50} (rats, mg/m^3 for 1 h)	<2000

*LD_{50} is the lethal dose required to produce death in 50% of the exposed test population within a specified time.
**LC_{50} is the lethal concentration in the air of a substance that produces death in 50% of the exposed test population within a specified time.

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Before starting experiments with highly toxic chemicals, check all work phases and steps, including storage and handling, experimental protocol, decontamination, disposal, and clean up of spills. Each experiment should be evaluated individually, as the circumstances and amounts of the toxic chemical used will affect the types of precautions required. Experimental work should be carried out in a designated area of the laboratory such as a fume hood or glove box. All laboratory personnel are made aware of the nature of the toxic chemicals being used and the necessary precautions to take. Warning signs to alert others in the area should be posted and they clearly define boundaries. In addition to the abovementioned, the following protocols should be followed:

- Make sure that fume hoods are working properly all the time during running the experiment.
- Handle glove boxes under negative pressure to prevent the escape of toxic vapor, specks of dust, or aerosols.
- Avoid releasing toxic dust, vapors, or aerosols to the atmosphere or into the apparatus such as vacuum pumps and lines by having a high-efficiency particulate air filter, or cold trap in the system.
- Choose equipment that can be easily decontaminated. For example, use vacuum pumps can be decontaminated easier than vacuum lines. Any used equipment should be labeled and isolated from the general laboratory equipment and decontaminated before being removed from the designated work area.
- Wear long-sleeved clothing and appropriate PPE and select gloves that are suitable for the chemicals being handled.

4.2 Flammable and Combustible Liquids

Flammable (or Class I) liquids are the ones with a flashpoint below 37.8 °C. Combustible (Class II or III) liquids are those with a flashpoint between 37.8 and 93 °C.

The great challenge of handling these liquids in the laboratory lies in their potential to cause fire or explosion. It is dangerous to heat flammable liquids with an open flame, and it is advisable to handle them in a free ignition area. For liquids with very low flash points such as diethyl ether and carbon disulfide, hot surfaces are avoided.

Appropriate ventilation should be used to prevent the formation of flammable or explosive gas mixtures in the air. Keep containers of flammable liquids always closed except during transfer of contents.

Ground metal lines and containers are used to dispense flammable liquids to prevent the buildup of static electricity. In the flammable liquid storage area, drums should also be grounded during dispensing. Drums are grounded by connecting the container to an already grounded object that will conduct electricity.

Static electricity can also be built up in plastic or other nonconductive containers. The splashing and turbulence of the liquid can cause a static charge to build up in the liquid. To minimize static buildup, use a slow pour rate and limit free fall when transferring flammable liquids.

4.3 Highly Reactive and Explosive Chemicals

Highly reactive and explosive chemicals are those that may be detonated by mechanical shock, elevated temperature, or chemical action to produce a violent release of energy and a large volume of gas, heat, and possibly toxic vapors. In many cases, it is not the total energy released that is a concern, but the extremely high rate of reaction. Even milligram quantities of some highly reactive substances can turn small fragments of glass or other materials into potentially serious injuries or lethal missiles.

Their use is limited to only minimum amounts with adequate shielding and personnel protective equipment. Examples of highly reactive and explosive chemicals usually encountered in the laboratory are listed as follows:

- Shock-sensitive materials such as azides, organic nitrates, nitro compounds, perchlorates, and peroxides
- Highly reactive or unstable chemicals that have the potential to polymerize, decompose, condense, or become self-reactive under conditions of shock, pressure, temperature, or light
- Water-reactive chemicals such as sodium, magnesium, lithium, and potassium are serious fire and explosion hazards
- Oxidizers or oxidizing agents such as halogens, oxy-halogens, permanganates, nitrates, or chromates

When working with and handling the abovementioned chemicals, precautions must be taken and the following protocols are advised:

- Minimize the need for handling of reagents and equipment while experiment is in progress.
- When setting up the experiment make sure that, in case of emergency, immediate removal of heat source, cooling or quenching of the reaction, stopping the addition of reagent, and closing of the fume hood sash are all possible.
- Use barriers such as shields, barricades, and guards. These should completely surround the hazardous area. Do not rely on the fume hood sash because it is designed to protect against chemical splash and minor explosions.
- Wear a face shield when working with explosive or highly reactive chemicals.
- Wear heavy gloves if necessary to reach behind a shielded area while a hazardous experiment is underway.

4.4 Corrosives

Corrosive chemicals result in an immediate, acute erosive effect on the body tissue. Corrosives include strong acids and bases of 1 M or greater concentration, nonmetal halides, dehydrating agents, halogens, and oxidizing agents. Precautions while handling corrosive chemicals include:

- Always add acid to water, not water to acid.
- Wear eye protection and suitable gloves. In certain cases, a face shield and acid-resistant rubber apron must be used.

4.5 Compressed Gases

Due to their high pressure, compressed gas cylinders represent additional physical hazards. In the case of a leak, inert gases in the cylinders can create an oxygen-deficient atmosphere, while toxic gases can create toxic atmospheres, and flammable gases can result in fire. The following precautions are advised when handling the cylinders:

- Transport cylinders with a handcart equipped with a restraining strap.
- Never drag, roll, or slide cylinders.
- Keep the valve cap in place during transport and remove it only when the cylinder is securely strapped to the wall.
- Use only approved cylinder regulators as per the specifications.
- Do not lubricate oxygen regulators, as the cylinder contents may oxidize the oil or grease and cause an explosion.

Static ignition, fireback, and flashbacks should be prevented by having a flash arrestor installed in the line, and all cylinders and gas lines and equipment used with flammable gases should be grounded. Cylinder connections and gas lines should be checked regularly for any leaks. This can be done by a leak detector or a soapy water solution around all joints. In case of leaks, bubbles will be seen around the leaking area. If a leak is detected, shut off the gas before doing any repairs. If, after shutting off the cylinder valve, leak continues, treat the situation as an emergency uncontrolled release.

To prevent possibly dangerous flashbacks or backflow of air or other contaminants, cylinders should not be completely emptied. When removing a cylinder from use:

- Close the main valve
- Bleed the system
- Shut off and remove the regulator, and replace the valve cap
- Mark the cylinder “empty” or “MT” and return it to the appropriate storage area for pickup by the supplier

4.6 Cryogenic Liquids

Cryogenic liquids are liquefied gases that exist in their liquid state at very low temperatures. They are extremely cold. Examples of cryogens include nitrogen, helium, hydrogen, argon, methane, and carbon monoxide. When handling these chemicals, the following precautions should be followed:

- Wear full-coverage clothing with no cuffs, pockets, which could catch the liquid in the event of a spill.
- Use insulating gloves and wear chemical splash goggles or a face shield for protection in case of cryogenic liquid splash.
- Store and transport cryogens only in Dewar flasks designed for that purpose. Always fill Dewar flasks slowly to reduce temperature shock effects and minimize splashing.
- Keep cryogens always covered to prevent condensation of atmospheric moisture that may cause a plug to form in a narrow vessel neck, resulting in an over-pressurized vessel.
- When using cold traps, ensure they do not become plugged with the frozen material.

4.7 Transporting Chemicals

Improper transport of chemicals from storerooms to laboratories, and between laboratories may lead to a chemical spill. To avoid that the following protocols are set as a guide when chemicals are transported outside the laboratory:

- Carry bottles in a designed bottle carrier or a leak-resistant, unbreakable secondary container.
- Use a cart that is suitable for the load and has high edges or spill trays to contain leaks or spills.
- Transport chemicals in freight elevators to avoid the possibility of exposing other people in the elevators. Do not use the stairs.

Chapter 5
Storage of Chemicals

5.1 Chemical Inventory

Maintaining an inventory of the laboratory used and stored chemicals is a crucial step in their safe handling. An updated record of hazardous chemicals helps in implementing proper storage and safe work procedures and emergency planning.

Chemical inventory should be updated when new chemicals are received or when chemicals are used or disposed of. This review process should be done at least once a year. For any chemical inventory, the following specific required information should be included:

- Chemical name
- Storage location
- Approximate amount
- Date received
- Supplier name
- Hazard group
- MSDS (known also as SDS)

For large chemical quantities and volumes, digital tracking can be applied in the inventory, in which the tracking can be done with containers, barcodes, RFID, and other unique identifiers.

5.2 Storage of Laboratory Chemicals

Storing of chemicals should be done according to their compatibility. Incompatible materials should not come in contact with each other in case of breakage or accidental spill. Usually, chemicals are separated into compatible groups and these groups are segregated from each other by boundaries, and distance is kept between them. Generally, store like materials with like and store liquids separated from solids. Chemicals should be separately stored as follows:

- Solids
  - Oxidizing solids
  - Flammable solids
  - Water-reactive solids

- Liquids
  - Acid liquids
  - Caustic liquids

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  - Oxidizing liquids
  - Perchloric acid solutions
  - Flammable or combustible liquids
  - Water-reactive liquids

- Gases
  - Toxic gases
  - Flammable gases
  - Oxidizing and inert gas

When storing chemicals in different separate locations is not feasible, they can be segregated by different boundaries such as glass, porcelain, or plastic container or tray. The secondary container must be large enough to contain any possible spills. Compatible dry chemicals can be stored together in separate areas. Organic solvents, acids, and bases should be physically separated from each other. Ideally, acids and bases can be stored in corrosive storage cabinets and flammable materials in approved fire-resistant storage cabinets.

The following protocol should be remembered when storing chemicals:

- Ensure bottles are within easy reach of everyone in the laboratory, and not higher than the eye level. In particular, large bottles and containers should be stored as close to the floor as possible.
- Do not store chemicals directly on the floor unless they are in approved safety cans, or if the chemicals are still in their shipping container.
- Use only chemical-resistant, secure, and strong enough shelves to store chemicals.
- Check chemicals' MSDS and store them accordingly. Certain chemicals should be stored in the fridge, freezer, or away from direct sunlight if required.
- Avoid storing chemicals under sinks as this may lead to corrosion of pipes, or any potential problems in the event of leaking.

5.2.1 Acids and Bases

- Acids and bases should be stored separately. Reactions may readily occur between ammonia vapor and hydrochloric and nitric acids, which result in the formation of potential hazardous precipitates on the bottles and throughout the storage area.
- Inorganic acids such as nitric acid and sulfuric acid and organic acids such as acetic acid and propanoic acid should be segregated. Organic acids may be stored with other incompatible chemicals.
- Concentrated nitric acid and hydrofluoric acid should be segregated from each other and from all other chemicals. They can be stored in acid or corrosive-resistant

cabinets where polyethylene or polypropylene compartments are there to isolate these acids from each other within the same cabinet.

5.2.2 Flammable and Combustible Liquids

The volume of flammable and combustible liquids permitted in the laboratory should be regulated and limited to the minimum volumes. A single container of each required flammable or combustible liquid will be sufficient if the nature of work in the laboratory does require more.

Ethanol, methanol, hexane, diethyl ether, and toluene are flammable liquids, and acetic acid, dimethyl sulfoxide, *N*, *N*-dimethylformamide, ethylene glycol, kerosene, and phenol are combustible liquids. Their cabinets should not be vented, and must never be vented to the laboratory, as they are designed to protect the contents from an external fire.

Vents must either be sealed or vented to the outdoors using materials or piping that provides fire protection equivalent to the cabinet itself. Refrigerators and freezers used for storing flammable or combustible liquids must be rated as "flammable material storage" or "explosion-proof" models.

5.2.3 Compressed Gases

In order to minimize problems associated with storing compressed gas cylinders there are a number of steps that can be followed:

- Secure cylinders in an upright position by a chain or strap to a bench, wall, or rack.
- Use carts for transporting cylinders only.
- Secure cylinders individually and avoid the usage of single strap or chain around multiple cylinders.
- Position cylinders in a way where the valve is easily accessible and the contents label clearly visible.
- Never store gas cylinders in the laboratory.
- Only cylinders in use can be kept in the laboratory.
- Keep cylinders in a cool, dry, well-ventilated area away from incompatible materials and ignition sources.

5.2.4 Ethers and Other Peroxide-Forming Chemicals

A number of inorganic and organic chemicals can become dangerous with time due to a tendency to form peroxides, especially on exposure to light and air. Chemicals

which have undergone peroxidation are sensitive to heat, shock, and friction and may explode violently. Common peroxide-forming chemicals are listed in Table 5.1.

Table 5.1: Common peroxide-forming chemicals.

Chemicals that form explosive levels of peroxides without concentration	Chemicals that form explosive levels of peroxides on concentration
Isopropyl ether, butadiene, potassium metal, potassium amide, and sodium amide (sodamide)	Acetaldehyde, benzyl alcohol, 2-butanol, cumene, cyclohexanol, cyclohexene 3-Methyl-1-butanol, tetrahydrofuran, dicyclopentadiene, diethyl ether, ethylene glycol, dimethyl ether, methyl isobutyl ketone, 4-heptanol, 2-hexanol, isopropanol, and 2-pentanol

Never expose peroxide-forming chemicals to heat and light. Always keep them away from heat and light. Record on the bottles or the container the date when these chemicals are received and the date the bottles are opened. These chemicals must also be disposed of once they have exceeded their safe shelf life, as detailed in Table 5.2.

Table 5.2: Shelf life of peroxide-forming chemicals.

Unopened containers	Dispose after 1½ years
Opened containers that have chemicals capable of forming peroxides without concentration	Dispose after 3 months
Opened containers that have chemicals capable of forming peroxides on concentration	Dispose after 1 year

5.2.5 Perchloric Acid and Perchlorates

At room temperature, perchloric acid of 60–72% solution is like any other strong acid. However, at higher concentrations or upon heating, it develops very strong oxidizing properties. At this point, it is prone to undergo spontaneous and explosive decomposition. Due to these properties, perchloric acid of any concentration must be kept away from strong dehydrating agents, organic materials, and reducing agents. Any procedure that involves heating perchloric acid must be carried out in a properly designed perchloric acid fume hood.

Spills of perchloric acid represent a significant danger, especially if allowed to dry or come in contact with the combustible material. Do not mop up or soak up the

spill with dry combustibles, the absorbing material may dry out, and then explode or catch fire. The spilled acid should be neutralized with a weak base such as sodium bicarbonate, and then soaked up with a suitable absorbent. As an extra precaution, the used clean-up material should be kept wet and sealed in a plastic bag for disposal. If perchloric acid is spilled on a wooden laboratory surface, the wood should be physically removed to avoid the possibility of future spontaneous fire or explosion.

Avoid mixing perchloric acid waste with any other waste and store it separated from other chemical waste. Old bottles must not be opened as they may contain dry crystalline perchlorate salts which are very sensitive to both heat and shock. Since anhydrous perchlorate salts are dangerous, the hydrated forms should be used whenever possible.

5.2.6 Picric Acid and Nitro Compounds

Picric acid's general formula is $(NO_2)_3C_6H_2OH$. Its IUPAC name is 2,4,6-trinitrophenol. It is highly shock-, heat-, and friction-sensitive, so it is easily exploded. For safety reasons, it is stored as a water-wet paste. Picric acid exists in different salt forms and many of which are even more reactive and shock-sensitive than the acid itself. Picric acid old bottles must be disposed of carefully because crystals may have formed on the bottle's lid, and any attempt to open it could result in enough friction to produce an explosion. Therefore, inspection is required to see any sign of crystallization. Store picric acid in a cool, dry place. Inspect every 6 months and add water as needed and dispose of after 2 years.

Chapter 6
Hazardous Chemical Waste Management

6.1 Definition of Chemical Waste

Chemical laboratory waste is any material or chemicals leftover or generated from running different experiments. It can be hazardous or nonhazardous and it can include organic, inorganic, glass, sharp materials, or carnage as shown in Figure 6.1.

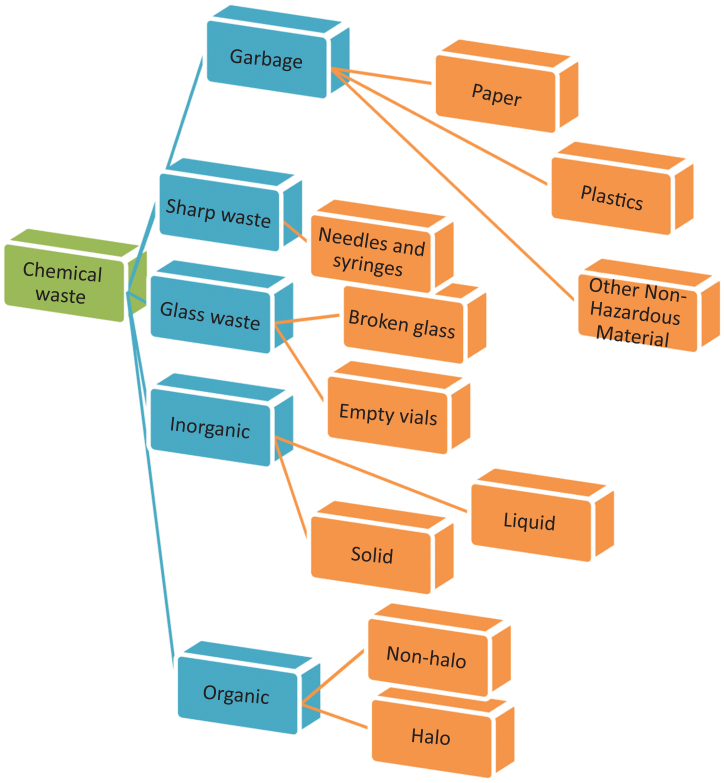

Figure 6.1: Different types of waste materials.

Hazardous chemical waste may include any solids, liquids, or gases containing or contaminated with:

- Flammable or combustible liquids
- Reactive chemicals such as oxidizers, reducing agents, cyanides, or water-reactive materials

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- Acute or chronic toxic material
- Corrosive materials

Unattended leftover chemicals are potentially hazardous if mishandled by any person and also harmful to the environment. It is of great interest to everyone working in the chemical laboratory to minimize the number of chemicals used, and subsequently, the amount of waste generated. It is advisable to practice the following three principles to help in controlling chemical waste:

- Reduce chemicals. Keep only a minimum amount of chemicals in the laboratory. Bring to the laboratory only the amount of chemicals required for the experiment if possible. Use the smallest possible amount for the experiment.
- Reuse chemicals. Borrow and lend chemicals to fellow researchers, technicians, and chemists. This will reduce the accumulation of chemicals by purchasing the same ones by different individuals.
- Recycle chemicals. Recycle chemical waste whenever possible.

6.2 Handling and Storage

Generally, all the precautions one has to follow when handling, storing, and using laboratory chemicals are applied to hazardous laboratory waste. Safe handling and storage of hazardous waste generated at the worksite through proper identification and worker education is a must in any workplace. Laboratory leaders and/or supervisors have to put in place safe work procedures to deal with hazardous waste from receiving through storage until disposal. They must ensure that all laboratory personnel are trained on those procedures. A few points to keep in mind when storing hazardous laboratory waste are:

- Keep containers free of chemical contamination.
- Segregate chemicals according to compatibility.
- Do not store incompatible chemicals together.
- Leave 10–20% air space in the chemical waste containers to allow for vapor expansion, and to reduce the spills from occurring when moving overfilled containers.
- Never accumulate large volumes of hazardous waste and have it disposed of regularly.

Waste containers should be kept closed at all times, except when contents are being added. Do not leave filter funnels in the open necks of containers, even if the waste is in a fume hood. Fume hoods are not to be treated as a worry-free method of waste containment or disposal. Wastes should be separated as follows:

- Separate liquid and solid waste.
- Separate liquid organic waste from liquid aqueous waste.

- Separate strong acids and bases from other aqueous waste.
- Separate halogenated from nonhalogenated waste.

6.3 Labeling Hazardous Waste

The individual who generates the waste is responsible for proper waste labeling. All waste containers must be properly labeled to accurately identify the contents of the container. Containers should have the minimum following information:

- Building name and room number
- Name of principal investigator or researcher working in the laboratory and a phone number
- The main contents should be broken down by approximate percentage

Waste containers should not be labeled with generic, vague terms such as “chemical waste,” “inorganic waste,” or “solvent waste.” Use specific names that clearly identify the contents and do not use abbreviations, acronyms, trademarked names, and chemical formulas. Attach a label to the container prior to being filled and maintain a list of contents as waste is added to the container. Deface or remove old labels on containers used for chemical waste.

6.4 Packaging Hazardous Waste

Proper packaging of waste has to be maintained by the waste generator. If possible, the original chemical containers should be preferably used for disposal. Otherwise, choose a container that has the following criteria:

- A sealable with a tight screw lid
- A waste compatible
- Not damaged or defected

6.5 Special Wastes

The procedures described above deal with common teaching and research chemical waste generated by academic laboratories. Other types of waste require additional or special handling as described further.

6.5.1 Solvent Drums

The chemical supplier's 5-gallon (22.7 L) drums must be carefully rinsed and cleaned, and their labels defaced before they can be properly disposed of.

6.5.2 Sharps

All needles and similar sharps are treated as biohazardous waste. Needles should not be recapped. All other sharp objects should be dropped into a specifically designed sharps disposal unit or another appropriate puncture-proof container.

6.6 Hazardous Waste Pickup

Depending on each academic institution's protocols, hazardous waste can be picked up either from an individual laboratory or from a central waste storage area.

6.7 Hazardous Pictograms

Hazardous pictograms show us if there are any hazardous chemicals. They give us details on the chemicals in use and what they might cause to people or the environment. Selected Classification, Labelling and Packaging (CLP) hazard pictograms are shown in Table 6.1.

6.8 The Control of Substances Hazardous to Health (COSHH)

Everyone who works with chemicals has to be aware of substances hazardous to health. In any workplace, it is essential that anyone encountering hazardous materials need to be protected from their risks and taught how to deal with them. One of the most important regulations is the Control of Substances Hazardous to Health or COSHH. According to these regulations, all employers require to ensure that they are sufficiently controlling hazardous substance exposure in the workplace. COSHH secures the health, safety, and welfare of persons exposed to hazardous substances at work and protects others who are in connection with them. COSHH also controls the storage and use of hazardous substances or other dangerous substances and generally prevents the unlawful acquisition, possession, and use of such substances. The eight-step approach to the COSHH requirements is summarized in Table 6.2.

Table 6.1: Selected CLP hazard pictograms.

Hazard symbol	Meaning
	Health hazard
	Acute toxicity
	Corrosive
	Explosive
	Gas under pressure
	Hazardous to the environment
	Serious health hazard
	Oxidizing
	Flammable

Table 6.2: The eight-step approach to the COSHH requirements.

Step 1	Assess any risks to health arising from hazardous substances used in, or created by, your workplace activities.
Step 2	Make necessary precautions and assess the risks first before allowing any work.
Step 3	Prevent or properly control employees' exposure to hazardous substances.
Step 4	Apply control measures and maintain them. Ensure that safety procedures are followed.
Step 5	Watch employees' exposure to hazardous substances.
Step 6	Carry out appropriate inspection and control on any COSHH-specific requirements.
Step 7	Put in place emergency procedures to handle any accidents, incidents involving hazardous substances.
Step 8	Make sure that employees are properly informed, trained, and supervised.

6.9 Health Risk Control Measures

Risk control measures are protocols followed or put in place to eliminate, prevent, or reduce the occurrence of hazards that are identified. A hierarchical approach presented in Figure 6.2 shows the five general categories of control measures: elimination, substitution, engineering controls, administrative controls (also known as work habits control), and personal protective equipment (PPE).

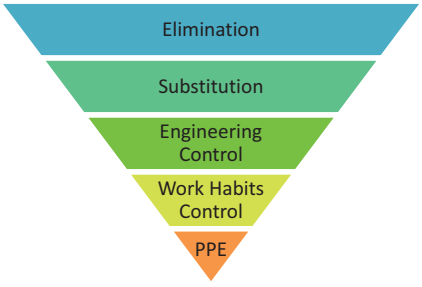

Figure 6.2: Hierarchy of health risk control measures.

6.9.1 Elimination or Substitution

The most effective way in the prevention control is to eliminate the use of hazardous agents. Sometimes it is not practicable or possible to eliminate the use of such agents, but instead, the hazardous agents are substituted with relatively innocuous ones. For example:

- Benzene is replaced with toluene.
- Carbon tetrachloride is replaced with dichloromethane.
- Talc is replaced with chalk.
- Sandblasting is replaced by steel shot blasting.
- Dry handling techniques are replaced by wet handling techniques that suppress dust emission.

6.9.2 Engineering Control

This is a process capable of reducing exposure to hazardous substances such as ventilation. It is commonly controlled by one of the mechanical air-handling methods discussed below or a combination of both.

- Local exhaust ventilation (LEV). Application of mechanical air-handling techniques whereby potential airborne contaminants are captured near the source of emission, extracted, and discharged to either a safe location or subjected to some form of "air cleaning" technique.
- General or dilution ventilation. General or dilution ventilation reduces the concentration of air contaminants or controls the amount of heat that accumulates in hot industrial environments, by mixing (diluting) the contaminated air with fresh, clean, uncontaminated air. This is widely used throughout the industry for the ventilation of control rooms, photographic laboratories, office spaces, and printing rooms. It is not normally suitable for the control of dust, the mist of fume or for substances of moderate to high toxicity, or in situations where the rate of generation of contamination is nonuniform or high.

6.9.3 Administrative Control (Work Habits Control)

Administrative controls or work habits control are workplace policies, procedures, and practices that minimize the exposure of workers to risk conditions. Great care is needed to ensure that procedures, once adopted, are observed, particularly in the longer term, as shortcuts, and nonobservance can become "custom and practice" over time, and once established can be difficult to overcome.

Good and continuous housekeeping is particularly important in processes and laboratories where hazardous materials may be handled. Clear labeling, with relevant health and safety advice, careful and appropriate storage and good work techniques all need to be addressed.

Good housekeeping can also help to minimize airborne contamination from spilled materials and waste off-cuts. The untidy workplace may also prevent access to essential system controls, such as LEV on–off switches, which could discourage their proper use, and this, in turn, affect the ventilation efficiency with the work area.

Education of employees on any health hazards in the workplace and the importance of correctly using all the control measures provided, adopting recommended operating procedures, and wearing personal protection, if required, are needed in order to minimize the risks to health.

Training of employees on the use of appropriate control measures, operating practices, and the factors involved in the correct selection, use, and maintenance of PPE.

Good hygiene practices are also important steps workers should take to protect their health. This includes the following established decontamination procedures, where applicable, regular laundering of clothing, using approved methods and facilities, and good personal hygiene such as frequent washing and showering particularly before meal breaks.

6.9.4 Personal Protective Equipment (PPE)

PPE is the last control and only applicable when the preceding measures are insufficient or not reasonably practicable in achieving a satisfactory work protection environment. It is important to ensure that the protection is effective and comfortable. Regular maintenance is vital for many types of PPE if effective protection is to be obtained.

PPE management programs need to be adopted whenever the option of PPE use is deemed necessary.

Chapter 7
Hazard Control Measures

The three major categories of hazard control measures – engineering controls, administrative controls, personal protective equipment (Figure 7.1) – that were partially discussed in the previous chapter will be elaborated thoroughly in this chapter. They have also been known as the safety three lines of defense.

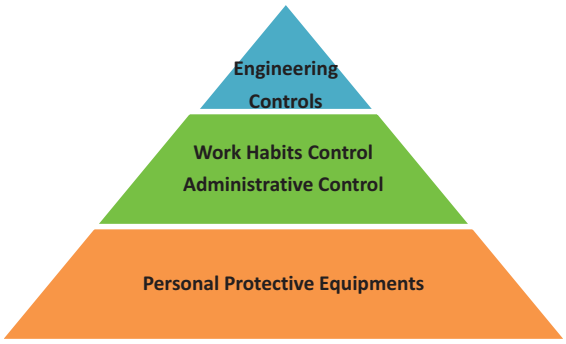

Figure 7.1: Safety three lines of defense.

The type and level of control required depend on the hazard present, the level of exposure, the toxicity of the product, and other factors related to the process on hand.

- Engineering controls refer to substituting with less hazardous material or process, isolating the hazard, enclosing it, or using ventilation to remove the hazard at the source.
- Administrative controls include work scheduling changes to reduce the amount of time spent in contaminant areas, experiment planning process, use of safe work procedures, and training.
- PPE is generally used as a control method when it is not feasible to protect the worker by using either engineering or administrative control. Since some hazards in the laboratory cannot be completely controlled through engineering or administrative controls, PPE such as eye protection, hand protection, laboratory coat, and closed-toed shoes are all essential for working with chemicals.

7.1 Fume Hoods

Fume hoods (Figure 7.2) are designed to control chemists and laboratory technicians' exposure to hazardous chemicals. They should not, however, be treated as a worry-

https://doi.org/10.1515/9783110779127-007

free method of waste disposal. Apparatus used in the hood should be equipped with appropriate condensers, traps, and scrubbers to collect or contain wastes and vapors.

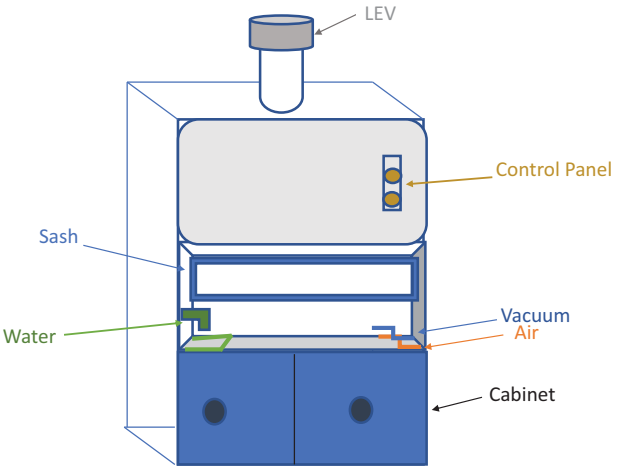

Figure 7.2: Fume hood.

Before beginning any work in the fume hood, confirm that the hood is operational. Check that the local on–off switch is in the "on" position and check the airflow.

In the absence of an airflow gauge or velometer, tape a strip of inch wide tissue to the lower corner of the sash to qualitatively confirm the airflow by noting that the tissue is pulled gently into the hood.

A fume hood that is not performing properly is more dangerous than no hood at all since the user will likely have a false sense of security about its ability to provide protection. Never carry out any work in a fume hood that is tagged as being out of service, as this could potentially result in the exposure of maintenance workers to hazardous chemicals. An average face velocity of 100 feet per minute (fpm), 0.5 meter per second (mps), is recommended for a standard chemical fume hood at a sash opening of 30 cm. The face velocity at any point should not be less than 80 fpm (0.4 mps). Fume hoods used for highly toxic chemicals require an average face velocity of 120 fpm with no less than 100 fpm at any point at the face. Adequate airflow and the absence of excessive turbulence are necessary for safe operation. To ensure this:

- The sash openings should be kept at a distance of 30 cm or less while working in the hood. When the hood is not in use, the sash must be completely closed.
- Do not block the air barriers behind the fume hood. Do not place anything closer than 3 cm to the back of the hood.
- Keep the device at least 15 cm from the front of the fume hood. Use mounts to lift bulky apparatus to avoid interfering with airflow through the hood.

- Keep the fume hood clean and tidy. Instruments and chemicals should usually be kept in a fume hood only if they are part of the process for which the hood is used. Fume hoods should not be used for the long-term storage of chemicals or apparatus.
- Do not modify the interior of the hood, for example, by installing shelves.
- Minimize traffic around the fume hood. Anyone passing through the hood can cause turbulence, causing vapors to flow.
- Close windows and doors near the hood. Open windows and doors can disrupt airflow.
- Do not use fans near hoods. Laboratory fans can cause turbulence that can disrupt the proper flow of air through the hood.

7.2 Other Laboratory Ventilation

There are many types of laboratory equipment and apparatus that generate vapors and gases but cannot be used inside a traditional fume hood. Some examples include gas chromatographs, atomic absorption spectrometers, and ovens. Local exhaust ventilation should be used to contain and remove potentially hazardous or noxious fumes and vapors. Ideally, a separate dedicated exhaust system should be used. If connected to an existing hood duct, the fan capacity must be increased and airflow to both hoods is properly balanced. Also note that each new exhaust hood requires the provision of more make-up air supply to the lab.

The general laboratory ventilation system controls the quality and quantity of air supplied to the lab at such a rate that the air is continuously replaced to minimize the concentration of odoriferous or toxic substances. Labs are also designed so that they are at negative pressure to the rest of the building, to prevent movement of odoriferous or toxic substances to other parts of the building.

7.3 Safe Work Procedures

Safe work procedures are step-by-step descriptions of how to safely perform certain high-risk work-related activities. Hazards related to chemicals, processes, and equipment must be identified and assessed in the laboratory. Then safe working procedures are developed based on the identified hazards. They should be written, easily accessible to everyone in the laboratory, and staff should be aware that procedures exist.

Procedures should be specific to the laboratory or research group so that the unique circumstances in the laboratory or research program can be addressed. Situations that require safe work procedures include:

- Working with hazardous chemicals
- Working alone or after hours
- Emergency response to chemical spills or fire

7.4 Personal Protective Equipment

7.4.1 Eye and Face Protection

Eye protection should be worn in or around all laboratories when working with chemicals. The type of eye protection required depends on the risk. Safety goggles with side shields are sufficient for most situations. For more hazardous activities where there is a risk of chemical spray or explosion, safety goggles or face shields designed to protect against chemical spray should be used. This is especially true for working with corrosive chemicals.

7.4.2 Gloves and Hand Protection

The right type of gloves provides much-needed hand protection in the lab. It is recommended to wear appropriate gloves when handling hazardous chemicals, toxins, unknown toxicity, corrosive substances, and hot or cold objects. Particular attention should be paid to chemicals that have a "Skin" mark on the MSDS sheet.

When choosing a glove, consider the circumstances in which the glove will be used. The degree of protection required will depend on the hazards associated with the chemical, the type of experimental work performed, the scale, and the individual work habits.

Disposable gloves made from suitable material are generally acceptable for routine laboratory work with small quantities of chemicals, as they offer the best combination of tactile sensitivity, and barrier protection. They should be removed and replaced when contaminated. Reusable gloves should be inspected before each use, replaced each time they discolor or show signs of damage, and should be cleaned or disinfected after each use.

Wearing the wrong type of glove when handling chemicals can be more hazardous than wearing none at all. If a chemical permeates the glove, it can be held in prolonged contact with the wearer's hand and potentially cause serious damage.

7.4.3 Laboratory Coats and Aprons

Laboratory clothing or aprons are worn to absorb or deflect leaks and to prevent corrosive or toxic substances from reaching the skin. Cotton is the preferred material for

a standard coat; it is cheap and has a relatively slow-burning. Synthetic fiber layers are not recommended as they can melt and adhere to the skin in case of fire. For higher risk situations, use chemical-resistant or flame-retardant synthetic materials such as Tyvek or Nomex. Plastic or rubber aprons should be used when handling large amounts of concentrated acids and other corrosive substances.

7.4.4 Respiratory Protection

Respiratory protection is not normally required when working in the laboratory, due to the combination of engineering controls, such as hoods, safe working procedures, and relatively small amounts of chemicals used in the laboratory. In order to use respiratory protection, a hazard assessment must first be performed and, if the result of the assessment recommends the use of respiratory protection, then laboratory personnel in need of protection must be instructed in the proper use, care, and maintenance of respiratory equipment.

7.5 Emergency Showers and Eyewash Stations

All laboratories using corrosive or other chemicals that are dangerous to the eyes or skin must have access to an eyewash station and a safety shower in the immediate vicinity and be accessible at all times. Laboratory personnel should be aware of the location of safety showers and eyewashes and should have the knowledge of using the equipment effectively. Laboratory equipment must neither be stored under emergency showers nor must access to safety equipment be blocked in any way or at any time.

Signs should also be posted to clearly indicate the location of showers and eyewashes. In the event of a chemical spill, flush the affected body parts immediately and thoroughly for at least 15 min. This supplies the large quantities of water necessary to dilute and wash away the contaminants. Remove all contaminated clothing. Clothing can absorb chemicals and hold them close to the skin, compounding the effect of a chemical burn. After flushing the affected body parts, seek medical attention as soon as possible.

Most of the emergency showers and eyewash stations use cold running water. To a person standing under a shower that uses cold water, 15 min may seem like an eternity. It is therefore important that another person assist the victim, to make sure he or she does not quit emergency flushing before all chemical contamination has been washed off.

Likewise, there is a strong tendency for a person with chemicals in the eye to close the eyelid, which increases the risk and extent of the damage. It may be necessary for

the assisting individual to open the victim's eyelids to ensure that proper washing takes place.

Dosing or drench hoses are common fittings in many labs and complement eyewashes and showers. They can be used to wash a small spot when a full shower is not necessary, to help a victim who is unable to stand or is unconscious, or to irrigate under clothing before removing for a full emergency shower flush.

Eyewash bottles can be used as an accessory or as stand-alone. They provide immediate rinsing of contaminants or small particles, followed by regular 15-min rinsing at the eyewash station. Eyewashes and showers should be tested regularly by rinsing them for at least 3 min, once a week, to ensure they are functioning properly and to prevent microbial growth or the formation of any dirt, rust, or scale.

7.6 Fire Extinguishers

Only those individuals trained in the use of fire extinguishers should attempt to use it. Fire extinguishers are designed only for extinguishing small fires. Every laboratory worker should be aware of the location and type of fire extinguishers available in the laboratory, as well as the limitations of these fire extinguishers. There are four general classes of fire:

- Class A: Ordinary combustible materials
- Class B: Flammable liquids
- Class C: Electrical equipment
- Class D: Combustible metals

Each category of fire has its own type of fire extinguisher which is most effective for extinguishing it. Class D fires alone do not respond to regular fire extinguisher classes. Special extinguishing agents should be used, or the fire should be extinguished with a dry sand extinguisher. The following are the most common types of fire extinguishers.

- *Class A water-based*. They should never be used in the laboratory as they are not suitable for flammable liquids or electric fires in the case of two common laboratory fires.
- *Class ABC multipurpose dry chemical*. Commonly found in many laboratories due to its versatility in fighting nearly all types of fire.
- *Class BC carbon dioxide*. Commonly found in laboratories that do not contain substantial amounts of Class A materials.

Chapter 8
Fire and Explosion Safety

8.1 Fire Safety

8.1.1 Introduction

Fire can be defined as the rapid combination of a flammable substance with oxygen, with the rapid development of heat and light. When most substances burn, the actual combustion occurs when the solid or liquid evaporates or is composed by heat to produce gas. The visible flame is burning gas or vapor. All burners and other sources of ignition must be protected from all flammable materials. You need three things to produce a fire:

- Fuel
- Oxidizer (oxygen, in the case of air)
- An ignition source (to bring the temperature up to the ignition point of the fuel)

8.1.2 Fire Terminologies

Flashback. The rapid combustion of heavy vapor of organic compounds that collect in areas distant from their source and when burning lead the flame back to their source to cause a large fire or explosion.

Flash point. The lowest temperature at which compounds in an open vessel gives off sufficient vapor to produce a momentary flash of fire. This happens when a flame, a spark, an incandescent wire, or another source of ignition is brought near the surface of the liquid.

Ignition temperature. The lowest temperature at which the vapor over the surface of the liquid ignites.

Auto-ignition temperature. The lowest temperature at which a vapor will ignite spontaneously when mixed with air.

8.1.3 Ignition Sources

Static electricity. To eliminate static electricity, all electrical equipment must be grounded. The two basic sources of ignition that arise from electrical equipment are:

- *Arcing*. Occurs between contacts, switches, and circuit breakers.
- *Surface temperature*. Results from the resistance of a conductor to the passage of electricity.

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Friction. The slippage of power-transmitting equipment such as belt drives or the rubbing of metal-to-metal surfaces.

Mechanical sparks. To eliminate mechanical sparks, non-sparking tools must be used. If applicable, non-sparking materials like fans, fan housings, scoops, or other moving parts should be used where an impact might produce a spark.

Flames and hot surfaces. A solid fuel, gas, oil, or electrical heating equipment that involves exposed flame must not be used when you are working with volatile flammable liquids or combustible dust.

8.1.4 Makeshift Safety Measures

You cannot minimize the inherent dangers of ignition of flammable substances by moving controls, lights, switches, and relays to nearby areas with the mistaken idea that this renders them no longer dangerous. This type of "jerry-rigging" gives you a false sense of security.

Although containers of flammable substances are supposed to be tightly closed, many of the lids and covers are loose or become so. In some instances, cotton balls or porous corks are substituted for proper stoppers and covers; sometimes, bottles may even be broken. Thus, it is possible for explosive gas concentrations to meet the arcing devices thought to be safely moved to another location, and the result could be a fire, explosion, injury to personnel, or damage to the laboratory facilities.

8.1.5 Precautions

- Do not use electrical equipment that is defective or has defective wiring.
- Use explosion-proof equipment, wiring, and controls where applicable.
- Shut off all non-explosion-proof electrical equipment before working with volatile or flammable substances.
- Never overload electric circuits, particularly multiple-socket installations.
- Turn off all lights and lamps that are not equipped with explosion-proof enclosures.

8.1.6 Relative Flammability of Selected Organic Compounds

Many organic compounds are flammable because of their vapor, not the liquid itself. Prior to the combustion of flammable organic compounds, they must be converted to vapor and mixed with oxygen or air in the right proportions to support combustion.

Air has a lower limit of vapor concentration, where there is not enough vapor to support combustion, and an upper limit, where the concentration of vapor is too high to support combustion. The flammability categories of the selected solvents are shown in Table 8.1.

Table 8.1: Flammability categories of selected solvents.

Solvent	Flammability category
Ethyl ether	4
Benzene	3
Gasoline	3
Petroleum ether	2
Acetone	3
Toluene	3
Kerosene	3
Carbon tetrachloride	0
Hexane	2

8.1.7 National Fire Protection Association Classifications

Laboratories routinely use chemicals that the National Fire Protection Association (NFPA) describes as combustible Class I, Class II, and Class III liquids. The quantity and flammability of Class I and Class II liquids especially make the laboratory potentially hazardous. The total laboratory storage of these combustible materials is determined by company policy and local fire codes, but as a rule, these combustible liquids should be limited to 1 L or less in unprotected glass or plastic containers, and the total stored volume limited to 1 gallon per 100 square feet of floor space. Combustible Class I, Class II, and Class III liquids' flash points are shown in Table 8.2.

Table 8.2: Combustible Class I, Class II, and Class III liquids' flash points.

Class of liquid	Flash point
I	At or below 100 °F
II	At or above 100 °F but below 140 °F
III	At or above 140 °F

8.1.8 Types of Fire Extinguishers

There are four basic types of fire extinguishers, which are classified by the type of fire for which they are suited:

Water extinguishers. These are effective against Class A type fires but should never be used for extinguishing organic liquid Class B, electrical Class C, or metal Class D fires. Obviously, this type of fire extinguisher would be of very limited use and possibly even hazardous in a chemistry laboratory. Fire class types are shown in Table 8.3.

Table 8.3: Fire class types.

Class of fire	Materials involved
A	Routine combustibles such as wood, cloth, paper, rubber, and plastics
B	All flammable liquids and gases common to most laboratories (Class I, Class II, and Class III liquids, greases, solvents, and paints)
C	Energized electrical equipment and apparatus (hot plates, ovens, and instruments)
D	Combustible metals (magnesium, potassium, sodium, and lithium aluminum hydride)

Carbon dioxide extinguishers. They are effective against Class B and Class C fires. They are especially recommended for use around delicate electronic systems and/or chemical devices with optics. This type of fire extinguisher is not very effective against paper or trash fires and should not be used on some flammable metal and metal hydride fires such as sodium, potassium, and lithium aluminum hydride as it produces water from atmospheric condensation.

"Caution should be exercised with such extinguishers as the force of the exhaust gas can shatter expensive glassware."

Dry powder extinguishers. They are effective against Class B and Class C fires and are particularly effective against large amounts of flammable liquids. These extinguishers are usually filled with inorganic compounds such as sodium bicarbonate or mono-ammonium phosphate under nitrogen pressure. This type of fire extinguisher is not very effective against paper and rubbish fires. Although effective against electrical fires, they are not recommended for instrumentation fires because of the difficulty in removing the resulting residue from delicate electronics and/or optical systems.

Met-L-X extinguishers. These are specialized for burning metal Class D and similar fires. They contain a granulated sodium chloride formulation, which tends to be very effective against burning metals, metal hydrides, and difficult organometallic compound fires. However, these extinguishers tend not to be very effective against Class A, Class B, or Class C types of fire. Dry sand is also very effective for this type of fire.

8.2 Explosion Safety

8.2.1 Introduction

Explosions invariably accompany a fire where combustibles are stored. An explosion differs from a fire due to the introduction of pressure. Explosions occur in closed volumes, requiring fuel, oxidizer, and ignition. They yield heat, light, and pressure.

8.2.2 Explosive Mixtures

The most common explosion hazards are:

- Exothermic reactions that get out of control.
- Ether explosions during evaporation of ether-containing solutions because of peroxide residues. Elemental iron, ferrous salts, and sodium bisulfite can be used to decompose any peroxides as they form.
- Acetylene forms an explosive mixture with air in a very wide range of concentrations.
- Aluminum chloride is a potentially explosive reagent. Decomposition of this salt in the presence of moisture can produce hydrogen chloride gas under considerable pressure.
- Benzoyl peroxide, in the dry form, can be sensitive to shock and easily ignited. It tends to decompose quickly at temperatures above 50 °C.
- Ammonia gas when reacting with iodine crystals can produce nitrogen triiodide, which is shock-sensitive and explosive.
- Dry ice can produce an explosive situation if improperly stored. Never store this cooling agent in a container not designed to vent or withstand high pressures.
- Ethylene oxide gas mixed with air has been known to explode when heated in a closed container under high pressure.
- Elemental alkali metals can form potentially explosive quantities of hydrogen gas upon contact with water or acids. Destroy waste alkali metals such as lithium, sodium, potassium, rubidium, and cesium properly by adding them slowly to absolute ethanol with cooling.

8.2.3 Exothermic Reactions and Explosions

Exothermic reactions evolve heat. As the rate of reaction increases, the rate of evolution of heat increases. If the rate of evolution of heat is greater than the rate at which the heat can be removed by cooling, the temperature rises and the mixture may boil over, vaporize, or explode.

Chapter 9
Laboratory Equipment Safety

9.1 Glassware Safety

Laboratory glassware may be made of several different types of glass. Select the appropriate glassware based on the application:

- Borosilicate glass such as Pyrex, Kimax, or similar is used for situations involving thermal and mechanical shock use.
- Soft glass may be used for applications in which the glassware is not exposed to these conditions, such as for reagent bottles, glass tubing, and measuring equipment.

Before beginning any experimental work, check glassware for flaws such as chips, star cracks, scratches, and etching marks, which may result in structural failure. To prevent cuts from trying to force glass tubing into rubber or cork stoppers or tubing, do the following:

- Use appropriate hand protection and a soap solution, glycerin, or other lubricants on the ends of glass rods or tubing before inserting into a stopper.
- Insert the rod or tubing into the stopper with a turning motion – never by force.
- Keep the rod or tubing away from the palm of the hand which holds the stopper.
- Ensure that the stopper hole is large enough to accommodate the rod or tubing.

9.2 Electrical Equipment Safety

Electrical equipment in the laboratory may cause electrical shock and act as an ignition source for flammable or explosive chemicals. To minimize the possibility of either of these, a number of precautions can be taken:

- All laboratory receptacles and equipment should be equipped with three-prong grounded plugs.
- Equipment should be located safely to minimize the possibility of chemical spills on or under it.
- Inspect cords on a regular basis for frayed and/or damaged connections.
- Devices equipped with motors used where there are flammable vapors present should be either non-sparking induction or air-driven motors.
- On–off switches, rheostat-type speed controllers, and similar devices can produce sparks every time they are adjusted. If electrical equipment is to be used in the fume hood, all controls should be outside the hood.
- Unplug electrical equipment before making repairs or modifications.

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Electrical devices such as stirrers and mixers are often operated over extended periods of time with the possibility of mechanical failure, electrical overload, or blockage of the stirrer. If they are to be left unattended, the associated equipment should be fitted with a suitable fuse or thermal protection device that will shut down the apparatus in the event of such problems.

9.3 Vacuum Pumps and Systems Safety

Working at reduced pressure carries with it the risk of implosion and the subsequent dangers of flying glass, splashing chemicals, and possibly fire. Any apparatus under reduced pressure should be shielded to minimize that risk. When using a rotary pump or a building vacuum line:

- Place cold traps between the apparatus and the vacuum source to minimize the amount of volatile material that enters the system.
- Vent rotary pumps to an air exhaust system, not directly into the laboratory.
- Belt-driven pumps must have protective guards, to prevent accidental entanglement.

9.4 Heat Sources Safety

Whenever possible, use suitable electrically heated sources such as hotplates, heating mantles, or similar devices in place of gas burners as they are inherently safer. Steam baths are best for temperatures below 100 °C, since they present neither shock nor spark risks and the temperature is guaranteed not to rise above 100 °C.

9.4.1 Heating Mantles

Heating mantles incorporate a heating element in layers of fiberglass cloth and do not present a risk of shock or fire if used properly. Some precautions that should be taken when using mantles include:

- Do not use if the fiberglass cloth is worn or broken, exposing the heating element.
- Be careful not to spill water or other chemicals on the mantle, as this poses a serious shock hazard. Depending on the spilled chemical, it may also present a fire or explosion hazard.
- Always use a variable transformer to control the input voltage. Never plug directly into an electrical outlet. High voltage will cause the mantle to overheat, damaging the fiberglass insulation and exposing the heater.

9.4.2 Oil, Sand, and Salt Baths

Electrically heated oil baths are commonly used in situations where a stable temperature is required, or a small or irregularly shaped vessel must be heated. Some precautions that should be taken when using oil baths include:

- Avoid spilling water or volatile substances into the bath, which may result in a splattering of hot oil or smoking or ignition of the bath.
- Saturated paraffin oil is suitable for up to 200 °C, and silicone oil should be used for temperatures up to 300 °C.
- Always monitor the temperature of the bath to ensure it does not exceed the flash point of the oil.
- Mix well to prevent "hot spots" from forming.
- Support with a laboratory jack or similar apparatus so the bath can be lowered and raised easily without recourse to manually lifting the hot bath.

Molten salt baths can be treated similarly to oil baths, except that they have a higher operating range, up to 450 °C. The bath container and the reaction vessel being heated must be able to withstand these temperatures. It is also imperative that the bath be kept dry since hazardous sputtering and splattering may occur if the absorbed water vaporizes during heat-up.

9.4.3 Ovens and Furnaces Safety

Ovens are most commonly used for drying laboratory glassware and chemical samples. Only laboratory-approved ovens that have the heating elements and temperature controls separated from the interior atmosphere should be used. Laboratory ovens generally vent directly into the laboratory. If toxic vapors or gases may be released while using the oven, the vapors should be vented into a fume hood.

Furnaces are used for high-temperature applications. Ensure reaction vessels and other equipment used are designed to withstand high temperature.

9.5 Refrigerators and Freezers Safety

Refrigerators and freezers used in the laboratory must be carefully selected for specific chemical storage needs. Commercial refrigeration units are not designed to meet the special hazards presented by flammable materials. The interior of a commercial refrigerator contains a number of electrical contacts that can generate electrical sparks. Frost-free models often have a drain, which could allow vapors to reach the compressor, and electrical heaters used to defrost the refrigerator are also

a spark hazard. For these reasons, only specially designed lab refrigerators or modified commercial units should be used for cold storage of flammable chemicals.

Those classified as “flammable” do not have internal switches or unprotected wires that can act as a source of ignition. An “explosion-proof” unit has switches and wires protected both inside and outside and is suitable for use in environments where flammable vapors may reach explosion and/or ignition limits outside the refrigerator. For storage of flammable materials in most laboratories, a unit rated for “flammable storage” is sufficient. Commercial refrigerators and freezers are acceptable for the storage of nonflammable materials but must be visibly labeled as unsuitable for the storage of flammable materials.

Laboratory refrigerators should be clearly labeled as being for chemical storage only. A major concern with chemical storage refrigerators is that as tightly sealed spaces, they can allow the buildup of toxic and/or flammable vapors. Containers must be adequately sealed to minimize the likelihood of this happening. Beakers, flasks, and bottles covered with aluminum foil or plastic wrap are unacceptable for the storage of volatile chemicals in the refrigerator. Likewise, corks and glass stoppers are also inadequate. Screw top caps with a seal inside are best suited for refrigerator storage. Refrigerators should also be regularly defrosted and cleaned to minimize the accumulation of ice and hazardous vapors inside the unit. Chemicals no longer used must be disposed of as hazardous waste.

9.6 Decontamination of Laboratory Equipment

Any equipment used in a laboratory that contains hazardous materials will become contaminated over time. Thus, laboratory equipment should be decontaminated prior to removal. This applies whenever equipment is transferred to another laboratory, sent out for repairing or calibration, or disposed of as waste or surplus equipment.

Decontamination includes removing all hazardous products, containers, or other potentially contaminated items such as refrigerators and cupboards. The equipment should then be visually inspected for stains, residues, or other evidence of chemical contamination, and such contamination, if found, should be removed by washing with soapy water, decontamination solution, or other necessary means.

Chapter 10
Emergency Procedures

There is an emergency when an incident occurs that involves a high risk of injury or contact with persons or damage to the property or the environment. Special information is required from the person who reported the incident. The following should be obtained:

- Identity of the reporter
- Nature of incident (fire, explosion, chemical spill, gas leak)
- Location of the incident (building and room number)
- The number of injuries
- When and how did the incident occur?

The basic steps to be taken for all emergencies are the same: warn others, evacuate the area, and contact authorities.

10.1 Chemical Spills

A chemical spill is defined as an uncontrolled release of a hazardous chemical, whether in the form of a gas, liquid, or solid. In the event of a leak in the laboratory:

- Stay away and warn others in the immediate area of the leak. Isolate the area around the drain.
- Assist injured or contaminated persons if you are instructed to do so, but do not expose yourself to the risk of injury or contamination in this process.
- Assess the situation and determine if it constitutes an emergency situation or even though it is not an emergency, whether assistance is required to clean up the spill.
- If the spill is minor, and trained local personnel, personal protective equipment, and spill abatement material are available, the spill may be cleaned up according to the procedures given by local authorities.

10.2 Fire and Explosion

Ensure that you are familiar with the locations and operation of the fire alarms, fire extinguishers, and emergency evacuation plans in your building. You know at least two exits from your area and the building, and you know which lanes have “deadlocked,” so you can avoid them in the event of a fire. Find out where the refuge areas are. These are temporary fire shelters. Exit staircases provide a convenient escape, as they are surrounded by solid walls. Certain floors or parts of floors can be

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designated as areas of refuge. Find out the location of the evacuation collection points for your building in case the building needs to be evacuated. Check with your building's chief emergency officer to find such areas for your building. In the event of a fire or explosion in the laboratory:

- Warn others in the vicinity of fire or explosion.
- Activate the building's fire alarm system.
- Contain the fire by closing doors and smoke covers in the fire area.
- Evacuate the fire or explosion area and the building. Use the stairs, not the elevator.
- Contact the communications control center and provide the above information about the fire or explosion.

10.3 Compressed Gas Leaks

Uncontrolled release of pressurized gas can be dangerous. This comes from the physical hazards of the high-pressure vessel and the specific chemical hazards of the contents. While flammable, toxic, and corrosive gases are more dangerous, inert gases such as nitrogen or argon can be deadly due to the risk of suffocation indoors and in poorly ventilated areas. A leaking gas cylinder is considered an emergency if closing the cylinder valve cannot stop the leak. In case of uncontrolled release of flammable, toxic, or corrosive gas, the following steps must be taken:

- Warn others in the immediate emission zone.
- If possible, stop the flow of gas on the cylinder valve.
- Activate the building fire alarm system.
- Evacuate the fire area and building. Use the stairs, not the elevator.
- Contact the communications control center.

Efforts should be made to stop the flow of gas on the cylinder valve only if there is no personal risk. Otherwise, evacuate the area and let the emergency response personnel handle the situation. Be aware that static electricity generated by flowing gas can cause flammable gases to catch fire.

Chapter 11
Chemicals and Compatibility Groups

When determining in which compatibility group a given chemical should be placed, it is often found that it will fall into more than one category. In these situations, it is necessary to determine what the primary hazard associated with the chemical is, and whether there are any specific incompatibilities that preclude storing with other chemicals in a given hazard group. This is best determined through consultation with the MSDS for specific reactivity and compatibility information. Note that this is not meant to be an exhaustive list, but a guide. For details on any chemical, always consult the MSDS.

11.1 Pyrophoric Chemicals

Pyrophoric chemicals are those that may spontaneously ignite upon exposure to air. They should be kept in a tightly sealed container and, in many cases, should be stored under an inert solvent or atmosphere to minimize the possibility of contact with air. Examples are:

- Grignard reagents, RMgX
- Alkali metals such as Na and K
- Metal powders such as Al, Co, Fe, Mg, Mn, Pd, Pt, Ti, Sn, Zn, and Zr
- Metal hydrides such as NaH, $LiAlH_4$, and $NaBH_4$
- Nonmetal hydrides such as B_2H_6 and other boranes
- Nonmetal alkyls such as R_3B and R_3P
- Phosphorus (white)

11.2 Oxidizing Agents

The primary danger associated with oxidants lies in their ability to act as an oxygen source and thus readily contribute to the combustion of organic matter. Typical oxidants include those chemicals with the following oxygen-containing groups:

- Bromates
- Chlorates
- Chlorites
- Chromates
- Dichromates
- Hypochlorites
- Nitrates
- Nitrites

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- Perborates
- Perchlorates
- Permanganates
- Peroxides
- Persulfates

In addition, the halogens (fluorine, chlorine, and bromine) also react as oxidizers and should be treated accordingly.

11.3 Reducing Agents

Reducing agents are those chemicals that are good sources of hydride and thus react vigorously with many other substances: Some of the strong reducing agents typically found in laboratories are:

- Hydrogen
- Metal hydrides (e.g., NaH, $NaBH_4$, and $LiAlH_4$)
- Grignard reagents, RMgX
- Boranes
- Alkali metals
- Alkyl lithium and alkyl sodium

11.4 Water-Reactive Chemicals

Chemicals reacting with water should be stored in a cool dry place, protected from water and fire sprinkler systems. Examples are:

- Alkali metals such as Na, Li, and K
- Metal hydrides such as LiH, NaH, CaH_2, $LiAlH_4$, and $NaBH_4$
- Metal alkyls such as lithium and aluminum alkyls
- Grignard reagents, RMgX
- Halides of nonmetals such as BCl_3, BF_3, PCl_3, and PCl_5
- Inorganic acid halides such as $POCl_3$, $SOCl_2$, and SO_2Cl_2
- Anhydrous metal halides such as $AlCl_3$, $TiCl_4$, $ZrCl_4$, and $SnCl_4$
- Phosphorus pentoxide

Part II: **Laboratory Techniques**

Chapter 12
Separation Techniques

12.1 Filtration

12.1.1 Introduction

Filtration is the process of removing a solid material from a substrate (liquid or gaseous) in which it is suspended. This process is a physical process. Filtration is done by passing the mixture to be processed through one of the many available filter media. These are of two types: surface filters and depth filters.

Surface filter traps particles larger than the filter pores or mesh dimensions on the surface of the filter; all other smaller matters pass through. The filter is usually made of paper, fabric, or other membrane kinds.

A depth filter is one that consists of either multiple layers or a single layer of a medium having depth, which retains particles within its structure. There are two types of depth filters. The first type is the deep bed filter which involves filtration vertically through a packed bed of granular or fibrous material. The second type is the thick media filter. This alternative form of a depth filter is predominately composed of a replacement filter cartridge.

Filtration is most commonly used in one of four ways:

- Solid–liquid filtration: The separation of solid particulate matter from a carrier liquid.
- Solid–gas filtration: The separation of solid particulate matter from a carrier gas.
- Liquid–liquid separation: A special class of filtration resulting in the separation of two immiscible liquids, one of them is water, by means of a hydrophobic medium.
- Gas–liquid filtration: The separation of gaseous matter from a liquid in which it is usually, but not always, dissolved.

In the laboratory, filtration is generally used to separate solid impurities from a liquid or a solution or to collect a solid substance from the liquid or solution from which it was precipitated or re-crystallized. This process can be accomplished with the help of gravity alone. The filtration can be speeded up by using vacuum techniques. Vacuum filtration provides the force of atmospheric pressure on the solution in addition to that of gravity, and thus increases the rate of filtration.

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12.1.2 Filtration Methods

The two methods of filtration are gravity and vacuum, also called suction. In gravity filtration, the filtrate passes, due to the combined forces of gravity and capillary attraction between the liquid and the funnel stem, through the filter medium.

In vacuum filtration, the pressure difference across the filter media is maintained by clearing the space below the filter medium. This is done by connecting the system to vacuum source. Vacuum filtration adds the force of atmospheric pressure on the solution to that of gravity, with a resultant increase in the rate of filtration.

The choice of the method to be used depends upon the following factors:

- Precipitate properties
- Filtration time
- The degree to which it is necessary to retain all the precipitate
- The extent to which one can tolerate the contamination of the precipitate with the filtrate

12.1.3 Filter Media

12.1.3.1 Paper

There are different grades of filter papers. These include qualitative grades, low-ash or non-ash quantitative grades, hard grades, and even glass-fiber "papers." The correct choice of filter paper grade is based on porosity and waste. Different grades of filter paper are made in different sizes and varying degrees of porosity. The main objective is to complete the filtration as quickly as possible while maintaining the speed on paper with minimal damage.

12.1.3.2 Membrane Filters

Membrane filters are highly porous, thin synthetic materials with extremely fine pores. They retain particulates larger than their defined pore size and they remove any gas or liquid particles, contaminants, or microorganisms that pass through them. Types of membrane filters include mixed cellulose ester filters, cellulose acetate filters, hydrophilic and hydrophobic PTFE filters, Nylon filters, and polycarbonate filters.

With proper filter selection, they yield a filtrate that is ultra-clean and/or sterile. Membrane filters are available in a wide variety of pore sizes in a number of different materials. When liquids pass through a Millipore membrane filter, all contaminants larger than the filter-pore size are retained on the surface of the filter, where they can be readily analyzed or counted. This is in sharp contrast with the action of a "depth" filter, which retains contaminants not only on its surface but also inside the filter matrix.

12.1.3.3 Fritted Glassware

The filtration of solids can be performed with funnels fitted with fritted-glass (also called sintered-glass) plates. Fritted glass is available in different porosities, and some of the problems encountered in using filter paper are minimized by using fritted-glass equipment. The grades of fritted glassware are listed in Table 12.1.

Table 12.1: The grades of fritted glassware.

Designation	Pore size in microns, µm
Extra-coarse	170–220
Coarse	40–60
Medium	10–15
Fine	4.0–5.5
Very fine	2.0–2.5
Ultra-fine	0.9–1.4

For best service, tools made of plastic should be carefully maintained. It is best to follow any manufacturer's instructions that may come with the device. The new vitrified filter should be washed by vacuum with hot hydrochloric acid and then rinsed with water before use. Clean all flat filters immediately after use. Many deposits can be removed from the filter surface simply by rinsing from the reverse side with water under pressure. Some sediment tends to clog the pores of the textured filter, and chemical means are required for cleaning.

12.1.4 Filtering Accessories

12.1.4.1 Filter Supports

Some solutions that are to be filtered tend to weaken the filter paper, and at times the pressure on the cone of the filter will break the filter paper, ruining the results of the filtration. Thin woven textile disks are used to support the tip of the filter-paper cone. They are approximately of the same thickness as the filter paper, and therefore ensure close contact of the reinforced paper with the funnel walls. They are folded along with the filter paper when it is formed into the normal conical shape, and they can easily be removed from the wet filter paper after the filtration has been completed.

12.1.4.2 Wash Bottles

The wash bottle is a squeeze bottle with a long-bent beak, often seen in chemistry and biology laboratories. It is generally made of semi-soft plastic that scatters when pushed. This pressure on the bottle compresses it and imposes the same amount of

pressure on the liquid inside it. Then the liquid quickly exits through a long, thin nozzle. Washing bottles are designed for one main purpose – to wash laboratory glassware. Beakers, test tubes, and flasks are often difficult to wash in the sink due to their shape and size.

There are three basic types of washing bottles that are found in most laboratories:

- Standard wash bottles: These are the most common type of wash bottles.
- LDPE washing bottles: These are transparent, thin, with a long, smooth spout.
- Self-releasing wash bottles: They have short tubes on their side. You don't need to press it to drop the liquid, just tilt the bottle.

12.1.4.3 Water Aspirator Pump

A traditional method for producing a vacuum in laboratories is a water suction device. This is a simple device, which is attached to a sink faucet and produces vacuum using the principles of the Venturi effect when cold water rushes through it.

12.1.5 Operations Associated with the Filtration Process

Regardless of whether gravitational or vacuum filtration is used, three processes must be performed: decantation, washing, and precipitation transfer.

12.1.5.1 Decantation

When a solid is easily deposited on the bottom of the liquid and has little or no tendency to remain suspended, it can be easily separated from the liquid by carefully pouring the liquid so that no solid is transferred to it. This process is called decantation. To decant a liquid from a solid:

- Hold the beaker that has the mixture in it in one hand and have a glass stirring rod in the other.
- Incline the beaker until the liquid has almost reached the lip.
- Touch the center of the glass rod to the lip of the beaker and the end of the rod to the side of the container into which you wish to pour the liquid.
- Continue the inclination of the beaker until the liquid touches the glass rod and flows along it into the second container.

12.1.5.2 Washing

Washing aims to remove the excess liquid phase and any soluble impurities present in the precipitate. Use a solvent that is miscible with the liquid phase but does not dissolve a significant amount of precipitate. The solids can be washed in the beaker after decanting the supernatant liquid phase. Add a small amount of washing liquid and mix it well with the precipitate. Allow the solid to settle. Decant the washing

liquid through the filter. Allow the precipitate to settle, with the beaker slightly tilted, so that the solid accumulates in the corner of the beaker under the drain. Repeat this procedure several times. Multiple washes with small volumes of liquid are more effective in removing soluble contaminants than a single wash using the total volume.

12.1.5.3 Transfer of the Precipitate

Most of the precipitate is removed from the beaker into the filter using a stream of washing liquid from the washing bottle. The mixing rod is used to direct the flow of liquid into the filtration medium. The last traces of precipitate are removed from the walls of the beaker with a mixing rod.

12.1.6 Gravity Filtration

Gravity filtration is carried out by using a stemmed funnel and filter paper. During filtration, the filtrate passes through the filter paper in the funnel as shown in Figure 12.1. This method is slow but preferable to vacuum filtering due to better retention of fine particles and less cracking or tearing of filter paper.

Gravity filtration is considered the fastest and most preferred method for filtering gelatinous precipitates because these precipitates tend to clog and pack the pores of the filter medium much more readily during vacuum filtration.

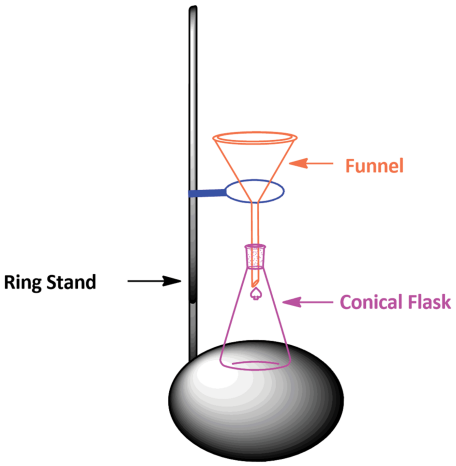

Figure 12.1: Gravity filtration setup.

12.1.7 Vacuum Filtration

Vacuum filtration is the best way to speed up the separation process, but the filter medium should keep the fine material intact. The vacuum is usually provided by an aspirator, although the vacuum pump, protected by appropriate traps, can be used. Due to the natural hazards of having a broken vessel from reduced pressure, a thick filter should be used, and technicians should always be alert for the possibility of drag. The standard setup of the vacuum filtration is shown in Figure 12.2.

This illustration shows the use of a Buchner funnel in which the wetted filter paper must be seated before the suction is applied. The funnel or crucible is fitted to a suction flask. The sidearm of the flask can be connected to a source of the vacuum such as a water aspirator.

A water-trap bottle should be inserted between the flask and the source of the vacuum. When the vacuum is turned on, the pressure difference between the filter medium and the atmosphere helps to speed up the filtration process.

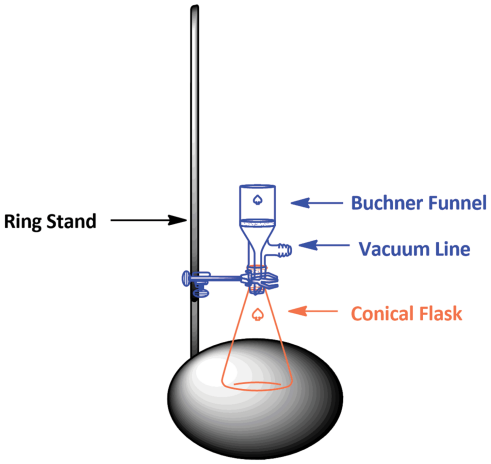

Figure 12.2: Vacuum filtration setup.

12.2 Recrystallization

12.2.1 Introduction

Recrystallization is a procedure whereby organic compounds which are solid at room temperature are purified by being dissolved in a hot solvent and reprecipitated by allowing the solvent to cool. The solvent may be a pure compound or a mixture, and the selection of the solvent depends upon a number of important factors.

If the growth of the crystals is very fast and not selective, the precipitation process does not aid in purification. When the crystals grow very slowly and consist of pure compounds, the precipitation process is a purifying one; this second type of precipitation is usually defined as crystallization.

In the laboratory, a solid is purified by recrystallization by dissolving it in a hot solvent, filtering the solution, and then allowing the desired crystals to form in the filtrate, while the impurities remain in the solution.

12.2.2 Solvent Requirements

In general, solvents should:
- not react with the material to be crystallized;
- form desirable, well-formed crystals;
- be easily removed from the purified crystals;
- have high solvency for the desired substance at high temperatures and low solvency for that substance at low temperatures;
- have high solvency for impurities.

12.2.2.1 Solvency

The substance to be purified should be sparingly soluble in the solvent at room temperature yet should be very soluble in the solvent at its boiling point. The solubility of a solute in a solvent is a function not only of the chemical structures of the solute and the solvent but also of the temperature. In the majority of cases, the solubility of the solute in a solvent increases as the temperature increases, and in some cases the increase in solubility is very dramatic. This is the basis for the recrystallization method of purification. The substance to be purified must not be completely soluble in the solvent at room temperature, but it must be highly soluble in the solvent at its boiling point. The solubility of a solvent depends not only on the chemical composition of the solute and solvent but also on temperature.

In most cases, the solubility of the solvent increases with increasing temperature, and in some cases the increase in solubility is very large. This is the basis of the recrystallization method for purification.

If the compound has been reported in the literature, its solubility in common solvents can be found in the reference. Normally, polar organic compounds tend to dissolve in polar solvents such as water, and the lower molecular weight alcohols, or combinations of them. Nonpolar compounds tend to dissolve in nonpolar organic solvents, such as benzene, petroleum ethers, hexanes, and dichloromethane.

Solubility follows the general rule like substances tend to dissolve in like substances. This is not always valid because the molecule as a whole must be considered before making the decision. For example, the long-chain carboxylic acid,

stearic acid, behaves more like a nonpolar substance than a polar one, because the nonpolar part of the molecule outranks the polar carboxyl group.

In general, the following points should be considered:

- A useful solvent is one that will dissolve a great deal of the solute at high temperatures and very little at low temperatures.
- If a solvent dissolves too much solute at low temperatures, it is unsuitable.
- If too much solvent is required to dissolve the solute even at its boiling point, it may be possible to recrystallize several grams, but extremely large volumes of solvent would be required to recrystallize several hundred grams.
- Quick tests of solubility are unreliable and are misleading because some solutes dissolve very slowly in boiling solvents. A quick observation may be misleading and cause you to reject the solvent as being unsatisfactory.
- The suitability of a solvent depends upon the establishment of equilibrium. The maximum solute will dissolve when equilibrium has been attained between the dissolved and solid solutes.

12.2.2.2 Volatility

The volatility of a solvent determines the ease or difficulty of removing any residual solvent from the crystals which have formed. Volatile solvents may be removed easily by drying the crystals under a vacuum or in an oven.

Solvents with a high boiling point should be avoided, if possible. They are difficult to remove, and the crystals usually must be heated mildly under a high vacuum to remove such solvents.

12.2.3 Recrystallization of a Solid

12.2.3.1 Selecting the Funnel

For recovering crystals by gravity filtration, use either a short-stemmed or a stemless funnel. Long-stemmed funnels tend to cool the filtering solution, and crystallization then takes place in the stem, decreasing the flow rate and even clogging up the funnel, but for recovering crystals by vacuum filtration using a Buchner funnel, either porcelain or plastic. Jacketed Buchner funnels may be desirable to minimize any crystallization of the solute caused by evaporation under reduced pressure.

12.2.3.2 Heating the Funnel

If a hot recrystallization solution is poured through a cold funnel, the solvent cools, and sometimes crystallization can occur in the funnel and its stem, clogging the funnel. Funnels and therefore solvents can be heated or kept hot in one of the following ways:

- Place a stemless or short-stemmed funnel in a beaker with pure solvent heated in a steam bath. The hot solvent can be spilled, and the reflux of the boiling solvent will heat the funnel.
- Place a funnel and fluted filter paper in the neck of an Erlenmeyer flask which is heated in a steam bath to reflux the pure solvent in it. The reflux ring will heat the funnel. When the recrystallization procedure is to be started, the heated funnel and filter paper are transferred to funnel support.
- Pass hot water or steam through a jacketed Buchner funnel during vacuum filtration.

12.2.3.3 General Procedure of Recrystallizing

- Select the most desirable solvent.
- Add the determined volume of solvent to the flask (no more than two-thirds the volume of the flask) and heat. Add a few boiling stones if required.
- Add the minimum amount of hot solvent to the solute slowly to dissolve it. Boil, if necessary, to dissolve all the solute.
- Preheat the filter funnel to prevent crystallization of the solids in the funnel.
- Filter the boiling solution through the preheated funnel. Add the solution in small increments and keep the filtrate hot and in a state of reflux to prevent premature crystallization. Steam baths are suitable for those solvents that have a boiling point lower than 100 °C.
- Collect the filtrate in a flask; allow it to stand and cool. Cool or chill rapidly in a cooling bath for small crystals, but cool slowly to get large crystals.
- Isolate the crystals by gravity or suction filtration. Concentrate the mother liquor to get more crystals.
- Dry the crystals in a warm oven or better in the desiccator because overheating in the oven may melt down the crystals.

12.2.3.4 Decolorization

Colored contaminants may sometimes be removed by adding finely powdered decolorizing charcoal, which adsorbs the contaminants. Soluble contaminants, not adsorbed, remain in solution in the mother liquor filtrate. Decolorization can be achieved as follows:

- Place the substance to be purified in a suitably sized flask.
- Add a determined volume of solvent.
- Add decolorizing carbon, 1% by weight of solute, if needed.
- Boil until all crystals have dissolved.
- Filter as quickly as possible through a fluted filter in the funnel. Stemless funnels are best to use because there is no stem in which crystallization can take place and clog the system. If necessary, warm the filter funnel to prevent the crystallization of hot filtrate in the funnel.

– Collect the filtrate in a flask; allow it to stand and cool.
– Dry the crystals in a warm oven.

12.3 Extraction

12.3.1 Introduction

Solutes dissolve in different solvents by different solubility rates. The process of selectively removing a solute from a mixture with a solvent is called extraction. A simple setup is shown in Figure 12.3. For successful extraction, the compound must be more soluble in the solvent than in the mixture. The solvent used for the extraction may be water, a water-miscible solvent, or a water-immiscible solvent. The selection of the solvent to be used depends upon the solute and the requirements of the experimental procedure.

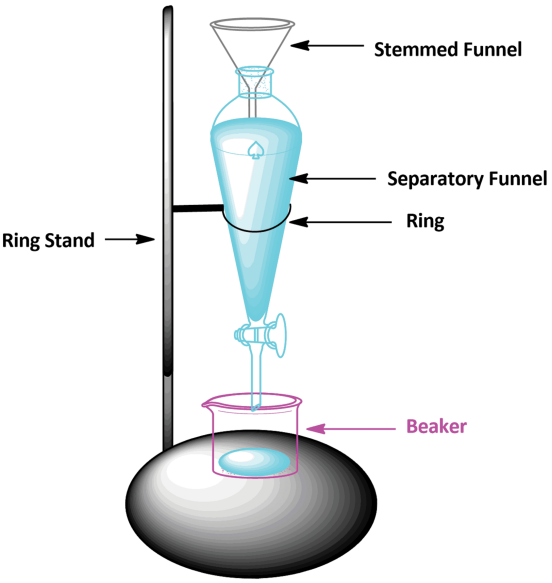

Figure 12.3: Extraction setup.

12.3.2 Extraction of Solute Using Immiscible solvents

A solute may be soluble in many solvents that are immiscible. When a solution of that solute in one of two immiscible solvents is shaken vigorously with the other immiscible solvent, the solute will be distributed between the two solvents in such

a manner that the ratio of the concentrations in moles per liter of the solute is constant. This ratio is called the distribution coefficient, and it is independent of the volumes of the two solvents and the total concentration of the solute.

This type of extraction transfers a solute from one solvent to another. It can be used to separate reaction products from reactants and to separate desired substances from others in the solution. The separatory funnel is used for this purpose. Immiscible solvents, which are incapable of mixing with each other to attain homogeneity and will separate from each other into separate phases, must be used.

Miscible solvents, which are capable of being mixed in any ratio without separation into two phases, cannot be used. Multiple extractions with smaller portions of the extraction solvent are more effective than one extraction with a large volume. The choice of the extraction solvent determines whether the solute remains in the separatory funnel or is in the solvent which is drawn off. The solvent that has the greater density will be the bottom layer and the less dense extraction solvent remains in the separatory funnel, and the denser extraction solvent is drawn off. If the extraction solvent of higher density is used, the extraction can proceed as follows:

- Use a clean separatory funnel.
- Pour the solution to be extracted into the funnel, which should be large enough to hold at least twice the total volume of the solution and the extraction solvent.
- Pour in the extraction solvent and close with the stopper.
- Shake the funnel gently.
- Invert the funnel and open the stopcock slowly to relieve the pressure built up.
- Close the stopcock while the funnel is inverted and shake again.
- Repeat steps as needed.
- Place the funnel in ring-stand support and allow the two layers of liquid to separate. Remove stopper closure.
- Open the stopcock slowly and drain off the bottom layer.
- Repeat the operation, as needed, with fresh extraction solvent as many times as desired.
- Combine the lower layers that have been drawn off.

12.3.3 Extraction Procedures in the Laboratory

Extraction procedures are used to separate and purify substances. There are three principal methods to follow.

12.3.3.1 Using Water

Water is a polar solvent, and polar substances are soluble in it; examples of such substances are inorganic salts, salts of organic acids, strong acids, and bases, low-molecular-weight compounds, carboxylic acids, alcohols, polyhydroxy compounds,

and amines. Water will extract these compounds from any immiscible organic solvents containing them.

12.3.3.2 Using Dilute Aqueous Acid Solution

Dilute hydrochloric acid (between 5% and 10% HCl) will extract basic substances such as organic amines, cyclic nitrogen-containing ring compounds, and alkaloids. The basic compound is converted to the corresponding hydrochloride, which is soluble in the aqueous solution, and therefore extracted from the immiscible organic solvent. After the acid extraction is completed, the organic solvent is extracted with water to remove any acid that might be left in the organic solvent.

12.3.3.3 Using Dilute Aqueous Basic Solution

Dilute NaOH or 5% $NaHCO_3$ will extract acidic solutes from an immiscible organic solvent by converting the acidic solute to the corresponding sodium salt solution which is soluble in water. After the basic extraction is completed, the organic solvent is extracted with water to remove any base that might be left in the organic solvent.

12.3.3.4 Considerations in the Choice of Solvent

Some characteristics of selected solvents commonly used for the extraction of aqueous solutions are presented in Table 12.2. The following points should be considered when choosing extraction solvents:

- Like substances tend to dissolve like substances.
- Organic solvents tend to dissolve organic solutes.
- Water tends to dissolve inorganic compounds and salts of organic acids and bases.
- Organic acids, soluble in organic solvents, can be extracted into water solutions by using bases such as NaOH, Na_2CO_3, or $NaHCO_3$.

12.3.3.5 Peroxides in Ethers

The safety of diethyl ether can be increased by detecting and removing any peroxides that form. Ethers tend to form peroxides upon standing, and these peroxides can cause severe and destructive explosions. Always test the ethers for peroxides before distilling them, either in concentrated solutions or purifying the ethers. This can be done by observing that the KI color changes to yellow or brown as follows:

- Prepare 10% aqueous KI solution.
- Add 1 mL of KI solution to a sample of the ether to be tested. Let the mixture stand for 1 min.
- The appearance of yellow color indicates peroxides.

Table 12.2: Some characteristics of selected solvents commonly used for extraction of aqueous solutions.

Solvent	Characteristics
Diethyl ether	Generally good solvent that absorbs 1.5% water and has a strong tendency to form peroxides. Easy to evaporate.
Methylene chloride	May form emulsions; is easily dried.
Petroleum ether	Can be easily dried but poor solvent for polar compounds.
Benzene	Tends to form emulsions.
Ethyl acetate	Good for polar compounds and absorbs large amounts of water.
2-Butanol	Good for highly polar compounds and can be dried easily.
Tetrachloromethane	Good for nonpolar compounds and can be easily dried.
Chloroform	Can be easily dried but tends to form emulsions.
Diisopropyl ether	Tends to form peroxides.

12.3.3.6 Removal of Peroxides from Ethers

There are several convenient methods that can be used:

- Pass the ether through a column containing activated alumina. Do not allow alumina to dry out. Elute or wash the alumina with 5% aqueous $FeSO_4$.
- Store the ether over activated alumina.
- Shake ether with a concentrated $FeSO_4$ solution (100 g $FeSO_4$ + 42 mL concentrated HCl + 85 mL H_2O). Some ethers produce aldehydes when so treated. Remove them by washing with 1% $KMnO_4$ followed by 5% aqueous NaOH extraction to remove any acids formed; follow again with a water wash.
- Wash ethers with cold triethylenetetramine (make the mixture 25% by mass of ether).
- In cases of water-soluble ethers, reflux with 0.5% (by mass) CuCl and follow by distillation of the ether.

12.3.4 Breaking Emulsions

Emulsions are caused by a too small difference in the densities of the water and organic layer. They can be broken by the addition of a high-density organic solvent such as carbon tetrachloride. Pentane can also be added to reduce the density of the organic layer, if so desired, especially when the aqueous layer has a high density because of dissolved salts. This can be achieved by adding saturated NaCl or Na_2SO_4 to form salt solutions "salting." The salt dissolves in the water layer and decreases the solubility of organic liquids in it.

One or more of the following techniques may also be of value in breaking emulsions:

- Add a few drops of silicone defoamer.
- Add a few drops of dilute acid (if permissible).
- Place the emulsion in a suitable centrifuge tube and centrifuge until the emulsion is broken.
- Filter by gravity or with a Buchner funnel (using an aspirator or pump, for higher vacuum).
- Add a few drops of a detergent solution.
- Allow the emulsion to stand for a time.
- Place the emulsion in a freezer.

12.4 Distillation

12.4.1 Introduction

Distillation is heating a liquid to form vapors that can be cooled and then collected and separated from the initial liquid. It can also be defined as the process of separating the components of a mixture based on their boiling points. In both cases, the liquid is vaporized, recondensed, and collected in a container. The liquid that has remained in the flask and has not vaporized is called a residue. The resulting condensed vapor is called the distillate. This process of purifying liquids and separating one liquid from another is based on the differences in volatility.

12.4.2 Simple (Atmospheric) Distillation

An experimental setup for simple distillation is shown in Figure 12.4. The glass equipment may be standard and require corks or may have ground-glass-fitted joints.

Please check the following points for a correct setup:

- The distilling flask should be large enough to accommodate twice the volume of the liquid to be distilled.
- The thermometer bulb should be slightly below the side-arm opening of the flask to have the correct temperature reading that will not be accurate.
- The glass-to-glass or glass-to-cork connections should be firm and tight.
- The flask, condenser, and receiver should be clamped independently in their proper relative positions on a steady base.
- The upper outlet for the cooling water exiting from the condenser should point upward to keep the condenser full of water.

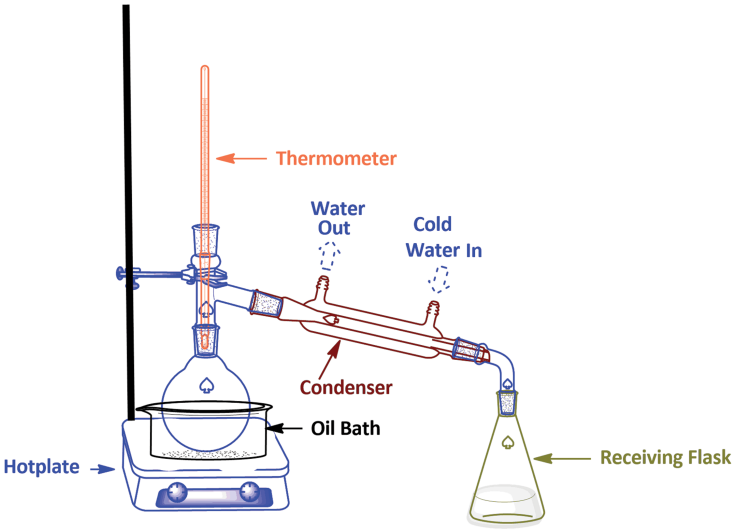

Figure 12.4: Simple (atmospheric) distillation setup.

Please check the following points for correct setup:

- The distillation flask should be large enough to hold twice the volume of the distilled liquid.
- The bulb of the thermometer should be slightly below the side opening of the bulb so that the correct temperature reading is accurate.
- Glass-to-glass or glass-to-cork connections must be strong and tight.
- The flask, condenser, and receiver must be fixed independently of each other in their respective positions on a stable base.
- The upper outlet of the cooling water leaving the condenser must be directed upward so that the condenser is filled with water.

And the below-mentioned procedure should be followed:

- Pour the liquid into the distilling flask with a funnel that extends below the side arm.
- Add a few boiling stones to prevent bumping.
- Insert the thermometer.
- Open the water valve for condenser cooling.
- Heat the distilling flask until boiling begins; adjust the heat input so that the rate of distillate is a steady two to three drops per second.
- Collect the distillate in the receiver.
- Continue distillation until only a small residue remains. Do not distill to dryness.

Distillation can be used to test the purity of liquids or to remove the solvent from a solution. The composition of the condensate should be the same as the original liquid and the same as the residue, and the boiling temperature remains constant throughout the distillation. The process affects the separation of the nonvolatile dissolved solids because they remain in the residue and the volatile liquid is distilled, condensed, and collected.

When a nonvolatile substance is in the liquid being distilled, the temperature of the distilling liquid (the head temperature) will be the same as that of the pure liquid since the vapor being condensed is uncontaminated by the impurity. The temperature of the pot liquid will be higher, because of the decreased vapor pressure of the solution containing the nonvolatile solute. The temperature of the pot liquid will continue to increase as the volatile component distills away, further lowering the vapor pressure of the solution and increasing the concentration of the solute.

When evaporating a solution to recover the solute or when using heating source to distill off large volumes of solvent to recover the solute, do not evaporate completely to dryness. The residue may be superheated and begin to decompose. If two liquids with different volatilities are to be separated, the receiver has to be changed several times during the distillation, thus collecting several portions of distillate. The first portion collected while the boiling temperature is near that of the more volatile liquid may contain that liquid with little impurity. The last portion collected when the distillation temperature is nearly equal to the boiling point of the less volatile liquid may contain that liquid and little of the other. Intermediate portions will contain both liquids in varying proportions.

12.4.3 Azeotropic Distillation

Azeotropic mixtures distill at a constant temperature without a change in composition. Simple distillation cannot separate azeotropic mixtures. For example, pure ethanol (bp 78.37 °C) cannot be obtained by fractional distillation of aqueous solutions that contain less than 95.5% of ethanol because this is the azeotropic composition; the boiling point of this azeotropic mixture is 0.30 lower than that of pure ethanol. Absolute ethyl alcohol can be obtained by distilling azeotropic 95.5% ethyl alcohol with benzene. The water is removed in the volatile azeotrope formed.

12.4.4 Fractional Distillation

Fractional distillation is a physical separation method based on the difference in boiling points of two or more components. By noting the boiling point of collected fractions and other physical properties, fractional distillation can also be used to identify components in a solution of unknown composition.

In a mixture of the two components, the low-boiling component will first rise to the top of the column and will eventually be replaced by the high-boiling component. If the fractionation column provides good separation, the low-boiling component will leave the column at a constant temperature. Then the second component of the higher boiling will come off from the column at a constant temperature.

A simple setup is shown in Figure 12.5. A fractionating column is essentially an apparatus for performing a large number of successive distillations without the necessity of actually collecting and redistilling the various fractions. Fractional distillation can be run as follows:

- Select the type of fractionating column to be used.
- Set up the equipment.
- Open the inlet cooling-water valve.
- Apply heat.
- Keep a large volume of liquid condensate continually returning through the column.
- Distill slowly to affect efficient separation.

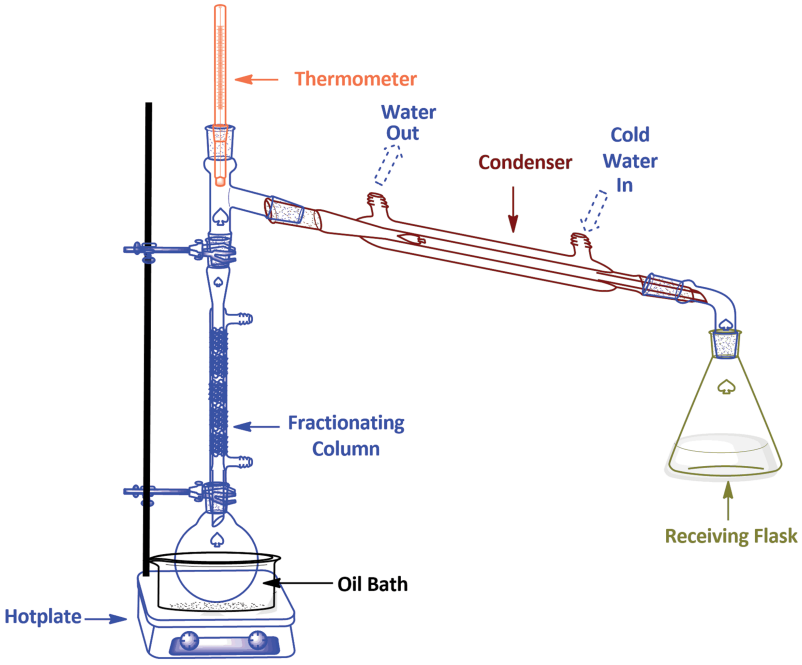

Figure 12.5: Fractional distillation setup.

12.4.5 Vacuum Distillation

Many substances cannot be satisfactorily distilled at atmospheric pressure because they are sensitive to heat and decompose before the boiling point is reached. Vacuum distillation, distillation under reduced pressure, allows distillation at much lower temperatures. The boiling point of the material is affected by the pressure in the system. The lower the pressure, the lower the boiling point, the higher the pressure, the higher the boiling point.

The setup of this kind of distillation is shown in Figure 12.6. The general requirement for the setup includes:

- Efficient vacuum sources such as water pumps can reduce the pressure in the system to the pressure of the water vapor passing through the pump. Mechanical oil vacuum pumps can also be used. Dry ice or liquid nitrogen should be used for the trap when using oil pumps.
- There is a need for safety traps to protect the manometer and the source of discharge from contamination caused by excess fluid. The trap must be connected correctly.
- A pressure gauge is also required. Air must be allowed to enter the vacuum system slowly to avoid breakage when the column of mercury rises to the top of the closed tube.
- Manostat (pressure regulator) is required to maintain constant pressure in the system, it automatically opens and closes needle valves, permitting air to enter or keeping the system airtight because of vacuum variations.
- Capillary air inlet or spin bar.
- Special vacuum distillation flasks to minimize contamination of the distillate caused by frothing of the boiling solution.
- Heating baths or electric mantles.
- Special distilling heads permit the removal of distillate fractions without interrupting the distillation.

12.4.6 Steam Distillation

Steam distillation deals with the separation and purification of organic compounds by volatilization. The organic compound should be insoluble or slightly soluble in water. When the steam is passed into a mixture of compound and water, the compound will vaporize. In the distillate, this distilled compound separates from the condensed water because it is insoluble in water. Most compounds distill by steam distillation at a temperature below that of pure boiling water. Some high-boiling compounds decompose at their boiling point. Such substances can be successfully

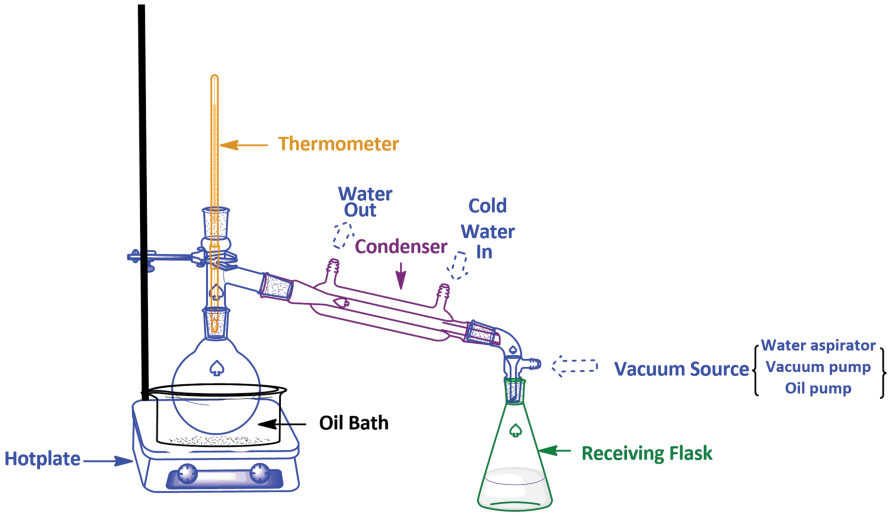

Figure 12.6: Vacuum distillation setup.

distilled at low temperatures by steam distillation. The steam distillation setup is shown in Figure 12.7. Steam distillation can be done as follows:

- Place the compound or mixture in the distilling flask with a little water. Pass cooling water through the condenser. A Claisen flask may be substituted for the round-bottomed flask. The Claisen still head helps to prevent any contamination of the distillate caused by spattering of the steam-distilled mixture. If there is no readily available source of piped steam, the steam can be generated in an external steam generator and then passed into the mixture to be steam-distilled.
- Pass steam into the distilling flask with the steam outlet below the surface of the liquid. The distilling flask itself may be heated gently with a burner. If steam is available from a laboratory steam line, insert a water trap in the entering steam line to trap condensed water. Otherwise, the condensed water may fill up the distilling flask.
- Continue passing steam into the flask until no appreciable amount of water-insoluble material appears in the condensate.

12.5 Refluxing

Reflux involves heating a chemical reaction for a period of time, while constantly cooling the steam produced back to liquid form, using a condenser. The vapors produced above the reaction condense constantly, returning to the flask as a condensate. In this way, the reaction temperature always remains constant. The temperature at

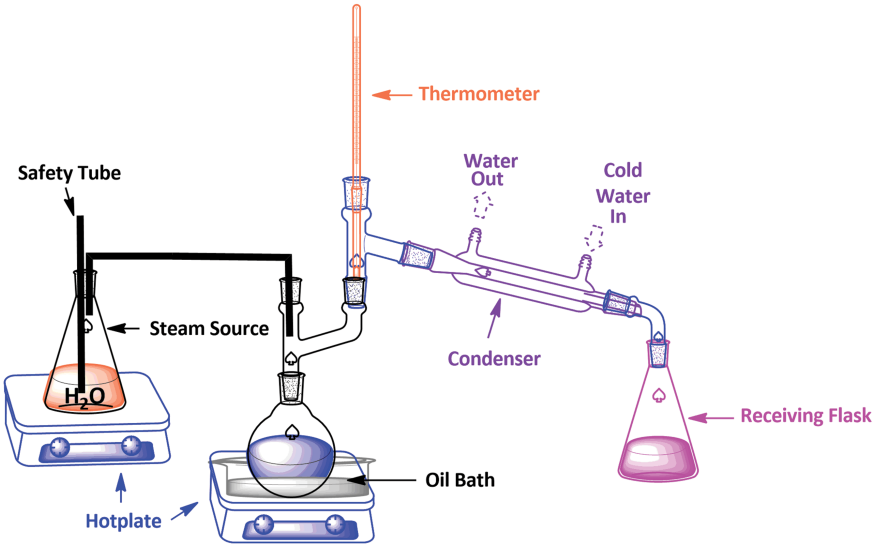

Figure 12.7: Steam distillation setup.

which the reaction is heated depends on the boiling point of the solvent. The general setting for reflux mixtures is shown in Figure 12.8.

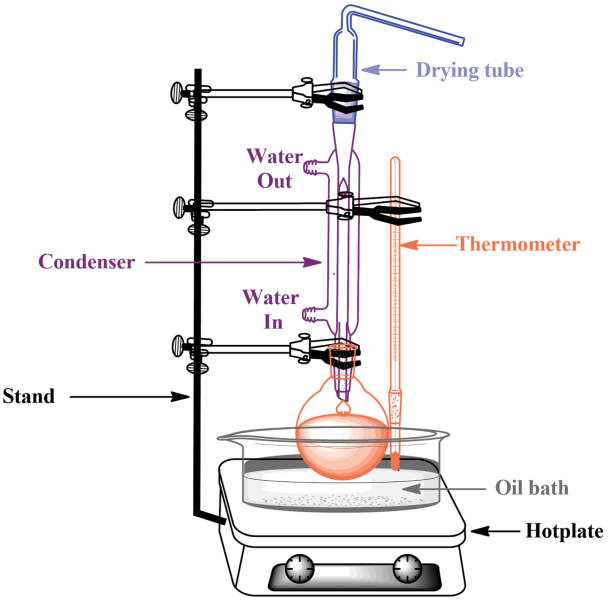

Figure 12.8: General setup for refluxing mixtures or solvents.

The reflux procedure allows you to heat a reaction mixture for an extended period of time without loss of solvent. The condenser, which is fixed in a vertical position directly above the heated flask, condenses all vapors to liquid so that the volume of liquid remains constant. Refluxing is also used for drying solvents over hydrides to get anhydrous solvents that are required for certain sensitive reactions. It can be carried out as follows:

- The water inlet to the condenser is the lower one. The water outlet to the condenser is the upper one.
- Fill the heating flask not more than half full and add a few boiling stones.
- Turn on the cooling water.
- Heat to reflux for the desired period of time.

12.6 Evaporation

Evaporation of solvents is necessary at times to concentrate solutions and to obtain crystallization of solutes.

Evaporation of small volumes can be done as follows:

- Pour the small volume of solution into the watch glass (or evaporating dish) placed over a beaker of water.
- Boil the water. The heat transfer through the steam formed evaporates the solvent of the solution.

Evaporation of large volumes can be done as follows:

- Pour the solution that is to be concentrated by boiling off solvent into a suitably sized beaker that is covered by a watch glass resting on glass hooks.
- Heat the solution to evaporate the solvent.

12.7 Rotary Evaporator

Rotary evaporators provide a very rapid means to evaporate solvents and concentrate solutions. The flask rotates while the system is under vacuum providing a very large surface area for evaporation. The walls of the flask are constantly rewetted as the flask rotates, minimizing superheating and bumping. Heat is supplied to the flask by a steam bath, oil bath, heating mantle, or other heat sources to meet the need. Rotary evaporators can be used for evaporation and vacuum drying of powders and solids, and for low-temperature distillation of heat-sensitive substances. Substances can be degassed and distilled under inert atmospheres. The rotating flask ensures good mixing and good heat transfer from the heating bath.

12.8 Sublimation

The vapor pressure of solids increases as the temperature increases, and because of this, some solids can go from the solid to the vapor state without passing through the liquid state. This phenomenon is called sublimation. Simple description of this technique is shown in Figure 12.9. The process can be used for purifying solids if the impurities in the solids have a much lower vapor pressure than that of the desired compound. The advantages of sublimation as a purification method are:

- It does not require any solvent.
- It is faster than crystallization for purification.
- It can remove more volatile impurities from the desired substance.
- Nonvolatile or less volatile solids can be separated from more volatile materials.

The disadvantage of sublimation as a purification method is that the process is not as selective as crystallization because the vapor pressures of the sublime solids may be very close together. Sublimation can be done as follows:

- Place 1 g dry crude material (e.g., naphthalene) in a small dry beaker. Put on the top of the beaker a round bottom flask that is smaller than the largest diameter of the beaker and contains ice for cooling (**A**) as shown in Figure 12.9.
- Heat the beaker gently so that the material in the beaker receives a steady uniform supply of heat. The material vaporizes and the vapor passes up into the cold surface of the round bottom flask here it cools and condenses as a fine crystal (**B**).
- Stop heating and let the system cool for a while (**C**).
- Then collect the pure crystals formed on dry clean watch glass or filter paper (**D**).

12.9 Freeze-Drying

Freeze-drying is a process in which drying is done under low temperature and vacuum. The sample's water is turned into ice and then removed as vapor. This drying is carried out under a vacuum and without going through the liquid phase. The main advantage of freeze-drying is that samples are always kept at lower temperatures and kept frozen during the entire drying process to prevent thermal breakdown. By drying the water through this technique, the dried product can be stored safely for long periods without risk.

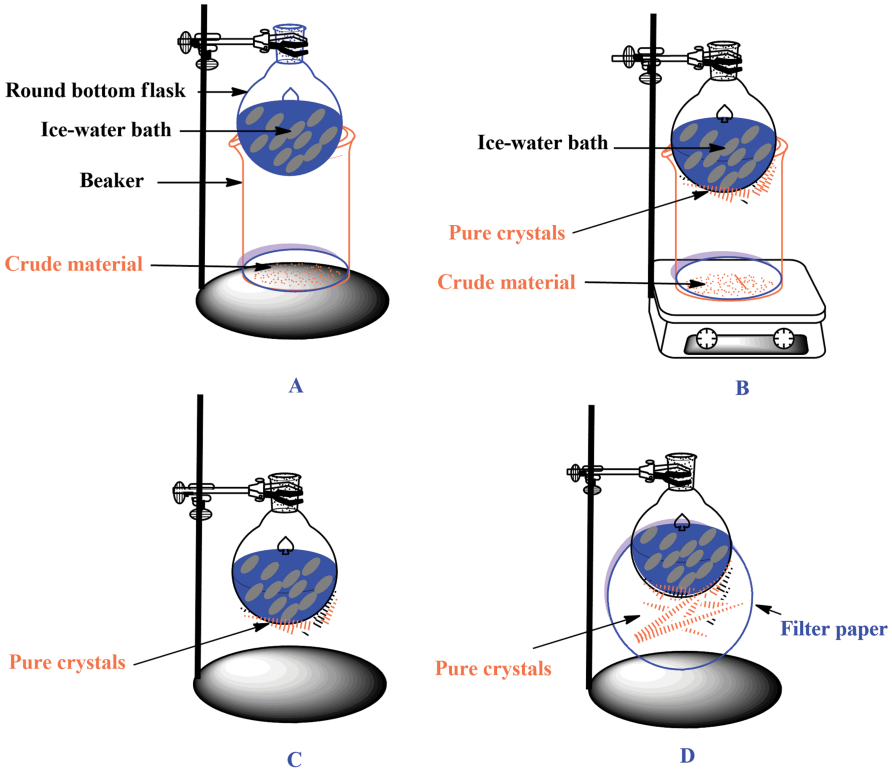

Figure 12.9: Sublimation.

The freeze-drying, also known as lyophilization, process differs from other dehydration techniques by taking place while the product is in a solid state and under a vacuum. Under these conditions, the product is stabilized, and degradation is minimized. Due to the above-mentioned advantages, freeze-drying has become a method of choice for processing and storing heat-sensitive products. Regardless of the usages of the freeze-drying process, there are four basic steps that are summarized in Figure 12.10.

Figure 12.10: The four basic steps of the freeze-drying process.

Chapter 13
Good Laboratory Practice

13.1 Introduction

Good laboratory practice, GLP, is a compilation of procedures and practices designed to promote the quality and the validity of all laboratory studies.

Good Manufacturing Practice, GMP, was developed long before GLP and regulates the manufacturing and associated quality control of products. However, GMP did not address all areas of quality assurance, such as laboratory research, archiving test samples and data, and the validation of equipment and methods.

13.2 What Is ISO 9000?

The International Organization for Standardization, abbreviated ISO, based in Geneva, Switzerland, issued a series of ISO 9000 standards in 1987. ISO 9000 is a set of five individual international standards for quality management and quality assurance. They cover all aspects of the company's business, from research to sales and services:

ISO 9000	is a common or basic standard.
ISO 9001	provides quality assurance in the design, manufacture, and supply of products or services. It is the most comprehensive of all the standards and covers all the requirements found in ISO 9002 and ISO 9003.
ISO 9002	is a model for quality assurance in production and installation, but not for research and development.
ISO 9003	is a model for quality assurance when only final inspection and testing are required.
ISO 9004	is a model that deals with guidelines for the development of quality management.

Adoption of the ISO 9000 system requires that a manufacturer must have documentation for managing an effective quality system. Documentation should be legible, readily identifiable, easily accessible, and include revision dates. All out-of-date documentation should be removed and disposed of according to the set procedures.

13.3 Common Deficiencies at ISO 9000 GLP Audit

Documents

- Unapproved
- Procedures not corresponding to practice
- Documents not located according to the distribution record

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- Approved suppliers list incomplete (ISO 9000 only)
- Product release protocol faulty

Equipment
- New/alternate equipment not qualified
- Calibration incomplete
- Performance measurement inadequate
- Inadequate response to *"Exceptions"*

Material
- Inadequate or no identification
- Material from unapproved sources
- Material in poor condition
- Inadequate shelf-life control
- Inspection status not clear
- Nonconforming material not controlled

People
- Not trained
- Unaware of requirements
- Nonconforming with documented requirements
- Training program or records are inadequate
- Organization or responsibilities nonconforming

Administration
- Methodology incomplete or inconsistent
- Nonconformance not dealt with (not identified, not documented, and/or not communicated)
- Corrective action not identified or specified, action slow or not documented
- Management reviews ineffective or infrequent
- Deviation from documented procedures
- Records incomplete or disorganized

13.4 Chemical Tracking and Inventory

The proper labeling of both chemicals and samples is extremely important. Labels should be clearly legible and permanent. Proper labeling will:
- assist in compliance with regulatory requirements, such as hazard communication and chemical waste disposal;
- reduce the need for identification and analysis prior to disposal or reuse;

- allow surplus quantities to be reused rather than requiring disposal because they are unknown;
- decrease the risks of accidents and injuries from improper handling or storage;
- assist with the overall management of chemical waste and inventory;
- track samples from initial receiving to proper storage in the archives.

A chemical tracking and inventory system that includes a program of comprehensive chemical waste minimization is absolutely necessary for modern chemical processing industries. The system can include information about the kinds, quantities, location, and status of chemicals within a particular facility. Tracking a chemical from purchase to disposal can benefit any organization by reducing duplicate purchases and perhaps reusing waste chemicals. By allowing redistribution of surplus materials, careful inventory control also minimizes the waste generated from partially used containers of chemicals. These partially used chemicals can present a real hazard associated with shelf-life degradation, which can increase the cost of proper storage and disposal. Some laboratories use data networks, tailored to the needs and resources of the respective facility.

The costs of the computer hardware and software needed for such a system have dropped dramatically over the last decade and may well offset the cost of excess chemical disposal and poor inventory practices.

There are a number of standard systems that utilize a barcoding system for chemical tracking and inventory control. Costs can be further controlled by linking chemical purchasing requests into the computerized inventory system so that orders can sometimes be filled with surplus chemicals. Some major chemical suppliers provide electronic access to their catalogs. Safety information can be added to the inventory system to promote the proper handling of chemicals and to aid in compliance with hazard communication and waste management regulations. For example, laboratory personnel who request a chemical could be supplied with the hazard information contained in its MSDS.

A computerized system that can maintain records of materials destined for disposal can be very useful. For example, this system could also maintain records showing that significant quantities of a particular chemical may have been discarded on a regular basis, which would indicate that combined purchases along with the in-house redistribution of the chemical may provide considerable cost savings.

13.4.1 Barcoding

A barcode is a series of thin and thick lines or bars printed on a lighter background. A barcode reader can translate the series of bars into a string of digits, letters, or ASCII characters. Currently, more than 30 different standardized barcodes are in

use. Chemical and sample barcode inventory systems have proven to be effective in some facilities-particularly when a centralized storage and data management system is utilized. The barcode system used in chemical management is similar to the Universal Product Code systems used in most commercial products. This system allows tracking of the sample as it moves throughout the organization.

A computer inventory can then be made available to laboratory workers, who may search the database by chemical formula, chemical name, trade name, and location of the container.

Several barcodes are currently in wide industrial use; for example, barcode system number 49 is useful for labeling very small packages such as medicine vials. Code 49 is not very practical for chemical laboratories because it stacks the numbers into three rows, and the code cannot be scanned by hand with a wand or other fixed-beam device and thus requires a more expensive laser scanner. Barcode 39 is currently the most popular barcode used in laboratories. Laboratories can simply purchase preprinted labels or computer software that will print barcodes on dot-matrix or laser printers.

13.4.2 Barcode Readers

A barcode reader is a hardware device that can read barcodes and transfer the data from the code to a computer. Some advantages of preprinted barcode labels are that they are guaranteed to have no duplicates within a numerical sequence and are more durable. If you print your labels, you must use software to ensure that no duplicates are accidentally printed. If your laboratory requires a large volume of labels that will last for 8 or more years or that will withstand harsh environments, it needs preprinted, laminated labels. These labels are printed and laminated with a plastic seal that allows them to last for many years. Laboratories can also purchase laminated label printers. Several manufacturers sell a device that prints and applies barcode labels on irregularly shaped containers such as test tubes and vials.

Two methods exist for reading barcodes. One method uses fixed-beam devices such as wands, swipe readers, and charge-coupled device scanners that emit a focused light beam that users pass over the barcode.

The other method uses gun-type readers that have a moving beam of light source that automatically sweeps across the stripes of the barcode. A wand reader looks like a pen. Its tip must be in actual contact with the surface as it moves over the stripes of the barcode. The optical sensor at the end of the wand sends the signal to a decoder and then transfers the decoded data to the computer.

13.5 The Laboratory Notebook

The laboratory notebook is another place where all the information is written by matter experts. A complete laboratory notebook should contain the following:

- Table of contents
- Testing or verifying name and number (if applicable)
- Dates
- Goals
- Data, including categories
- Calculating and calculating the formulas used
- Drawer for tools or setups, if selected
- Results
- Summary and/or conclusion
- Technician and/or manager signatures

The above laboratory notebook guide is provided with all the rules. Each company or manufacturer will have its own laboratory manual systems and formats. The notebook is a diary and an expert record. All data are recorded directly in the notebook as they are retrieved. Data should not be recorded on lost papers because there may be cases where a notebook can play an important role in a court decision.

Many cases have been won or lost because of the credibility of the data contained in a laboratory notebook. Therefore, it is extremely important that the following rules be observed:

- The laboratory notebook should be a numbered, permanently bound book, preferably with automatic carbon or other duplication methods. The pages should be consecutively numbered, and no original pages should ever be removed. The data should be recorded in waterproof or permanent ink, never pencil. The technician should also prepare a duplicate notebook that may be kept at the technician's disposal for ready reference. The original bound book can be placed in the proper place for security and ready reference for all other members of the staff. The cover of each record book should indicate the dates of the first and last entries made in that volume.
- All available information must be included no matter how small the information.
- Each page must be drafted and signed by the professional and administrator.
- The purpose of the process should be stated on the first page of the sequence of pages used.
- A diagram of the apparatus or equipment to be used should be sketched, followed by a short summation of the procedure to be followed.
- All data should be entered into the notebook immediately. All raw data should be recorded neatly and directly in the notebook. Mistakes should be "lined through" and remain legible. Mistakes should never be erased or totally obscured.

- Entries should always be specific. The technician should never generalize so as to minimize questions in the future. One of the main purposes of a record book is to enable duplication of what has been done, and the omission of relevant data can cause needless delays and costly repetitive work.
- Information obtained from automatic recording devices, such as charts, should be noted and recorded in the notebook with the appropriate reference indexed on the charts or recording paper for easy retrieval when needed. Charts and graphs can then be stored in separate, appropriate, secure locations.
- Calculations of raw data that are carried out on other paper or on a calculator must be recorded in the laboratory notebook with the results. All calculations should be checked by either the person who performs the work or a competent coworker.
- It should be understood that if raw data entries are transferred to a computer database, electronically stored neither data nor its hard copies can be considered legal substitutes for the original notebook data entries. If raw data are captured directly by a computer such as a chromatographic system connected directly to a computer, the laboratory may elect to treat the electronic data or hard copy printout as raw data. If the magnetic media are treated as raw data, the laboratory must retain the ability to display these data in a readable form for the entire period required by the appropriate agencies.
- Calculated results such as theoretical yield, limiting reagent, and percent yield should be included on reaction or synthesis-type experiments and recorded in the laboratory notebook.
- Include all pertinent physical, chemical, and safety information in the notebook. In most cases, this information should be gathered before the experiment is started.

13.6 Laboratory Statistics

Statistics are an absolute necessity in all scientific measurements for determining the accuracy and precision of data. Many new and specific mathematical terms are encountered in the study of statistics. For example, in the laboratory, accuracy means the “correctness” of a given analysis, while precision indicates the “reproducibility” of an analytical procedure.

A major source of error in laboratory results can be the sampling procedure itself. The question to be asked is: Does the laboratory sample truly represent the material being tested? Many professional societies and governmental agencies have very specific instructions on obtaining, preparing, and storing representative samples.

13.6.1 Statistical Terminology

Absolute error. The difference between the true value and the measured value, with the algebraic sign indicating whether the measured value is above (+) or below (–) the true value.

Relative error. The absolute error is divided by the true value and is usually expressed as a percentage.

Indeterminate errors. Random errors result from uncontrolled variables in an experiment that cannot be determined normally due to the lack of a single source.

Determinate errors. Errors that can be ascribed to a particular cause are usually determined as being personal, instrumental, or method uncertainties.

Mean (m). An average is obtained by adding together the numerical values of analysis and dividing this sum by the number *n* of measurements.

Median. This is the middle value in an increasing or decreasing series of data. The advantage of the median over the mean is that the median will always be one of the actual measurements.

Mode. A measurement value that appears most frequently in the series of values.

Deviation. A measurement that defines how much each measured value differs from the mean.

Relative deviation (d_R). A measurement that relates the deviation to the mean in order to indicate the magnitude of the variance. If the mean is a rather large number, then the deviation is not as critical as it would be in the case of a smaller mean.

Average deviation (d_A). The precision of all the measurements is calculated by dividing the sum of all the individual deviations (*dx*, *dy*, *dz*, etc.) by the number *n* of deviations calculated.

Standard deviation (d_S). A deviation-averaging technique that indicates *confidence limits*, or the *confidence interval*, for analyzing all data.

13.6.2 Quality Control

Statistics are not only useful for plotting graphs and rejecting unreliable laboratory statistics data, but they are also routinely used in laboratory quality control programs. Control samples are routinely analyzed along with all other laboratory samples. These standards, or *control samples*, have usually been analyzed many times or have been purchased as a standard from a commercial source. The laboratory management establishes a confidence level (e.g., three standard deviations) within which these control samples must fall, and a daily plot is maintained of the analytical results. With the central line normally representing the known concentration of the control, these *quality control charts* will indicate any sudden or even gradual trend

from which the analytical results deviate. These control charts are also used in interlaboratory comparisons and auditing.

13.6.3 Rejection of Laboratory Data

A wide variety of statistical tests have been developed to determine whether data should be retained or rejected. The Dixon's Q test is one of the more popular methods and is useful even with a limited quantity of data.

The ratio Q is calculated by arranging all data in increasing order and determining the difference between the questionable number and its nearest neighbor. This difference is then divided by the range (highest number minus lowest number) of all the experimental data as shown by the following equation:

$$Q = \frac{\text{difference}}{\text{range}}$$

This calculated ratio Q is compared to the standard table values of Q at a 90% confidence level for varying numbers of observations as shown in Table 13.1.

If the calculated Q ratio is equal to or exceeds the tabulated value for a given number of observations, the measurement is discarded. For example, the following calcium ion results were obtained from a water sample analysis: 203, 204, 207, 206, 205, and 214 mg/L. Should the last result (214 mg/L) be discarded? The questionable observation differs from its nearest neighbor, 207 mg/L, by 7 mg/L. The range in this experiment is from 214 to 203 mg/L, or 11 mg/L; Q would calculate to be 7/11 or 0.64. According to Table 13.1, the tabulated value for six observations is 0.56. Since the calculated Q (0.64) is greater than the tabulated value for six observations (0.56), the questionable number should be rejected.

Table 13.1: The rejection quotients (Q) at the 90% confidence limit.

Number of observations	Q
3	0.94
4	0.76
5	0.64
6	0.56
7	0.51
8	0.47
9	0.44
10	0.41

Chapter 14
Pressure and Vacuum

14.1 Introduction

Pressure is defined as force per unit area. Thus, the appropriate units would be pounds per square inch (lb/in^2 or psi) and, in the SI system, the pascal (Pa) or newton per square meter (N/m). The SI unit of force equals the SI unit of mass times the SI unit of acceleration (kg · m/s^2) and is called the newton.

14.2 Measuring Atmospheric Pressure

14.2.1 Mercury Barometer

Atmospheric pressure is measured by a barometer, shown in Figure 14.1, which measures the weight of the air above the instrument. In a mercury barometer, the mercury will drop, forming a vacuum over the mercury, until the weight of the mercury column is fully counteracted by the pressure of the surrounding air.

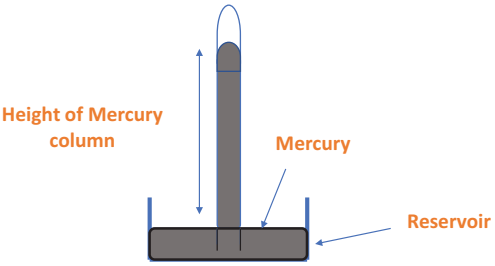

Figure 14.1: Simple mercury barometer diagram.

14.2.2 Aneroid Barometer

Atmospheric pressure can also be measured with a simple device called an aneroid barometer, shown in Figure 14.2, which has a thinly removed cylinder made of very thin metal, enclosed in a circle, and adjusted to the center.

Inside the pressure is a spring that prevents the total drop of pressure. As atmospheric pressure increases, pushing on gravity, lever, and coupling mechanisms enhance movement toward the point of view on the calibrated scale. When the pressure decreases in the spring, the bells increase, and again the movement is directed to the

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pointer. This type of barometer is not exactly like a mercury barometer, which should be used to perform a specific work.

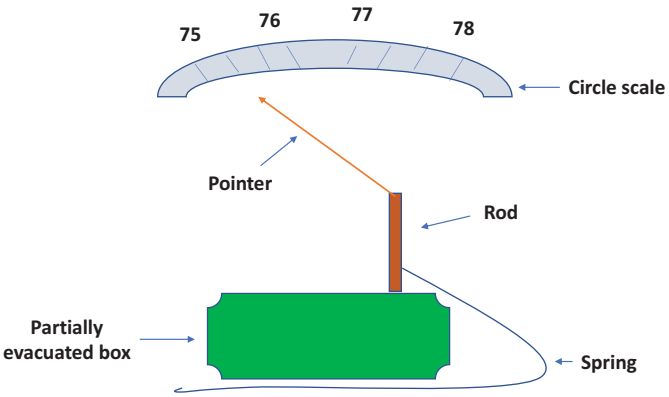

Figure 14.2: Aneroid barometer diagram.

14.3 Gas Laws

Boyle's law states that the pressure (P) of ideal gas times its volume (V) gives a constant value if the temperature (T) is held constant:

$$PV = \text{constant } (T \text{ constant})$$

Charles' law states that the volume (V) of a given mass of gas is proportional to its temperature (T) expressed in Kelvin:

$$V \propto T \ (T \text{ in Kelvin})$$

Gay-Lussac's law states that the pressure *(P)* of any gas changes directly as the temperature (T) changes if the volume is held constant:

$$P \propto T \ (V \text{ constant})$$

Avogadro's law states that equal volumes (V) of gases at the same temperature (T) and pressure (P) contain equal numbers of molecules. If standard temperature and pressure conditions (STP) of 0 °C (273 K) and 1 atm are used, then Avogadro's law can be restated as 1 mol of any gas at STP occupies 22.4 L.
Dalton's law states that the total pressure of a gas mixture is the sum of the pressures from the individual gases under the same conditions:

$$P_{\text{total}} = P_1 + P_2 + P_3 + \ldots$$

Ideal gas law is a mathematical application of Avogadro's law, which provides a means for calculating the pressure, temperature, volume, or moles of any ideal gas:

$$PV = nRT$$

where P is the pressure of the gas in atmosphere units, V is the volume of the gas expressed in liters, n is the number of moles of the gas, T is the temperature of the gas in Kelvin, and R is the *ideal gas constant* ($0.08206\ \text{L} \cdot \text{atm/mol} \cdot \text{K}$).

Pascal's law states that in a confined fluid, any externally applied pressure is transmitted equally in all directions.

14.4 Vacuum

A vacuum is considered a space that contains relatively few molecules. There is no absolute vacuum; every substance does exert a definite vapor pressure. Generally, a vacuum is a state of reduced atmospheric pressure, i.e., some point below normal atmospheric pressure.

14.4.1 Sources of Vacuum in the Laboratory

There are three sources to produce a vacuum in the laboratory:
- The water aspirator
- The mechanical vacuum pump, a rotary pump
- The vapor-diffusion pump

14.4.1.1 The Water Aspirator

The water aspirator, shown in Figure 14.3, is the most commonly used medium vacuum source in the laboratory because it is inexpensive and does not require heavy traps to prevent its damage. The aspirator, however, cannot provide a lower pressure than the water vapor that flows, and the pressure corresponds to the water temperature. The aspirator can be used safely as follows:
- Always insert a bottle trap between the aspirator and the apparatus under a vacuum. The water pressure may drop suddenly, and when it does, the pressure in the apparatus may become less than that of the aspirator. Water would be drawn back from the aspirator into the apparatus, causing contamination.
- Always disconnect the aspirator from the apparatus before turning off the water; otherwise, the water will be drawn back into the apparatus as described above.
- If water does backup for any reason, immediately disconnect the tubing from the aspirator.

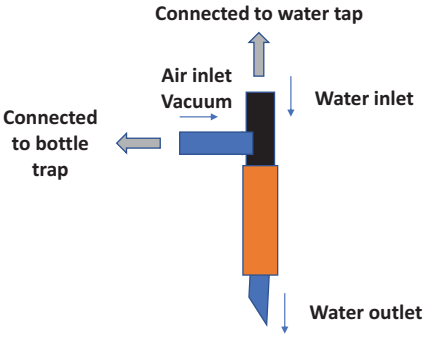

Figure 14.3: Water aspirator diagram.

14.4.1.2 The Mechanical Vacuum Pump

A mechanical pump uses a rotary vane to produce a rough vacuum (approximately 10 torr, which is slightly better than the water aspirator). This device relies on the sweeping action of multiple vanes turning within a cylindrical housing. An electric motor usually provides the driving force.

14.4.1.3 The Diffusion Pump

A vapor-diffusion pump is similar in principle to a water aspirator; the steam which entrains the undesired gases consists of a heavy vapor generated by the evaporation of pump oil. The pump oil vapor is condensed after serving this purpose and is returned to the boiling pot, thus comprising a closed cycle.

Chapter 15
Chemicals, Reagents, and Preparation of Solutions

15.1 Introduction

Preparation of solutions that are needed for different experiments in the laboratory is part of the chemist or the technician's job. It is important that directions be followed exactly and that all cautions are observed. Labels should always be rechecked to avoid the misuse of chemicals because the use of wrong chemicals can ruin the experiment.

15.2 Grades of Purity of Chemicals

Chemicals are manufactured in varying degrees of purity. Select the grade of chemical that meets the need of the work to be done. It is wasteful to use costly reagent grades when technical grades would be satisfactory. The various grades are listed and explained below.

15.2.1 Commercial or Technical Grade

This grade is used industrially but is generally unsuitable for laboratory reagents because of the presence of many impurities.

15.2.2 Practical Grade

This grade does contain impurities, but it is usually pure enough for most organic preparations. It may contain some of the intermediates resulting from its preparation.

15.2.3 USP

USP-grade chemicals are pure enough to pass certain tests prescribed in the U.S. Pharmacopeia (UPS) and are acceptable for drug use, although there may be some impurities that have not been tested for. This grade is generally acceptable for most laboratory purposes.

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15.2.4 CP

CP stands for chemically pure. Chemicals of this grade are almost as pure as reagent-grade chemicals, but the intended use for the chemicals determines whether or not the purity is adequate for the purpose. The classification is an ambiguous one; read the label and use caution when substituting for reagent-grade chemicals.

15.2.5 Spectroscopic Grade

Solvents of special purity are required for spectrophotometry in the UV, IR, or near-IR ranges as well as in NMR spectrometry and fluorometry. Specifications of the highest order in terms of absorbance characteristics, water, and evaporation residues are given. The principal requirement of a solvent for these procedures is to have as low as possible background absorption. Most of these chemicals are accompanied by a label that states the minimum transmission at given wavelengths. Residual absorption within certain wavelengths is mainly due to the structure of the molecule.

15.2.6 Chromatography Grade

Chemicals of this grade have a minimum purity level of 99+ mol%. This is determined by gas chromatography. Each chemical is accompanied by its own chromatogram, indicating the column and parameters of the analysis, and chemicals' impurity should not exceed 0.2%.

15.2.7 Reagent Grade

Reagent-analyzed, or reagent-grade, chemicals are those that have been certified to contain impurities in concentrations below the specifications of the Committee on Analytical Reagents of the American Chemical Society. Each bottle is identified by batch number. These chemicals are used in chemical analysis.

15.2.8 Primary Standard

Substances or chemicals of this grade are sufficiently pure that they may serve as reference standards in analytical procedures. You may use them directly to prepare standard solutions by dissolving massed amounts in solvents and then diluting

them to known volumes. Primary standards must satisfy high requirements of purity; they usually contain less than 0.05% impurities.

15.3 Common Hazardous Chemicals

Consider all chemicals, reagents, and solutions as toxic substances. Many of the hazards of chemicals are not obvious or evident by smell, odor, appearance, or immediately detectable by the organs of the body.

Common chemical poisons and symptoms they induce are:

- Acids and bases: Burn and corrode the tissues.
- Alcohols: Strong depressant of CNS.
- Cyanide: Very dangerous, can cause collapse and death.
- Hydrogen cyanide and CO: May cause death (asphyxiation or asphyxia) by combining with the oxygen-carrying system in the blood.
- Hydrogen sulfide, H_2S: Inflammable, poisonous gas with the odor of rotten eggs. Very hazardous, cause collapse and death if inhaled. Low concentration may cause irritation of mucous membrane, headache, and nausea.
- Lead: Acute lead poisoning may lead to anorexia, vomiting, and permanent damage.
- Mercury: Very dangerous.
- Methyl alcohol: Dangerous to the optic nerve and may cause permanent damage and blindness.
- Silver nitrate: Contact with the skin or mucous membrane can be caustic and irritating.
- Benzene: It is extremely toxic and acts as an acute or chronic poison.
- Carbon tetrachloride (CCl_4): Exposure to CCl_4 may cause depression in the central nervous system (CNS) followed by hepatic and renal damage.
- Chloroform and dichloromethane ($CHCl_3$ and CH_2Cl_2): Act as CNS depressants and cause liver damage.

15.4 Laboratory Solutions

The solutions of chemical reagents used in the laboratory are prepared so that their concentrations or compositions are known and can be used in appropriate calculations. General definitions of selected terms related to preparation of laboratory solutions are shown in Table 15.1.

Table 15.1: General definitions of selected terms related to preparation of laboratory solutions.

Term	Definition
Solute	A substance that is dissolved or has gone into solution in a smaller amount than the solvent
Solvent	A substance that does the dissolving. It is the liquid in which a solute is dissolved to form a solution
Solution	Homogeneous system of two or more substances that may be present in varying amounts
Composition	Mass of solute per unit mass of solvent

15.4.1 Chemical Calculations and Computations for Preparation of Laboratory Solutions

Mass percent. Grams of solute per 100 g of solution, for example, 20 g of NaCl in 100 g of H_2O is a 16.66% by mass solution.

Mass NaCl = 20 g (solute)
Mass NaCl + H_2O = 20 g + 100 g = 120 g (mass of solution)
Mass percent = mass of solute/mass of total solution
20 g NaCl ÷ 120 g solution = 1 ÷ 6 = 16.66%

Volume percent. Milliliters of solute per 100 mL of solution. For example, 10 mL of ethyl alcohol plus 90 mL of H_2O is a 10% by volume solution.

Molality (m), molal concentration. The number of gram-molecular masses of solute per 1000 g of solvent. For example, a solution containing 58.44 g of NaCl per 1000 g of water is a 1 molal (1 m) solution. A solution that contained 29.22 g of NaCl in 1000 g of water would be a 0.5 m solution.

Molarity (M), molar solution. The number of gram-molecular masses of solute per liter or 1000 mL of solution. This is a concentration term. For example, if 58.44 g of NaCl is dissolved in water and the volume of the solution is 1000 mL, it is a 1 molar (1 M) solution.

Normality (N), normal solution. The solution which has a specific number of equivalent masses of the acid or base dissolved in the solution per liter. A 1 N solution contains 1 equivalent mass per liter; a 2 N solution contains 2 equivalent masses per liter, and so on.

For example, for the preparation of 3 L of 0.1 N solution of H_2SO_4 14.7 g ($0.1 \times 49 \times 3 = 14.7$ g) are required.

15.4.2 Preparation of Standard Laboratory Solutions

A list of commonly used acids, bases, and standard laboratory solutions, and their preparation is shown in Table 15.2.

Table 15.2: Commonly used acids, bases, and standard laboratory solutions, and their preparation.

Name	Formula	Molecular mass	Molarity	Preparation
Acetic acid, glacial (99.7%)	CH_3COOH	60	17.4 M	
Acetic acid, diluted			1 M	Dilute 58 mL of 17.4 M to 1 L
Hydrochloric acid, concentrated (37.2%)	HCl	36.4	12.1 M	
Hydrochloric acid, diluted			1 M	Dilute 83 mL of 12.1 M to 1 L
Nitric acid, concentrated (70%)	HNO_3	63.01	15.8 M	
Nitric acid, diluted			1 M	Dilute 63 mL of 15.8 M to 1 L
Sulfuric acid, concentrated (96.0%)	H_2SO_4	98.08	18 M	
Sulfuric acid, diluted			1 M	Dilute 56 mL of 18 M to 1 L
Phosphoric acid (85.5%)	H_3PO_4	98.00	14.8 M	
Phosphoric acid, diluted			1 M	Dilute 68 mL of 14.8 M to 1 L
Ammonium hydroxide, diluted	NH_4OH	35.05	1 M	Dissolve 35 g in water and dilute to 1 L
Potassium hydroxide, diluted	KOH	56.11	1 M	Dissolve 56 g in water and dilute to 1 L
Sodium hydroxide, diluted	NaOH	40.0	1 M	Dissolve 40 g in water and dilute to 1 L
Aluminum chloride	$Al_3{\cdot}6H_2O$	241.43	0.1 M	Dissolve 24.1 g in distilled water and dilute to 1 L
Aluminum nitrate	$Al(NO_3)_3{\cdot}9H_2O$	375.13	0.1 M	Dissolve 37.5 g $Al(NO_3)_3{\cdot}9H_2O$ in distilled water and dilute to 1 L

Table 15.2 (continued)

Name	Formula	Molecular mass	Molarity	Preparation
Aluminum sulfate	$Al_2(SO_4)_3 \cdot 18H_2O$	666.42	0.1 M	Dissolve 66.6 g $Al_2(SO_4)_3 \cdot 18H_2O$ in distilled water and dilute to 1 L
Ammonium acetate	$NH_4C_2H_3O_2$	77.08	0.1 M	Dissolve 7.7 g in distilled water and dilute to 1 L
Ammonium carbonate	$(NH_4)_2CO_3$	96.10	0.1 M	Dissolve 9.6 g $(NH_4)_2CO_3$ in distilled water and dilute to 1 L
Ammonium chloride	NH_4Cl	53.49	0.1 M	Dissolve 5.4 g NH_4Cl in distilled water and dilute to 1 L
Barium chloride	$BaCl_2 \cdot 2H_2O$	244.28	0.1 M	Dissolve 24.4 g $BaCl_2 \cdot 2H_2O$ in distilled water and dilute to 1 L
Barium hydroxide	$Ba(OH)_2 \cdot 8H_2O$	315.50	0.1 M	Dissolve 31.5 g $Ba(OH)_2 \cdot 8H_2O$ in distilled water and dilute to 1 L
Calcium acetate	$Ca(C_2H_3O_2)_2 \cdot H_2O$	176.19	0.1 M	Dissolve 17.6 g $Ca(C_2H_3O_2)_2 \cdot H_2O$ in distilled water and dilute to 1 L
Calcium chloride	$CaCl_2 \cdot 2H_2O$	147.0	0.1 M	Dissolve 14.7 g $CaCl_2 \cdot 2H_2O$ in distilled water and dilute to 1 L
Calcium hydroxide	$Ca(OH)_2$	74.10	0.1 M	Dissolve 7.4 g $Ca(OH)_2$ in distilled water and dilute to 1 L
Copper(II) chloride	$CuCl_2 \cdot 2H_2O$	170.49	0.1 M	Dissolve 17.0 g $CuCl_2 \cdot 2H_2O$ in distilled water and dilute to 1 L
Copper(II) sulfate	$CuSO_4 \cdot 5H_2O$	249.7	0.1 M	Dissolve 24.9 g $CuSO_4 \cdot 5H_2O$ in distilled water and dilute to 1 L
Iron(III) chloride 1.0 M	$FeCl_3 \cdot 6H_2O$	270.3	0.1 M	Dissolve 27.0 g $FeCl_3 \cdot 6H_2O$ in distilled water and dilute to 1 L
Magnesium chloride	$MgCl_2 \cdot 6H_2O$	203.33	0.1 M	Dissolve 20.3 g $MgCl_2 \cdot 6H_2O$ in distilled water and dilute to 1 L
Magnesium hydroxide	$Mg(OH)_2$	58.34	0.1 M	Dissolve 5.8 g $Mg(OH)_2$ in distilled water and dilute to 1 L
Potassium carbonate	K_2CO_3	138.21	0.1 M	Dissolve 13.8 g $Mg(OH)_2$ in distilled water and dilute to 1 L

Table 15.2 (continued)

Name	Formula	Molecular mass	Molarity	Preparation
Potassium chloride	KCl	74.56	0.1 M	Dissolve 7.5 g KCl in distilled water and dilute to 1 L
Potassium chromate	K_2CrO_4	194.2 g	0.1 M	Dissolve 19.4 g K_2CrO_4 in distilled water and dilute to 1 L
Potassium dichromate	$K_2Cr_2O_7$	294.22	0.1 M	Dissolve 29.4 g $K_2Cr_2O_7$ in distilled water and dilute to 1 L
Potassium permanganate	$KMnO_4$	158.04	0.1 M	Dissolve 15.8 g $KMnO_4$ in distilled water and dilute to 1 L
Sodium dichromate	$Na_2Cr_2O_7{\cdot}2H_2O$	298.03	0.1 M	Dissolve 29.8 g $Na_2Cr_2O_7{\cdot}2H_2O$ in distilled water and dilute to 1 L

Chapter 16
Determination of Physical and Other Properties

16.1 Density

The density of any given substance is calculated by dividing the mass of the substance by the volume that it occupies. Density is expressed in grams per cubic centimeter, g/cm^3, or grams per milliliter, g/mL:

$$\text{Density} = \frac{\text{mass of the substance}}{\text{volume of the substance}}$$

16.1.1 Density of Solids

Determination of regularly shaped density of solids is done as follows:
- Determine the mass of the object.
- Measure the object and obtain relevant dimensions.
- Calculate the volume, using mathematical formulas for box, sphere, or cylinder.
- Divide the mass by the volume.

Determination of irregularly shaped density of solids is done as follows:
- Determine the mass of the object.
- Determine the volume by water displacement.
  - Use a graduated cylinder containing a measured amount of water (original volume).
  - Submerge the weighed solid completely in the cylinder containing the water and record the larger volume reading (final volume).
  - Subtract the original volume from the final volume and obtain the volume of the object.
  - Divide the mass of the object by the volume.

16.1.2 Density of Liquids

Liquid densities are commonly reported at 20 or 25 °C. To determine the density, simply weigh a 1 mL vessel to the nearest milligram. Pipet, quantitatively, 1 mL of the liquid to be measured into the weighed vessel. Reweigh the vessel. Divide the net weight by the volume to determine the density of that given liquid. Different methods to determine density of liquids are described in the paragraphs to come.

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16.1.2.1 Density-Bottle Method

– Determine the weight of the dry and empty density bottle shown in Figure 16.1.

Figure 16.1: Density bottle.

– Fill the density bottle with liquid. Make sure the neck of the floor is covered by about a third.
– In a thermostatic bath, set the temperature of the bottle and contents to 20 °C.
– Align the stopper, respectively, the density bottle thermometer according to the mark and carefully insert it. The capillary tube is filled, and the displaced fluid comes out.
– Dry the surfaces of the stopper and density bottle with a tissue.
– Determine the weight of a packed density bottle.
– Calculate the density from the mass (weight) and the volume of the liquid at a reference temperature of 20 °C. The size is engraved on the bottle.
– Use the following equation: density (ρ) = mass (m)/volume (v).

16.1.2.2 Westphal Balance Method

– The balance is standardized in distilled water by immersing the entire plummet or buoy in the water and the balance is equalized by adjusting the riders. When the scale is in equilibrium by uniformity with water, it becomes ready for the unknown liquid.
– The water bowl is removed, and the plummet is carefully dried.
– Replace the fluid to be tested. Completely immerse the plummet in the liquid.
– Adjust the riders so that the beam and tire indicators are level.
– Read the density by the position of the riders.

16.1.2.3 Float Method

- Fill a beaker, graduated cylinder, or any glass container with the liquid to be tested.
- Add floats and note which float remains suspended.
- Read the density of the liquid from that float.

16.1.3 Density of Gases

All gases have a much lower density than liquids, and determining the density of a gas is more difficult due to the extremely small mass.

16.1.3.1 Dumas Method

- The volume of the flask is checked by filling it with a liquid of known density and determining the mass of the filled ball.
- The flask is emptied, cleaned, dried, and evacuated.
- The test gas is introduced into the flask and the total mass of the flask and gas is measured:

$$\text{Density of gas} = \frac{\text{mass of gas}}{\text{volume of gas}}$$

The density calculated is the density of the gas at the temperature at which the determination is made. A thermometer should be hung in the immediate vicinity and read several times during the procedure.

16.2 Specific Gravity

When metric units are used, the specific gravity has a numerical value equal to the density; of particular importance is the mass of a substance which is divided by the mass equal to the amount of water. Significant gravity is represented by a number, since it is a ratio. It has no unit:

$$\text{Specific gravity} = \frac{\text{mass of a given volume of a substance}}{\text{mass of the same volume of water}}$$

16.2.1 Pycnometer Method

- Measure the mass of a pycnometer, a calibrated-volume ground, a glass vessel fitted with a closure, and a thermometer.

- Measure the mass when the pycnometer is filled with distilled water. Subtract the mass obtained in step 1 from this value. This gives the mass of the water.
- Repeat the procedure when the pycnometer is filled with the unknown liquid. Subtract the mass obtained in step 1 from this quantity. This gives the mass of the equal volume of the unknown liquid.
- Divide the mass obtained in step 3 by the mass obtained in step 2 to get the specific gravity. (All mass measurements should be made at the same temperature.)

16.2.2 Hydrometer Method

A hydrometer is a glass container, weighted at the bottom, having a slender stem calibrated to a standard. The depth to which the container will sink in a liquid is a measure of the specific gravity of the liquid. Specific gravity is read directly from the calibrated scale on the stem of the container.

16.3 Melting Point

The melting point of a crystalline solid is the temperature at which the solid substance begins to change into a liquid. Pure organic compounds have sharp melting points. Contaminants usually lower the melting point and extend it over a long range. The temperature of the melting point and the sharpness of the melting point are criteria of purity.

The melting point range is the temperature range between which the crystals begin to collapse and melt, and the material becomes completely liquid. The majority of organic compounds melt at convenient temperatures which range from about 50 to 300 °C, and their melting points are useful aids in identifying the compounds as well as indicating their purity. Many compounds have the same melting point, yet mixtures of different compounds having the same melting point will melt at lower temperatures. This depression is a characteristic feature of mixed melting points and is extremely useful when one is trying to identify a compound; the melting point may be as much as 50 °C lower than that of the pure compound.

As a rule, samples that melt at the same temperature and whose melting point is not depressed by admixture are usually considered to be the same compound. Narrow range melting points are indicative of the relative purity of a compound. Acceptably pure compounds have a 1 °C range; normal commercially available compounds have a 2–3 °C range. Extremely pure compounds have a 0.1–0.3 °C range. A wide melting-point range indicates that the compound is impure and contaminated. Melting points can be determined as follows:

16.3.1 Capillary Tube Method

The melting points are determined in this method by introducing a tiny amount of the compound, into a small capillary tube attached to the stem of a thermometer which is centered in a hot oil bath. For substances that sublime, seal both ends of the capillary tube. Substances that tend to decompose, when the temperature is a few degrees below the melting point, put capillaries in the heating bath.

The procedure is done as follows:

- Obtain commercially available capillary tubes or make them by drawing out 12-mm soft glass tubing.
- Fill the capillary tube with the powdered compound to a height of 3–4 mm:
  - Scrape the powder into a pile.
  - Push the powder into the open end of the capillary tube.
  - Shake the powder to the bottom of the tube by tamping lightly against the desktop or by gently scraping the tube with a file. Pack tightly.
- Attach the capillary to the thermometer with a rubber band and immerse it in an oil bath.
- Heat the oil bath quickly to about 5 °C below the melting point, stirring continuously.
- Now heat slowly; raise the temperature to about 1 °C/min, mixing continuously.
- Record the temperature when fusion is observed and record the melting point range.
- Discard the capillary after the determination has been made.

16.3.2 Electric Melting Point Apparatus

This is a metal block equipped with a thermometer inserted into a close-fitting hole bored into the block, which is heated by electricity controlled by a variable transformer or a rheostat. The metal block is so constructed that the temperature reading of the thermometer indicates the temperature of the metal block on which the solid melts.

Measurement can be done by the following procedure:

- Clean the surface of the block and place a very small quantity of finely powdered material on the proper area.
- Raise the heat quickly to about 5 °C below the expected melting point of the substance, and then increase the heat slowly.
- When the determination is complete, turn off the electricity.
- Multiple melting points may be determined simultaneously.
- Always clean the metal surface carefully after each use.

16.4 Boiling Point

The boiling point of a liquid is indicated when bubbles of its vapor arise in all parts of the volume. This is the temperature at which the pressure of the saturated vapor of the liquid is equal to the pressure of the atmosphere under which the liquid boils. Normally, boiling points are determined at standard atmospheric pressure: 760 mmHg (torr) or 1 atm. The boiling point of a liquid is sensitive to atmospheric pressure and varies with it. As the pressure decreases, the boiling point will drop; at approximately normal pressure, it will drop about 0.5 °C for each 10-mm drop in pressure. At much lower pressures, close to 10 mmHg, the temperature will drop about 10 °C when the pressure is halved. There are several methods for determining boiling points. These are summarized as follows:

16.4.1 Boiling Point Determination During Distillation

When a liquid is distilled, the boiling point of the distilling liquid can be read from the thermometer in the distilling head, which is constantly in contact with the vapors.

16.4.2 Test Tube Method

- Clamp a test tube containing 2–3 mL of the compound on a stand as shown in Figure 16.2.
- Suspend a thermometer with the bulb of the thermometer above the surface of the liquid.
- Apply heat gently until the condensation ring of the boiling liquid is above the bulb of the thermometer.
- Record the temperature when the reading is constant.

16.4.3 Capillary Tube Method

Boiling points of liquids can be determined in microquantities by the capillary tube method as shown in Figure 16.3. The method can be described as follows:

- Seal one end of a piece of 5-mm glass tubing or use a small test tube.
- Attach the thermometer with a rubber band.
- Use a pipette to deliver the liquid (a few milliliters) whose boiling point is to be determined.
- Drop in a small piece of capillary tubing (sealed at one end) so that the open end is down.
- Begin heating in a beaker half-filled with mineral oil.

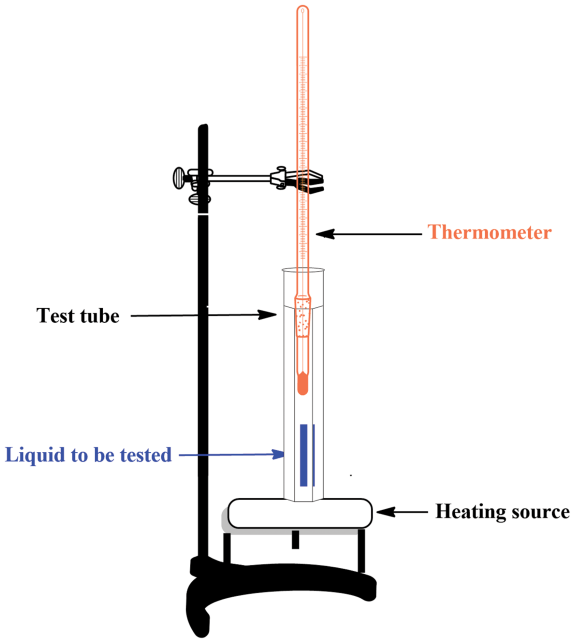

Figure 16.2: Boiling point determination by test tube method.

- Heat until a continuous, rapid, and steady flow of vapor bubbles emerges from the open end of the capillary tube, then stop heating.
- The flow of bubbles will stop, and the liquid will start to enter the capillary tube. Record this temperature as the boiling point of the sample to be tested.

16.4.4 Electronic Methods

The boiling points of very small amounts of liquid can be accurately and quickly determined with the help of electronic sensing devices using photocells. The material is placed in a special boiling point sample tube, designed to prevent superheating, and achieve smooth and continuous boiling.

The tube is illuminated from below by a dark-field light, and as long as no bubble is present (the compound does not boil), no light passes through the liquid to reach the photocell sensor.

When the boiling point is reached, the bubbles begin to grow and, when they reach the correct boiling point, they illuminate the light with the intensity and frequency required to turn on the readout indicator. Boiling points are set to 0.3 °C with extreme precision.

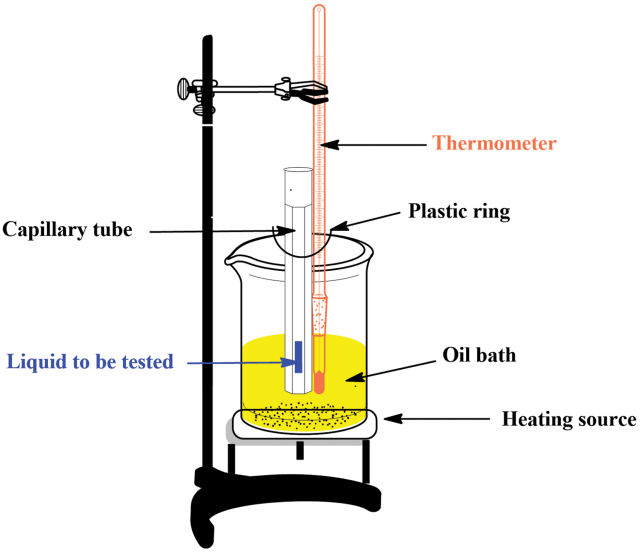

Figure 16.3: Boiling point determination by capillary tube method.

16.5 Viscosity

Viscosity arises when there is relative movement between the layers of a liquid. Viscosity can also be thought of as a measure of the thickness of a liquid or its resistance to objects passing through it. Viscosity, or internal friction, is a very important property of fluids. In the study of organic oils and liquids, viscosity is very important, because in industry, "heavier" oils and liquids have a higher viscosity and not higher densities. The unit of viscosity in the SI is the poiseuille (PI). Its other units are newton-seconds per square meter (N s m^2) or pascal seconds (Pa s.)

16.5.1 Newtonian and Non-Newtonian Fluids

If there is a linear relationship between the magnitude of the applied shear stress and the resulting deformation rate, the fluid is classified as a Newtonian fluid. Most oils fall into this category. If there is a nonlinear relationship between the magnitude of the applied shear stress and the resulting deformation rate, it is classified as a non-Newtonian fluid. Selected examples are shown in Table 16.1.

There are various experimental methods for determining viscosity. Selected methods are shown as follows:

Table 16.1: Newtonian liquids and non-Newtonian liquids.

Newtonian liquids	Non-Newtonian liquids
Oils	Synthetic oils
Solvents	Thermosetting resins
	Latex paints

16.5.2 Small-Bore Tube Method

Fluid flow through a tube of small diameter can be measured using a graduated cylinder and a stopwatch. Constant hydrostatic pressure is maintained by continuous charging and overflow. The volume of fluid passing through the capillary tube is collected in a graduated cylinder, and the required time is measured with a stopwatch:

$$\text{Coefficient of absolute viscosity} = \frac{\text{volume collected}}{\text{time}}$$

16.5.3 Saybolt Viscometer Method

The Saybolt viscometer, shown in Figure 16.4, has a container for liquids with a capacity of 60 mL, fitted with a short capillary tube of special length and diameter.

The liquid flows through the tube, under a falling head, and the time required for the liquid to pass through is measured in seconds. If the temperature is a critical factor, the viscometer is kept at a constant temperature in a temperature-controlled bath.

16.5.4 Ostwald Viscometer Method

- Wash the viscometer and make sure it is absolutely clean.
- Introduce sufficient distilled water into the large round bulb or reservoir.
- Allow the distilled water to come to thermal equilibrium in a constant- temperature bath.
- Apply suction with a rubber tube to the upper part of the viscometer. This is best done by inverting the viscometer. Draw the liquid up into the tube with the two bulbs to a level above the second bulb.
- Clock the time needed for the level of the water to pass the signal markings. Make several determinations using a stopwatch.
- Drain the viscometer and dry it completely.

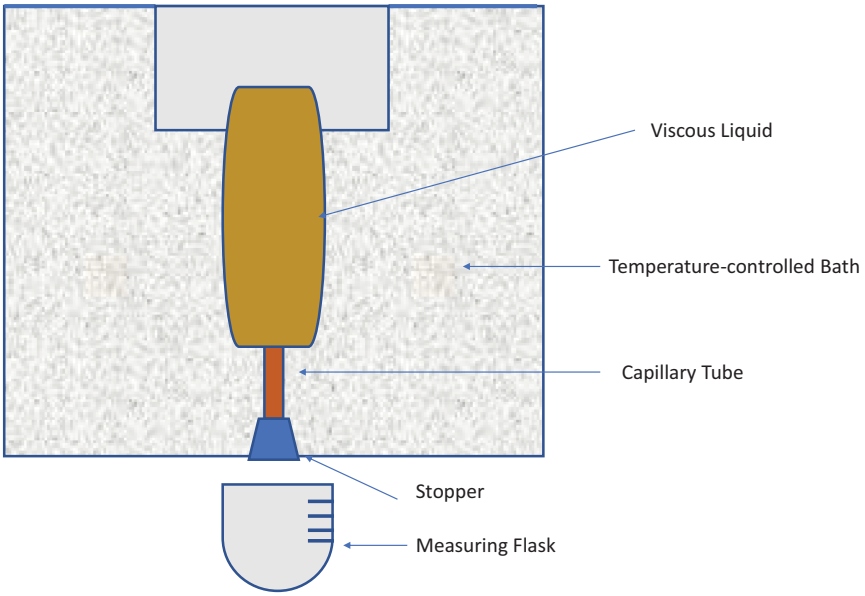

Figure 16.4: Saybolt viscometer.

- With a pipette, add an appropriate volume of the solution to be tested to the reservoir.
- Clock the time needed for the level of the liquid under test to pass the signal markings.
- Calculate the relative viscosity of the test liquid by comparing the average time required for its flow against that of water at 25 °C.

16.5.5 Viscosity Units and Conversions

Viscosity is the resistance of a fluid to flow. Fluids that cannot readily change their shape or form are said to be viscose. The dynamic unit of viscosity is the poise. Poise is the centimeter-gram-second (cgs) unit of viscosity and is defined as dyne-seconds per square centimeter:

$$\text{Poise} = \frac{\text{gram}}{\text{second} \times \text{centimeter}}$$

Kinematic viscosity is defined as the ratio of viscosity to density. The kinematic unit of viscosity is the stoke. The stoke can be calculated by dividing the viscosity expressed in poises by the density of the substance at the temperature. Units of centipoises and centistokes appear quite often in the literature and represent 0.01 poise and/or 0.01 stokes, respectively:

$$\text{Stoke} = \frac{\text{gram}}{\text{second} \times \text{centimeter} \times \text{density}} = \frac{\text{poise}}{\text{density}}$$

16.6 Methods for Determining pH

16.6.1 Colorimetric Determinations: Indicators

Hydronium-ion or hydrogen-ion concentration of a solution can be measured by adding an indicator. An acid–base indicator is a complex organic compound that has a weak acid or weak base. The molecular form of the indicator differs in color from the ionic form. Color changes are fast and inverse and occur in a pH range of 2 units. The color of the solution represents the pH of the solution. This can be done as follows:

- Choose the indicator that has a range covering the pH interval to be measured. A list of selected indicators with their preparations is shown in Table 16.2.
- Add several drops of indicator to the solution being tested.
- Compare the color of the solution with the color range of the indicator.
- Record the pH observed and determined by the color of the solution.

When color-changing indicators are used to indicate the equivalence point of acid–base titrations, the selection of the correct indicator for that particular system is most important. This is especially true when the strong acid–weak base or weak acid–strong base titrations are carried out.

16.6.2 pH Test Paper

The pH range over which the color of the indicator changes determines the correct indicator for the procedure. pH test papers are available for every value of pH. They cover both broad and narrow pH ranges. The paper is impregnated with the indicator. A strip of test paper is wetted with the liquid to be tested and then immediately compared with the standard color chart provided for each paper and range. The pH can be determined visually by a comparison of the colors.

16.6.3 pH Meter

Fortunately, in the case of hydrogen-ion measurements, a convenient and direct determination of the pH can be made with an instrument known as the pH meter (Figure 16.5).

Table 16.2: Selected indicators and their preparations.

Indicator	Acid color	Base color	Transition pH range *	Preparation
Thymol blue** (First transition)	Red	Yellow	1.2–2.8	Dissolve 0.1 g of thymol blue in 2.15 ml of 0.1 M sodium hydroxide and 20 ml of 95% ethanol then add sufficient water to produce 100 ml.
Thymol blue (Second transition)	Yellow	Blue	8.0–9.6	
Bromophenol blue	Yellow	Blue	3.0–4.6	Dissolve 5.0 g of bromophenol blue powder in 74.5 mL of 0.1 N sodium hydroxide (NaOH) solution. Dilute with water to 500 ml.
Methyl orange	Red	Yellow	3.2–4.4	Dissolve 0.1 g of methyl orange in 80 ml of water and add sufficient 95 % ethanol to produce l00 ml.
Universal Indicator	Red	Blue / Purple	4.0–10	Dissolve 0.18 g methyl red and 0.36 g phenolphthalein in 550 ml of 95% ethanol. In a separate container, dissolve 0.43 g bromothymol blue in 300 ml of distilled water. Mix the two solutions together and dilute using distilled water to a final volume of 1 L. Add 0.1 M sodium hydroxide (NaOH) dropwise until the indicator solution turns green.

Methyl red	Red	Yellow	4.8 –6.0	Dissolve 50 mg of methyl red in a mixture of 1.86 ml of 0.1 M sodium hydroxide and 50 ml of 95% ethanol then add sufficient water to produce 100 ml.
Bromothymol blue	Yellow	Blue	6.0 –7.6	Dissolve 50 mg of bromothymol blue in 4 ml of 0.02 M sodium hydroxide and 20 ml of 95% ethanol then add sufficient water to produce 100 ml.
Phenol red	Yellow	Bright pink	6.8 –8.4	Dissolve 0.1 g of phenol red in 2.82 ml of 0.1 M sodium hydroxide and 20 ml of 95% ethanol and then add sufficient water to produce 100 ml
Phenolphthalein colorless***	Colorless	Purplish red color (Bright magenta or fuchsia color)	8.2 –10	Dissolve 0.1 g of phenolphthalein in 70 mL of 95% ethanol; dilute to 100 ml with water.

** The transition range may shift slightly depending on the concentration of the indicator in the solution and on the temperature at which it is used.*
*** Thymol blue changes from red to yellow at pH 1.2–2.8 and from yellow to blue at pH 8.0–9.6.*
**** Phenolphthalein is naturally colorless but turns pink in alkaline solutions. It remains colorless throughout the range of acidic pH levels but begins to turn pink at a pH level of 8.2 and continues to a bright magenta at pH 10 and above.*

A pH meter measures the pH (acidity or basicity) of a liquid. A typical pH meter consists of a special measuring probe (a glass electrode) connected to an electronic meter that measures and displays the pH reading. pH measurement can be done as follows:

- Turn the switch on standby. Let warm for 30 min.
- Extend the electrode from the storage solution in the beaker. Always place the electrodes in distilled water when not in use.
- Rinse the electrodes thoroughly with distilled water. Wipe with an absorbent tissue.
- Standardize against an appropriate buffer solution.

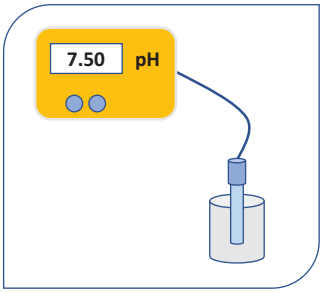

Figure 16.5: pH meter.

- Place the beaker of the solution to be tested beneath the electrodes. This is the measurement of the pH of the solution.
- Lower the electrodes carefully into the solution. Adjust the temperature compensator to the temperature of the solution.
- Rotate the selector knob to pH. Read the pH of the solution directly from the meter. Record the value.
- Once the determination is complete, switch to STANDBY, raise the electrodes, rinse the electrodes with distilled water, and store the electrodes in distilled water.

Always leave the pH meter connected to the power line at all times, except when it is not used for extended periods. This will ensure stable, drift-free performance, and the slight temperature rise will eliminate humidity troubles.

Component life will also be extended by the elimination of repeated current surges. Turn the selector switch to the balanced position when the instrument is not in use.

All pH meters must be standardized daily by means of a buffer solution of known pH value. For maximum accuracy, use a buffer in the range of the sample to be tested. A buffer solution is one that tends to remain at constant pH. For example, use a pH 4 buffer for standardizing when work is to be done in the acid range; a pH 7 buffer when the work is near neutral; and a pH 9 buffer when the work is in the alkaline range. The buffered temperature should be as close as possible to the sample temperature. Try to keep this temperature difference within 10 °C.

Chapter 17
Gravimetric Analysis

17.1 Introduction

Gravimetric analysis refers to the isolation of a specific substance from a sample and ultimately weighing the substance in a pure or known form. This substance is usually isolated by precipitating it in some insoluble form, by depositing it as a pure metal in electroplating, or by converting it into a gas which is then quantitatively absorbed. It is necessary that the sought substance be completely removed from the sample, the moisture content and other volatile components are determined, and the sample be representative of the material being analyzed.

17.2 Techniques of Representative Sampling

Sampling and analysis of raw materials and products are required to determine their purity. The size of the lot to be sampled can range from a few grams to thousands of kilograms, and yet the sample used in the analysis must represent as closely as possible the average composition of the total quantity being analyzed, and different sample sizes are shown in Figure 17.1.

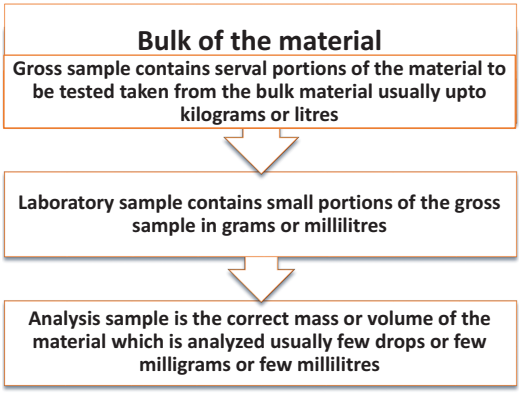

Figure 17.1: Different sample sizes.

The gross sample of the part to be analyzed is assumed to be the same in composition and particle size distribution. The laboratory size sample should represent the entire lot and should be suitable for all analytical procedures. Sampling techniques vary from one substance to another and depend on the physical characteristics of

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each particular substance. The basic sampling rules, gases, and sampling liquids are briefly presented in Figure 17.2.

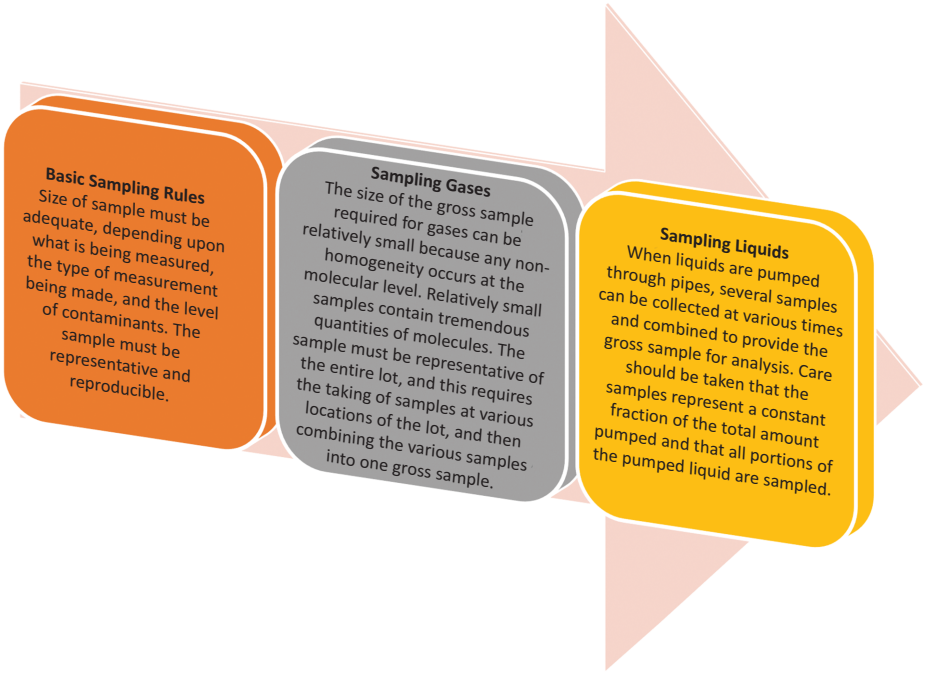

Figure 17.2: Sampling rules, sampling gases, and sampling liquids.

17.2.1 Basic Sampling Rules

- The sample size should be adequate, depending on what is being measured, the type of measurement being made, and the level of contaminants.
- The sample must be representative and reproducible; in static systems, multi-level sampling must be done.

17.2.2 Sampling Gases

The volume of the raw sample required for the gas can be relatively small because any heterogeneity can occur at the molecular level. Relatively small samples contain huge amounts of particles. The main problem is that the sample has to be representative of the entire batch, and this requires sampling with a “sample thief” at different locations in the batch and then merging different samples into a single raw sample.

17.2.3 Sampling Liquids

When fluids are pumped through tubes, a number of samples can be collected at different times and combined to provide the total sample for analysis. Care must be taken that samples represent a fixed portion of the total amount pumped and that all portions of the liquid pumped are sampled.

Homogeneous liquid solutions can be obtained relatively easily, provided the material is thoroughly mixed by agitators or cow mixers. After proper mixing, top and bottom samples can be taken and combined into a sample that is well mixed again; from this, the final sample is taken for analysis.

17.2.4 Sampling Nonhomogeneous Solids

The task of obtaining a representative sample from a lot of nonhomogeneous solids requires that:

- A gross sample is taken.
- The gross sample is reduced to a representative laboratory-sized sample.
- The sample is prepared for analysis.

17.2.4.1 Coning and Quartering

When very large quantities are sampled, a representative sample can be obtained by cone and quartering. The first sample is shaped like a cone, and the next sample is poured on top of the cone. Then the result is mixed appropriately, and a new cone is formed. As each successive sample is added to the reformed cone, the total is thoroughly mixed, and a new cone is formed before another sample is added.

After mixing all the samples by coning, the mass is flattened, and a circular layer of the substance is formed. This circular layer is then cut into quarters, and the alternate quarters are discarded. This process can be repeated as often as required until a suitable sample size for analysis is obtained (Figure 17.3).

17.2.4.2 Rolling and Quartering

A representative cone of the sample is obtained by the coning procedure, and this sample is then placed on a flexible sheet of suitable size. The cone is flattened, and then the entire mass of the sample is repeatedly rolled by pulling first one corner of the sheet over to the opposite corner, and then another corner over to its opposite corner as shown in Figure 17.4. The number of rollings required depends upon the size of the sample, the size of the particles, and the physical condition of the sample. To collect the sample, raise all four corners of the sheet simultaneously and collect the sample in the middle of the sheet.

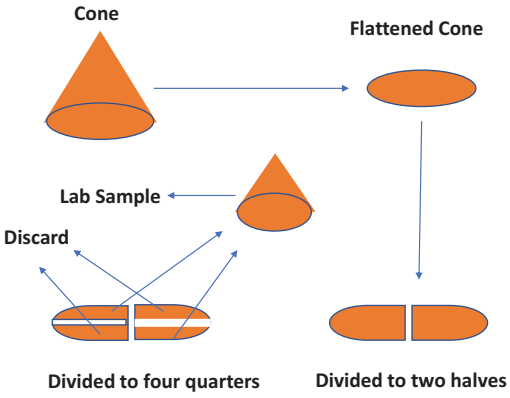

Figure 17.3: Coning and quartering.

The resulting rolled sample is flattened into a circular layer and quartered until a suitably sized sample is obtained.

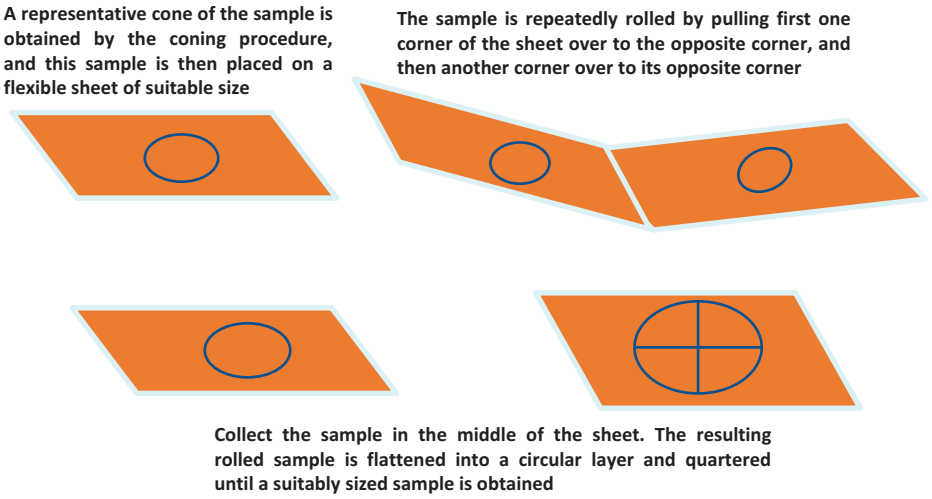

Figure 17.4: Rolling and quartering.

17.2.5 Sampling Metals

Minerals can be sampled by drilling the piece at regular intervals on all sides, making sure that each drill hole extends beyond half a point. Additional samples can be obtained by sawing the metal. All collected particles are then mixed well and quadrupled or melted in a graphite crucible to provide a sample for analysis.

17.3 Handling Samples in the Laboratory

The technician may analyze an already prepared sample or prepare a new sample that is to be tested, analyzed, or evaluated. Each sample should be completely identified, tagged, or labeled so that no question as to its origin or source can arise. Some of the information which may be on the sample is:

- The number of the sample
- The notebook experiment identification number
- The date
- The origin, the technician's name, and cross-reference number
- Weight or volume
- Identifying code of the container
- What is to be done with the sample, what determination is to be made, or what analysis is desired

17.3.1 Pretreatment of Samples

Most received samples require prior treatment before it is analyzed. One of the objectives of this pretreatment is to produce material so homogeneous that any taken portion for the analysis will be identical to any other portions. It involves the reduction of the size of particles to a few tenths of a millimeter and thorough mechanical mixing. The other objective of the pretreatment is to convert the substance to be analyzed to a form that can be attacked by the analysis reagents. Finally, the sample may have to be dried or its moisture content may have to be determined because this is a variable factor that is dependent upon atmospheric conditions as well as the physical state of the sample.

17.3.2 Crushing and Grinding

In dealing with solid samples, a certain amount of crushing or grinding is sometimes required to reduce the particle size. Unfortunately, these operations tend to alter the composition of the sample, and for this reason, the particle size should be reduced not more than is required for homogeneity and for ready attack by reagents.

Ball mills or jars are containers, usually made of porcelain, fitted with a lid and a gasket that can be attached tightly to the jar. The jar is half filled with flint, porcelain, or metal balls, and then enough of the material to be ground is added to cover the pebbles or balls and the spaces in between.

The lid is screwed on tightly to seal the grinder tightly, and the jar is rotated on a rotating assembly. The length of time the material is milled depends on the required

fineness and the hardness of the material. The jar is then emptied into a coarse mesh sieve to separate the pebbles or balls from the ground material.

17.4 Moisture in Samples

The presence of water in the sample is a common problem that the analyzer encounters often. This compound may exist as a pollutant from the atmosphere or from the solution in which the substance was formed, or it may be associated as a chemical compound, a hydrate. Regardless of its origin, water plays a role in determining the composition of the sample.

Thus, the sample composition may change significantly with the environment and handling method. In order to deal with variation in composition caused by the presence of moisture, the analyzer may attempt to remove water by drying prior to weighing the samples for analysis. Alternatively, the water content can be determined at the time samples are weighed for analysis. This way the results can be corrected on a dry basis.

Chapter 18
Laboratory Glassware

Glassware items used in chemical laboratories are commonly made from glass although some are made from plastics. Pyrex, Quickfit, SVL, and MBL are examples of glassware brands produced from borosilicate glass. Among the glass types, soda glass is produced by combining silica, calcium carbonate, and sodium carbonate; lead crystal glass is made by mixing silica with cerium oxide; potash glass is made by mixing silica and potassium carbonate with calcium carbonate; and Pyrex glass is made by combining barium silicate with sodium silicate. Selected glassware items are listed in Table 18.1.

Table 18.1: Selected laboratory glassware.

Name	Purpose	Picture
Reduction adapter	Useful for the connection of dissimilar sized ground glass joints	
Receiver adapter plain bend	Useful for the connection of condenser to receiving flask	
Three-way adapter or still head adapter	Used in distillation assemblies for connecting flasks to condenser	
Beakers	Useful as a reaction container or to hold liquid or solid samples	

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Table 18.1 (continued)

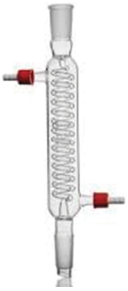
Name	Purpose	Picture
Reagent bottle	Used for mixing and storing liquids, reagents, and analytical standards	
Density bottles	Used in density measurement. These bottles have exact volume engraved on each bottle	
Dropping bottle	Used to transfer small amounts or drops of certain reagents	
Burette	Graduated glass tube with a tap at one end, for delivering known volumes of a liquid, especially in titrations	
Condenser	Suitable for either reflux or distillation	

Table 18.1 (continued)

Name	Purpose	Picture
Graduated cylinder	Used for measuring and transferring liquids	
Desiccator	Used for drying solids and preserving moisture-sensitive items	
Crystallizing dish	Used as heating and cooling baths	
Mortar and pestle	Used for crushing solids into powders for easier handling	
Filtration system	Used for filtration	

Table 18.1 (continued)

Name	Purpose	Picture
Conical flask	Used for collecting and transferring liquids	
Buchner flask	Used for vacuum filtration	
Round bottom flask	Used as distilling flasks and receiving flasks for the distillate and also to contain chemical reactions especially for reflux setups and laboratory-scale synthesis	
Three-neck round bottom flask	Used to connect three components for complex distillation or reaction	
Volumetric flask	Used for precise dilutions and preparation of standard solutions	

Table 18.1 (continued)

Name	Purpose	Picture
Stem funnel	Used for gravity filtration	
Sintered glass disk Buchner funnel	Used for suction filtration	
Fractionating column	Used in fractional distillation	
Dropping funnel	Used for adding reagents and liquids drop-wise	
Pressure-equalizing funnel	Used for adding liquids into vessels under vacuum	
Separating or separatory funnel	Used for liquid–liquid extraction	
Joint clip	Used to prevent a joint from separating during a reaction process	

Table 18.1 (continued)

Name	Purpose	Picture
Graduated pipette	Used to accurately measure and transfer a volume of liquid from one container to another	
Pipette filler	Used to release air, draw liquid into the pipette, and accurately release liquid	 
Test tube rack	Used to hold upright multiple test tubes at the same time	
Clamp and ring stand	Used to support other pieces of equipment and glassware such as burettes, columns, and flasks	
Stirrer bars or magnetic stir bars	Used to stir liquids in any container	
Stirring glass rods	Used for mixing liquids, or solids and liquids	
Stoppers	Used to seal containers	
Stopcock	Used to control the flow of a liquid	

Table 18.1 (continued)

Name	Purpose	Picture
Thermometer	Used to measure the boiling point of liquids during chemistry experiments	
Thermometer adapter	Allows the use of a standard laboratory thermometer in any chemistry reaction	
Centrifuge tube	Used to contain liquids during centrifugation	
Test tube	Used to handle chemicals, especially for qualitative experiments	
Tweezer	Used for grasping objects too small to be easily handled with the human fingers	
Watch glass	Used to evaporate liquids and cover beakers during sample preparation	
Weighing scoop	Used on weighing scales	
Scoopula	Used to transfer solids	
Spatula	Used to mix, spread, and lift solids	

Chapter 19
Volumetric Analysis

The volumetric method is the method in which the analysis is completed by measuring the volume of a solution of a specified concentration needed to completely react with the substance being determined.

19.1 Definitions of Terms

19.1.1 Units of Volume

Liters (L): A volume equal to 1000 cubic meters or milliliters.
Milliliters (mL or cm^3): One-thousandth (0.001) liters.
Cubic centimeters (cm^3): Can be used interchangeably with milliliters without effect.

19.1.2 Titration

This is the process by which a measured substance is combined with a reagent and is measured quantitatively. Usually, this is accomplished by the controlled addition of a reagent of known concentration to a solution of the substance until the reaction between the two is judged to be complete. Then the volume of the reagent is measured.

19.1.3 Back-Titration

A process by which an excess of the reagent is added to the sample solution and this excess is then determined with the second reagent of known concentration.

19.1.4 Standard Solution

A reagent of known composition is used in the titration. The accuracy with which the concentration of a standard solution is known sets a limit on the accuracy of the test.

Standard solutions are prepared by carefully measuring a quantity of a pure compound and calculating the concentration from the mass and volume measurements or carefully dissolving a weighed quantity of the pure reagent itself in the solvent and diluting it to an exact volume or by using a pre-standardized commercially available standard solution.

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19.1.5 Equivalence Point

This is the point at which the standard solution is chemically equivalent to the substance being titrated. The equivalence point is a theoretical concept. We estimate its position by observing physical changes associated with it in the solution.

19.1.6 End Point

This is the point at which the physical changes arising from alterations in the concentration of one of the reactants at the equivalence point become apparent.

19.2 Typical Physical Changes During Volumetric Analysis

- Appearance or change of color due to the reagent, the substance being determined, or an indicator substance
- Turbidity formation results from the formation or disappearance of an insoluble phase
- Conductivity changes in a solution
- Potential changes across a pair of electrodes
- Refractive index changes
- Temperature changes

19.3 Washing and Cleaning Laboratory Glassware

19.3.1 General Rules

- Clean your glassware immediately after use, as it is much easier to remove debris before it dries and hardens.
- Be careful when cleaning glassware, especially heavy flasks and long, thin columns.
- Rinse the glassware carefully with water to remove any soap or detergent residues to prevent any possible contamination.

19.3.2 Cleaning Volumetric Glassware

- Always rinse volumetric glassware equipment three times with distilled water after you have emptied and drained it. This prevents solutions from drying on the glassware, causing difficulty in cleaning.

- Dry volumetric glassware at room temperature, never in a hot oven. Expansion and contraction may change the calibration.
- The glass surfaces should be wetted evenly. Spotting is caused by grease and dirt. Grease can be removed by rinsing and scrubbing with a hot detergent solution followed by adequate distilled water rinses. Dirt can be removed by filling or rinsing with a dichromate cleaning solution. Allow standing for several hours, if necessary. Follow with multiple distilled water rinses.

19.3.2.1 Pipettes

Pipettes can be cleaned with a hot detergent solution or a cleaning solution. Pull the bulb into enough liquid to fill it to about one-third of its capacity. Holding it almost horizontally, carefully rotate the pipette to cover all the inner surfaces. Drain upside down, and rinse thoroughly with distilled water. Check for water leaks and repeat the cleaning cycle as often as needed.

19.3.2.2 Burettes

Clean the tube thoroughly with detergent and a long brush. If water breaks do not disappear after washing, clamp the burette upside down by lowering its end into a glass of washing solution. Connect the hose from the burette tip to the vacuum line. Gently draw the cleaning solution into the burette before reaching the stopcock.

Leave it on for 10–15 min, then rinse it well with distilled water. After some use, the lubricating oil on the stopcock tends to harden; small grease particles can break off and flow to the edges of the burettes and clog them. Degreasing can be done with a thin, flexible wire. Finally, wash off any remaining particles with water.

19.3.3 Cleaning Glassware Soiled with Stubborn Films and Residues

When you cannot completely clean glassware by scrubbing it with a detergent solution, more drastic cleaning methods must be used.

19.3.3.1 Dichromate-Sulfuric Acid Cleaning Solution

"Prepare and handle this cleaning solution with extreme care. Avoid contact with clothing or skin."

Dissolve 92 g of $Na_2Cr_2O_7{\cdot}2H_2O$ (sodium dichromate) in 458 mL H_2O, and cautiously add by stirring 800 mL concentrated H_2SO_4. The contents of the flask will get very hot and become a semisolid red mass. When this happens, add just enough sulfuric acid to bring the mass into the solution.

Cool the solution down before transferring it to another glass bottle. Clean the glassware first with detergent and rinse it carefully with water, then pour a small

amount of the chromate solution into the glassware, allowing the solution to flow down all parts of the glass surface. Pour the solution back into the stock bottle. Then rinse the glassware, first with tap water and then with distilled water, until the glass surface appears clean. This solution can be reused until it acquires the green color of the chromium(III) ion. Once this happens, it should be disposed of.

19.3.3.2 Diluted Nitric Acid Cleaning Solution

Residues inside bottles and flasks can be removed with dilute nitric acid, followed by multiple rinsing with distilled water.

19.3.3.3 Aqua Regia Cleaning Solution

The aqua regia consists of three parts of concentrated HCl and one part of concentrated HNO_3. This is a very powerful but extremely dangerous and corrosive cleaning solution. Use in the hood with extreme care.

19.3.3.4 Alcoholic Potassium Hydroxide or Sodium Hydroxide Cleaning Solution

Add about 1 L of 95% ethanol to 120 mL H_2O containing 120 g NaOH or 105 g KOH.

"This is a very good cleaning solution. Avoid prolonged contact with ground-glass joints on inter-joint glassware because the solution will etch glassware and damage will result. This solution is excellent for removing carbonaceous materials."

19.3.3.5 Trisodium Phosphate Cleaning Solution

Add 57 g Na_3PO_4 and 25.5 g sodium oleate to 470 mL H_2O. "This solution is good for removing carbon residue. Soak glassware for a short time in the solution, and then brush vigorously to remove the incrustations."

19.3.3.6 Nochromix Cleaning Solution

This is a commercial oxidizer solution, but it contains no metallic ions. The powder is dissolved in concentrated sulfuric acid, yielding a clear solution. The solution turns orange as the oxidizer is used up. Use with care.

19.3.4 Ultrasonic Cleaning

Ultrasonic cleaning units generate high-frequency sound waves (sound waves of higher frequencies than those detectable by the human ear) that penetrate deep recesses, turn corners, and pass through barriers. Laboratory glassware and optical equipment as well as narrow-bore pipettes, manometers, and similar items are easily

cleaned with such units. The items are immersed in the cleaning solution, and the power is turned on.

19.4 Laboratory Glass Drying

After the glassware is thoroughly cleaned and washed, it must be dried.

19.4.1 Drainage Plates and Drainage Shelves

Drainage boards and drainage racks are used for drainage and drying glassware of various sizes and shapes. The brackets have pins and wedges anchored in an inclined position to ensure drainage. Some drain plates are equipped with hollow wedges and a hot air fan to speed up the drying process. Place the glassware securely on the rack. Do not allow parts to touch each other and cause accidental breakage.

19.4.2 Drying Ovens

Drying ovens are designed to dry glassware at high speed. They have different sizes and power ratings; some of them are equipped with timers.

19.4.3 Quick Drying

Drying the inside of flasks or similar vessels can be done by lightly heating them on a Bunsen flame, and then gently passing a jet of compressed air through a glass tube leading to the bottom of the flask until they dry.

19.4.4 Rinsing Wet Glassware with Acetone

Water-wet glassware can be dried more quickly by rinsing them with several small portions of acetone and discarding the acetone rinse after each time. Then place them in a safety oven or gently pull air through the glassware by connecting a pipette with rubber tubing to an aspirator and inserting the pipette into the glassware.

19.5 Tools of Volumetric Analysis

Pipettes, burettes, and volumetric bottles are standard volumetric equipment. A volumetric apparatus calibrated to contain a certain volume is designated as TC (To Contain), and an apparatus calibrated to deliver a certain amount, TD (To Deliver). Only clean glass surfaces will support a uniform film of liquid; the presence of dirt or oil tends to cause fractures in this film. The appearance of water cracks is a sure indicator of an unclean surface.

Volumetric glassware is carefully cleaned by the manufacturer before it is labeled so that they have meaning; the equipment must be equally clean when in use. As a general rule, the heating of calibrated glass equipment should be avoided. Cooling too fast can permanently distort the glass and cause a change in volume.

19.5.1 Volumetric Flasks

The volumetric bottles are calibrated to contain a certain volume when filled to the line incised on the neck. Before use, volumetric bottles should be washed with detergent and, if necessary, a cleaning solution. Then they should be carefully and repeatedly rinsed in distilled water; they rarely need to be dried. However, if drying is needed, it is best to achieve this by clamping the flasks in the inverted position and using a mild vacuum to circulate air through them.

Direct preparation of a standard solution requires introducing a known mass of solute into a volumetric flask. To reduce the possibility of loss during transportation, insert a funnel into the neck of the vial. The funnel is then washed free of solids. After introducing the solute, fill the flask about half full, and rotate the contents to obtain the solution.

Add more solvent and mix well again. Bring the solution level to approximately the mark and allow time for it to drain. Then use of the dropper to make final additions to the solvent as necessary. Cap the vial firmly and turn it over frequently to ensure uniform mixing.

19.5.2 Pipettes

Pipettes are designed for the transfer of known volumes of liquid from one container to another. Pipettes that deliver a fixed volume are called volumetric or transfer pipettes. Other pipettes, known as measuring pipettes, are calibrated in convenient units so that any volume up to maximum capacity can be delivered.

The following instructions pertain specifically to the manipulation of transferring pipettes, but with minor modifications; they may be used for other types as well. Liquids are usually drawn into pipettes through the application of a slight

vacuum. Use mechanical means such as a rubber suction bulb. The pipette can be used as follows:

- Clean the pipette by rinsing it with distilled water.
- Drain completely and then rinse three times with the solution to be used in the analysis.
- Keep the tip of the pipette below the surface of the liquid.
- Draw the liquid up in the pipette using the pipette bulb.

For proper measurement proceed as follows:

- Disconnect the suction when the fluid is above the calibration mark. Quickly remove the suction unit and place the index finger of the hand holding the pipette over the exposed end of the pipette to the closed end.
- Release the pressure on the index finger to allow the meniscus to approach the calibration mark.
- At the mark, apply pressure to stop the flow of liquid, and drain the drop on the tip by coming into contact with the wall of the liquid-retaining container.
- Transfer the pipette to the container to be used and release the pressure on the index finger. Let the solution drain completely. Allow an interval of 10 s, or the period indicated on the pipette. Remove the last drop by touching the wall of the container.
- The amount of liquid titrated was transferred. Do not inflate the straw. In the case of color-coded pipettes, a polished ring indicates a full blast.

19.5.3 Burettes

Burettes, like measuring pipettes, deliver any amount up to their maximum capacity. Burettes of the traditional type must be filled in manually. The other side-armed burettes are gravity-filled. For more accurate work, Schellbach burettes are used. These have a white background with a blue bar and are readable at the lowest magnification point. When using unstable reagents, a burette with a reservoir bottle and pump can be used.

Before being placed in service, a burette must be scrupulously clean. In addition, it must be established that the stopcock is liquid-tight. Grease films that appear unaffected by cleaning solution can be rinsed with organic solvents such as acetone, although thorough washing with detergent should do the cleaning.

Chapter 20
Chromatography

20.1 Introduction

The term “chromatography” was first described as the washing of the impure compounds through a column packed with an adsorbent medium such as calcium carbonate. The least-adsorbed pigments are washed through the column quickly, while the strongly adsorbed pigments are immobilized by their attraction to the column packing.

In all chromatographic processes, one medium is fixed in the system and is called the stationary phase, while a second medium flows through the fixed medium and is called the mobile phase.

Adsorption in this column process is directly related to the affinity of the solute for either the stationary adsorbent or the flowing solvent, and the process is generally referred to as column chromatography. Today, all types of chromatographic processes are used primarily for the nondestructive separation of complex mixtures.

20.2 Adsorption Chromatography

Adsorption chromatography typically uses silica gel or alumina as the stationary solid phase and organic solvents for the mobile liquid phase. Adsorption chromatography occurs when the sample components transfer from the mobile phase to the stationary phase where they are selectively adsorbed on the surface. This chromatographic process has the advantages of being simple and applicable over a wide range of temperatures but is best for resolving heat-labile substances at low temperatures.

The main disadvantages are that many substances undergo chemical changes with these very active adsorbents, separations tend to be concentration-dependent, and the adsorbents have low capacities for adsorbing solutes.

20.3 Partition Chromatography

A second and more versatile type of chromatography is called partition chromatography. It is based on the differential distribution of the sample components between the two phases. Partition chromatography differs from adsorption chromatography, in that two liquid phases are used in which the sample components vary in their degree of solubility. The solubility and polarity of the individual components determine the distribution of these components in the mobile and stationary liquids.

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The stationary phase has a thin layer of liquid coated on a porous inert solid and the mobile phase can be a pure liquid or a mix of liquids. An example is the use of water adsorbed into silica gel as the stationary phase and a mixture of butanol and chloroform as the mobile phase to separate complex mixtures of amino acids. Other common adsorbents are cellulose, starch, diatomaceous earth, and even powdered rubber.

20.4 Thin-Layer Chromatography

20.4.1 Introduction

Thin-layer chromatography, TLC, is a simple, rapid, and inexpensive method for analyzing a wide variety of materials ranging from inorganic ions to high-molecular-weight biological compounds. The simple setup of TLC is shown in Figure 20.1.

TLC is widely used in chemical, biological, pharmaceutical, and medical industries, not only for quality control and research analyses but also for the preparative separation and isolation of compounds of interest.

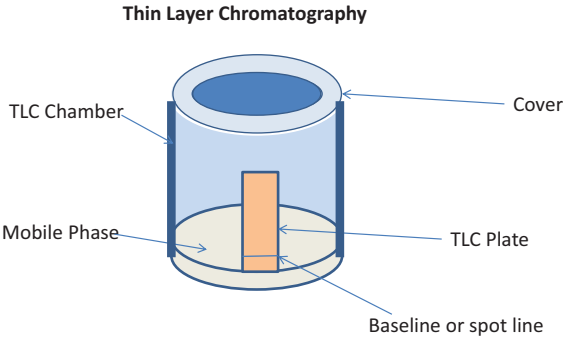

Figure 20.1: Thin-layer chromatography (TLC).

TLC is actually a subsection of liquid chromatography (LC) where the mobile phase is a liquid, and the stationary phase lies as a thin layer on the surface of a flat plate. TLC is grouped with paper chromatography under the term "planar liquid chromatography" due to the flat geometry of the paper or the stationary phases of the layer. Although paper chromatography has made valuable contributions to separation techniques, paper is not universally satisfactory for all separations. Being inert with chemicals, glass is the universal support for TLC.

Glass plates in different sizes, shapes, and thicknesses are used according to the specific needs of the user. Pyrex-branded glass panels are available for situations where high-temperature heating of the plate is required to make the composites

visible. In TLC, an absorbent is applied to a support plate in a thin layer. Typically, a binder is used to bond the absorbent to the backing, although some work is done without a binder using a highly flammable absorbent that adheres to the backing and forms a fairly smooth layer.

A thin slurry of absorbent and binder is applied, and excess moisture is removed under different conditions depending on the absorbent, binder, and desired degree of activity. Use of silica gel as an absorbent for TLC accounts for an estimated 70–80% of all TLC plates used.

Most commercial silica gel produced and sized for TLC use has consistently reproducible pore size, particle size, particle distribution, surface area, and impurity levels. With all of these variables carefully controlled, the most important factor influencing TLC separations is moisture.

20.4.2 Preparation of the Plate for Thin-Layer Chromatography

Before preparing the slurry, treat the mixing flask and glass rod with a hydrophobic substance, such as dimethyldichlorosilane, thus rendering them hydrophobic. Dissolve 2 mL of the dimethyldichlorosilane in 100 mL of toluene and thoroughly wash the mixing vessel and glass rod in it. Use this solution as a rinse to waterproof the mixing vessel, rod, and all other glassware to be used. Finally, rinse all glassware with methanol and distilled water prior to use.

Prepare a slurry of the adsorbent and put the required mass of adsorbent into the mixing flask and then add the specified volume of water. Shake thoroughly for about 5 s. Place a clean, dry, glass plate on a paper towel and pour the slurry evenly across the carrier plate near the bottom edge. Use the glass rod to spread the slurry with a smooth steady motion to the top edge of the plate (but not over it); slide the rod, do not roll it. A commercial spreader may also be used. Without allowing the further flow of the coating, dry the coated plate in an oven at 89–90 °C for about 1 h. This permits the plate to be handled and at the same time activates the coating. Store dried plates in suitable desiccators.

20.4.3 Thin-Layer Chromatography Procedure

Standard TLC procedure involves three steps.

- The substance to be separated into fractions is spotted on the edge of the plate with a micropipette in such a manner as to yield a minimum area. Better separation and development are obtained with small sample spots.
- The prepared solvent mixture is placed at the bottom of a developing tank and the plate (or plates) is positioned in the tank with the upper part of the carrier plate leaning against the side of the tank. The tank is securely covered with a

glass plate and the development begins as the solvent rises up the plate by capillary attraction.
- The spots must be located. Once the solvent front has reached the desired level, the plate is removed and allowed to dry. Now the location of the spot must be determined. This location can be used as a criterion for the identification of the substance, particularly if controls have been set up; the intensity of the spot is a quantitative measure of the concentration of the substance. Chromophoric substances can be located visually; colorless substances require other means. Some substances fluoresce under UV light, and irradiation of the plate will indicate the position of the spot. Other plates are coated with fluorescent materials; the spot will obscure this fluorescence when the plate is irradiated. Different spray reagents are selected to react with the spot and reveal its location. The spray must be applied uniformly to the dried plate. Finally, exposure of the plate to chemical vapors can also reveal the location of the spot.

20.5 Gas Chromatography

20.5.1 Introduction

Gas chromatography (GC) is one of the fastest and most useful separation techniques available in the laboratory. The GC analysis is basically limited to organic compounds that are volatile and not thermally labile (decomposable). There are two modes of GC: gas–solid (adsorption) chromatography (GSC) and gas–liquid (partition) chromatography (GLC). GLC is used more extensively than GSC. Both types of GC require that the sample be converted into vapor state and be transported by an inert carrier gas through a column packed with either a liquid phase coated on a solid support for GLC or simply a solid adsorbent with no liquid-phase coating for GSC.

A sample is injected into a heated block where it is immediately vaporized and swept as a concentrated vapor into a column. Separation occurs as the various compound vapors are selectively adsorbed by the stationary phase and then desorbed by the fresh carrier gas. This sorption–desorption process occurs repeatedly as the compounds move through the column toward a detector. The compounds will be eluted from the column with those having a high affinity for the column packing being slower than those with little affinity.

20.5.2 Instrument Design and Components

A typical gas chromatograph, shown in Figure 20.2, consists of the following:
- Carrier gas supply
- Sample injection port

- Column
- Column oven
- Detector
- Recorder-integrator system or computer data analysis system

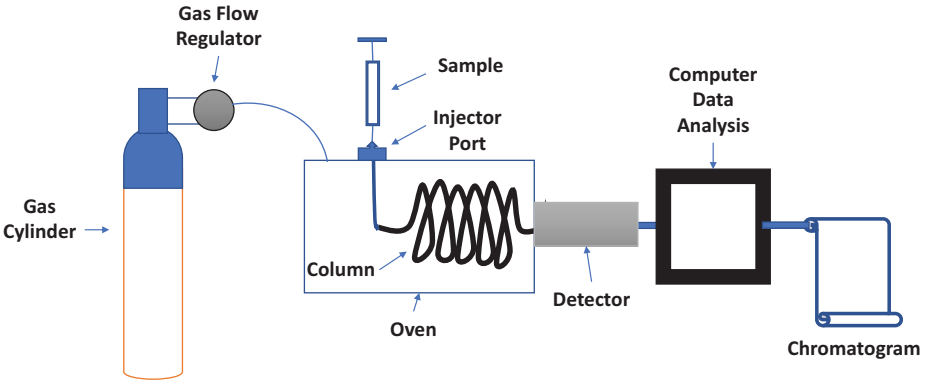

Figure 20.2: GC diagram.

In the GC system, the carrier gas is used to transport the sample molecules from the injection port to the detector and provide the means for partitioning the sample molecules from the stationary phase. The most common carrier gases are helium and nitrogen. These gases are supplied in high-pressure tanks which require a two-stage pressure regulator for reducing the inlet gas pressure and controlling the gas velocity through the column. This gas must be of high purity with minimal moisture or other contaminants present to reduce erroneous detector signals. Various commercial gas purifiers are available for removing carrier gas contaminants, especially oxygen and water. Refillable in-line traps are also available that contain molecular sieve 5A, and charcoal for removing oxygen, moisture, and hydrocarbon contaminants. These purifiers should be checked and reconditioned periodically, especially if a drifting baseline is being experienced. If hydrogen gas is being used for an FID detector or as the carrier gas, a hydrogen generator is strongly recommended (over a cylinder of compressed hydrogen) for high purity and laboratory safety.

A sample inlet system is provided to allow liquid samples in the range of 1–10 µL to be injected with a microsyringe through a septum into a block that is heated to a temperature in excess of the compound boiling point. The liquid sample is immediately vaporized and swept through the column by the carrier gas. The septum is a self-sealing rubber or an elastomer material that forms a leak-proof entrance into the injection port. Septa are manufactured in disks ranging in size from 5 to 16 mm to fit specific injection inlets and are available in very expensive high-puncture-tolerance low-bleed preconditioned types or in less-expensive simple rubber stock.

Some Teflon-faced septa are available to reduce septum-bleeding contamination into the column at higher temperatures. A leaky septum is one of the most common sources of trouble in GC; therefore, it should be changed periodically.

20.6 Liquid Chromatography

20.6.1 Introduction

LC is a separation technique consisting of two phases: a solid stationary phase and a liquid mobile phase. LC can be classified into liquid–solid chromatography (LSC), liquid–liquid chromatography (LLC), and high-performance liquid chromatography (HPLC). The fastest growing field of LC is HPLC, which has the faster flow rate allowed by higher pressure pumps. In HPLC, the sample is introduced as a liquid in the mobile phase, and for analysis, the sample does not have to be volatile. Therefore, LC is very useful for the analysis of mixtures of nonvolatile and thermally changeable compounds.

There are two types of HPLC columns: normal phase and reverse phase. In the normal phase of HPLC, the stationary phase is more polar than the mobile phase. In a reverse-phase HPLC column, the column contains a nonpolar stationary phase. Reverse-phase columns are widely used in the pharmaceuticals and petroleum industries to separate chemical compounds into individual components for refining or analysis.

For analysis, the sample is injected into a reverse-phase column, and then a solvent is added to wash the sample through the stationary phase. Since the stationary phase in a reverse-phase HPLC column is nonpolar, the polar components of the sample will exit the column first, followed by the nonpolar components.

The main components of a basic LC or HPLC system, shown in Figure 20.3, are:

- Reservoir for mobile phase (liquid)
- Pump
- Injection port (sample inlet)
- Column/HPLC column
- Detector (chromatography detector)
- Computer data station
- Waste container

The bottle contains the solvent, which is the mobile phase. A high-pressure pump is used to move the mobile phase at a constant rate through the column (typically mL/min). The injector introduces the sample into a continuously flowing mobile-phase stream which carries the sample to the column. The column contains a chromatographic filler, a stationary phase necessary to carry out the separation. Detector is used for observing separated bands of compounds as they elute from the column.

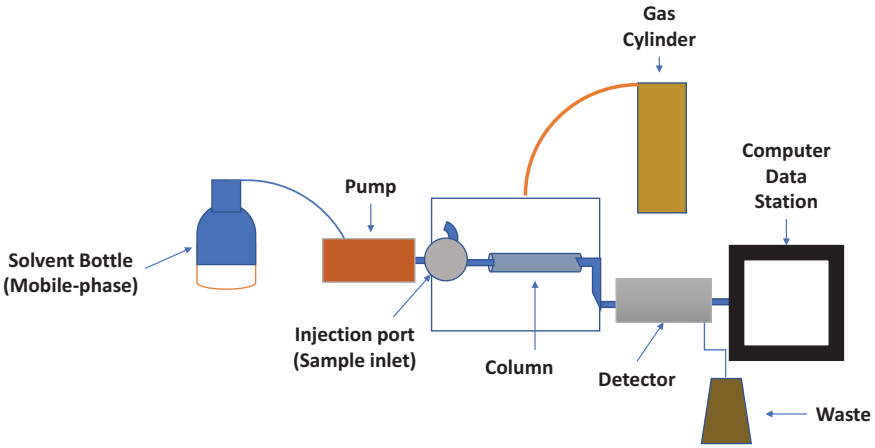

Figure 20.3: HPLC diagram.

20.7 Column Chromatography

A simple column chromatography setup is shown **in** Figure 20.4. The mobile phase is the *eluant* or solvent as it passes through the stationary adsorbent phase. The word *elute* means to wash out.

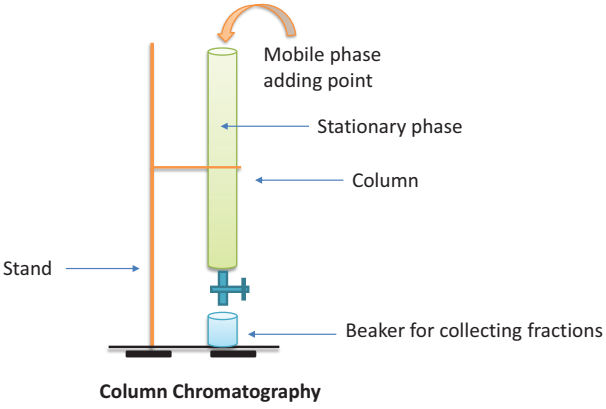

Figure 20.4: Column chromatography.

20.7.1 Liquid Column Techniques

Column chromatography is one of the most versatile chromatography techniques. Some techniques and tips for using column chromatography are summarized as follows:

- Use a column with a minimum length-to-diameter ratio of 20:1.
- Determine the optimum quantity of sorbent required to affect the separation. Generally, adsorption requires between 50 and 100 g of sorbent per gram of sample, and partition requires between 500 and 1000 g of sorbent per gram of sample.
- When you use a dry-packed column, cover the sorbent with solvent immediately after carefully packing the column; do not allow the solvent to evaporate so that the sorbent dries out. Allow any heat that has developed during the addition of the solvent to the sorbent to dissipate, and let the column come back to normal (or room) temperature. If you desire to shorten the cooling time, the use of cooling jackets will accelerate this heat dissipation.
- Slurry pack instead of the dry pack when you desire the highest resolution in a procedure. Gently tap or bump the column continuously while you fill it with a slurry of the sorbent in a suitable solvent by pouring in one small portion at a time. This disturbance will free any trapped air bubbles and pack the column more tightly and more uniformly so that it will yield better results.
- The sample should be introduced uniformly and symmetrically without disturbing the column sorbent. You can slurry the sample with some sorbent and pour this slurry on top of the column bed or seat a filter disk or pad of filter paper on top of the column bed and then gently pipette the sample onto the filter disk.

20.7.2 General Operating Procedure

There are almost limitless combinations of modes, solvents, sorbents, and procedures to select from, and yet there are no ironclad rules to guide you in your selection. Selected samples' category and their chromatographic modes are summarized in Table 20.1.

Table 20.1: Selected chromatographic techniques.

Categories of samples	Liquid chromatography modes
Positional isomers, moderate-polarity molecules	Liquid–solid
Compounds with similar functionality	Liquid–solid or liquid–liquid
Polar and polynuclear aromatics	Liquid–solid

Table 20.1 (continued)

Polysulfonated hydroxynaphthalenes	Ion exchange
High-polarity compounds	Liquid–liquid
Metallic chelates	Liquid–liquid
Compounds with differing solubility	Liquid–liquid
Mixtures of varied sizes of molecules	Gel permeation
Lubricating oils	Gel permeation

The general operating procedure and tips to keep in mind, while running the LC, are summarized as follows:

- The septum should be checked daily for leaks and must be changed often.
- Check the flow rate regularly at a specified pressure to detect any buildup of pressure or decrease of flow.
- Allow sufficient time for the LC system to stabilize after being turned on. Plan ahead.
- The activity of a solid stationary phase can vary with the purity of the solvents being used and the polarities of the samples. It may be necessary to regenerate the column if it appears to have lost its separating capability.
- If possible, samples should be dissolved in the liquid mobile phase.
- Exercise care with flammable and/or toxic solvents.
- Only high-purity solvents should be used as mobile phases. Some may require distillation prior to use.
- Try to dissolve samples in the mobile phase or in a less polar solvent than the mobile phase. This technique tends to concentrate the injection on the tip of the column and yields better resolution.
- When filling the pump, hold the funnel slightly above the opening in the pump; this maneuver allows air to escape from the reservoir.
- Never remove or loosen the lower 1/4-in column fitting; this disturbs the column bed and destroys column efficiency.
- If the syringe is pushed too far into the column packing, the needle becomes plugged. To clear the needle, hold the syringe with the needle pointed down, allow some solvent to collect around the plunger, and then rapidly remove the plunger, causing a vacuum to form inside the syringe barrel. The vacuum sucks in some of the liquid. If you now replace the plunger, pushing the liquid through the needle, you will force out the plug of packing material.
- After the standard column has been used for a period of time, its chromatographic properties may change. The column may be restored to its previous activity by pumping through it 50 mL each of ethyl alcohol, acetone,

ethyl acetate, chloroform, and hexane. This treatment should leave the column as active as it was when you received it.
- If you want to change from any solvent mobile phase to water, pump a solvent miscible in both solvents through the system before making the change. This removes all traces of the previous solvent remaining in the system.
- Stop-flow injections can be made easily by opening the three-way valve, releasing the pressure, and then making the injection and repressurizing the system by turning the three-way valve back to the OPERATE position.

20.7.3 General Precautions

General precautions for solvent compatibility, flow restrictions, and general attention should be read thoroughly before any analysis. Failure to do so may result in erroneous analytical information and may invalidate the column's usefulness. Careful attention will extend the life of the column and allow you to return to the stored column with knowledge of the purification steps required before analytical use. Always mark the last solvent that passed through the column. For long-term storage, see the column maintenance brochure that accompanies each column.

It is important to filter all solvents that are used in LC. LC is a high-precision instrument, and particulate matter (>0.5 μm) could be the source of problems. It is also important to filter all samples before they are injected into the instrument.

20.7.4 Sorbents for Column Chromatography

Since the sorbent used in column chromatography is packed in a vertical column, there is no need for any binders such as those used in TLC. However, the critical parameters for sorbents are particle size and size distribution. These factors directly affect the flow of the solvent, of which the driving force may be either hydrostatic or low pump pressure. A narrow particle size distribution will usually provide better separation, with all other factors remaining the same.

20.7.5 Solvent Mixtures for Use in Column Chromatography

The possible combinations of solvent mixtures are almost unlimited because of the number of solvents used and the possible proportions of the concentrations of the components of the mixtures. These may be used as a basis for creating special mixtures as they are needed. Solvent mixtures are formulated by experiment.

20.8 Ion-Exchange Chromatography

20.8.1 Introduction

Ion-exchange chromatography (IE chromatography shown in Figure 20.5) can be classified as a form of LC. This technique deals with the separation of ionic mixtures. Many naturally occurring inorganic substances such as clays and zeolites have a strong attraction for certain ions in solution. In addition, stationary phases composed of solid polymeric material of styrene cross-linked with divinylbenzene in "bead" form having anion or cation sites on the surface have been developed.

An acid functional group, such as sulfonic acid, SO_3H, hydroxyl, OH, thiol, SH, or carboxylic acid, COOH, binds to the polymer, and the acid–hydrogen group tends to separate, leaving a negative spot on the bead area to attract other cations. Similarly, major basic functional groups, such as secondary amines, R_2N, primary amines, and other NH_2 nitrogen-containing groups, tend to become quaternary ammonium groups that have a positive charge on the polymer bead to attract anions. Cationic and anionic functional groups are classified as strong or weak depending on the tendency to dissociate.

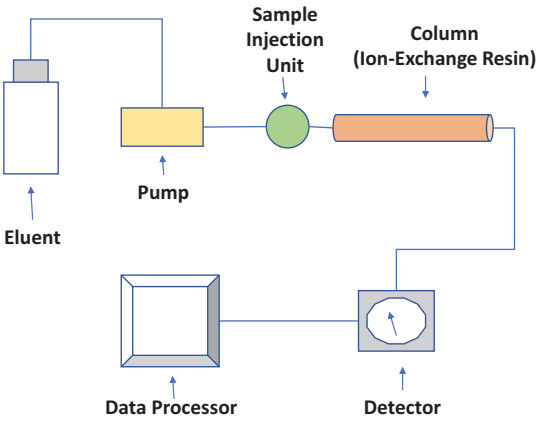

Figure 20.5: Ion-exchange chromatography diagram.

Ion-exchange resins are ridged polymer beads bonded or cross-linked with divinylbenzene and contain exchange sites. The sites may be strong or weak acid, strong or weak bases, or a combination of both acidic and basic groups. The resins are selected for the ion process to be used. The resin properties to be considered are cross-linkage, particle size, exchange groups, and ion-exchange capacity.

The cross-linkage affects resin's properties by making it more or less dense. The more cross-linkage there is, the tighter the gaps between the exchange sites. Therefore, ions larger in size are excluded, but at the same time, more exchange sites are

available. With less cross-linkage, the opposite is true. Smaller sized ions will be allowed to flow through the resins, and there will be fewer exchange sites. Particle size, mesh, will affect both the amount of solution and the number of ions that the resin can handle.

The larger the mesh, the faster the solution can flow through the column, and the fewer exchange sites the column can work. Conversely, the smaller the mesh, the less solution flow the column can handle, but there are more sites. Ion exchange occurs when ions in the mobile phase exchange with counter-charged ions in the stationary phase.

In an anion exchange, cationic exchange sites are attached to the stationary resin. In cation exchange, anionic exchange sites are attached to the resin. The exchange capacity of an ion-exchange resin can be defined as the total number of replaceable ions per unit of volume expressed in milliequivalents per milliliter.

The exchange capacity can be determined by:

- weighing a quantity of the dried resin (R-H) in the H^+ form;
- adding deionized water to hydrate (swell) the resin;
- pouring the hydrate resin into a column; avoid adding the dried resin first to the column because this could break it;
- adding a measured concentration of cations (e.g., K^+) causing the H^+ ions to be quantitatively displaced;
- determining the milliequivalents of H^+ by titration with a known concentration of base.

The used column can now be regenerated by washing the column resin with concentrated HCl, which reverses the equilibrium by flushing off the K^+ ions and restoring the H^+ groups.

Many laboratories use a combination of anionic and cationic resins to purify (deionize) tap water instead of using the more expensive and slower distillation process. Deionized water is not as pure as distilled water since this process removes only cation and anion contaminants. These deionizing columns release an equivalent number of H^+ ions for each cation adsorbed and an equivalent number of OH^- for each anion adsorbed. Thus, a molecule of water is released or substituted for each equivalent of cation and anion contaminants retained on the column. Since ion-exchange resins attract only charged particles, few organic contaminants are removed by this process.

20.8.2 Preparing an Ion-Exchange Column

The list shown in Table 20.2 gives information that might be found on a typical ion-exchange resin bottle label and an interpretation of each item.

Table 20.2: Typical ion-exchange resin bottle labels and their interpretations.

Strong acid resin	Contains acid functional group such as R-SO_3H or R-COOH that dissociates readily in water.
Sodium form	The exchangeable ion is Na^+. In other words, the resin exists as R-Na.
20–60 mesh	The bead spheres are 20–60 particles per inch.
10X	Polymer is cross-linked with 10% divinylbenzene.
Capacity 2.0 meq/g	The resin has an exchange capacity of ions up to an equivalent of 2.0 milliequivalents per gram of dried resin.

Fresh ion-exchange resins should be, respectively, washed with 2 M HCI, rinsed with water, washed with 2 M NaOH, and again rinsed with water until the wash solution is neutral and salt-free. Ion-exchange resins labeled "Analytical Grade" have already been treated.

- Soak a calculated quantity (based on equivalents of ions to be exchanged) of the freshly washed resin in water for at least 2 h in a large beaker. Resins with greater X values require less time for soaking. More highly cross-linked (e.g., 10X) resins swell less than those with lower X values (e.g., 2X).
- Using a conventional liquid chromatographic column, place a glass-wool plug in the bottom, and fill it half full of water.
- With the aid of a powder funnel, transfer the soaked resin into the column and drain the excess water without allowing any of the resin to "go dry."
- Back-flush the packed resin column with a stream of water to remove any air bubbles, and then allow the resin to settle.
- Determine the flow rate of the column. Never at any time allow the resin to go dry as "channeling" can occur, drastically reducing the efficiency of the packing.
- When the column is ready for use, a separatory funnel is a convenient device for adding samples at a controlled rate to the ion-exchange column.

One common IC packing material is 10-μm particles of styrene-divinylbenzene containing very polar functional groups to selectively remove cations or anions. A second common packing is silica gel which has been modified chemically to produce an ion exchanger. These silica-based packings can be prepared from 5- to 10-μm porous silica spheres; they have mechanical properties similar to those of the silica liquid chromatographic packings. These two types of packing have advantages and disadvantages. The styrene-divinylbenzene polymer bead exchangers can be used at almost any pH, whereas the silica packings are restricted to pH between 2 and 8. The silica-based packings are not as prone to dimensional changes with variations in ionic strength and solvent composition as the polymer beads, but they are sensitive to mechanical shock.

A second ion-exchange column sometimes used with IC is called a suppressor column. The purpose of the suppressor column is to decrease the concentration of conductive species in the mobile phase. Many ion chromatographic processes utilize the solution of high ionic strength as the mobile phase; thus, conductivity detectors cannot distinguish the analyte ions. The suppressor column packed with a second ion-exchange resin effectively converts the ions of the mobile phase to a molecular species of limited ionization without affecting the analyte ions. The suppressor column is normally very short in length and is located immediately after the analytical column. Currently, a "mixed bed" of ion-exchange resins is widely used to quantitatively remove all cations and anions while converting them to water molecules. In ion chromatography, the suppressor column removes all mobile-phase ions but does not affect the analyte ions.

Essential Terms

Absolute error. The difference between the true value and the measured value, with the algebraic sign indicating whether the measured value is above (+) or below (–) the true value.

Accident. An incident arising from carrying out the work that results in personal injury.

Auto-ignition temperature. The lowest temperature at which a vapor will ignite spontaneously when mixed with air.

Average deviation. Indicates the precision of all the measurements and is calculated by dividing the sum of all the individual deviations by the number *n* of deviations calculated.

Barcode. A series of thin and thick lines or bars printed on a lighter background.

Chemical laboratory waste. Any material or chemicals leftover or generated from running different experiments.

Boiling point. The temperature at which the pressure of the saturated vapor of the liquid is equal to the pressure of the atmosphere under which the liquid boils.

Corrosive chemicals. Chemicals that result in an immediate, acute erosive effect on body tissue.

Cryogenic liquids (cryogens). Liquids with a boiling point less than –73 °C.

Dangerous occurrence. Occurrence arising from work activities in a chemical laboratory that results in a hazardous situation.

Determinate errors. Errors that can be ascribed to a particular cause and thus can usually be determined as being personal, instrumental, or method uncertainties.

Deviation. A measurement that defines how much each measured value differs from the mean.

Distillation. A process in which the liquid is vaporized, recondensed, and collected in a receiver.

Dixon's Q test. A test used for identification and rejection of outliers or, in other words, a way to find outliers in very small, normally distributed, data sets.

End point. The point at which the physical changes arising from alterations in concentration of one of the reactants at the equivalence point become apparent.

Equivalence point. The point at which the standard solution is chemically equivalent to the substance being titrated.

Extraction. The process of selectively removing a solute from a mixture with a solvent.

Filtration. The process of removing a material from a substrate in which it is suspended.

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Flashback. The rapid combustion of heavy vapors of organic compounds that collect in areas distant from their source and when burning lead the flame back to their source to cause a large fire or explosion.

Flash point. The lowest temperature at which compounds in an open vessel gives off sufficient vapors to produce a momentary flash of fire. This is happened when a flame, a spark, an incandescent wire, or another source of ignition is brought near the surface of the liquid.

Fractional distillation. The separation and purification of a mixture of two or more liquids, present in appreciable amounts, into various fractions.

Freeze-drying. This process is also known as lyophilization, which involves the drying of the product under low temperature and vacuum.

Fume hoods. Equipment designed to control chemists' and laboratory technicians' exposure to hazardous chemicals.

Good laboratory practices. A compilation of procedures and practices designed to promote the quality and validity of all laboratory studies.

Good Manufacturing Practices. A procedure that regulates the manufacturing and associated quality control of products.

Gravity filtration. A process in which the filtrate passes through the filter medium under the forces of gravity and capillary attraction between the liquid and the funnel stem.

Hazard. Anything that can cause harm

Health risk control measure. A hierarchical approach combining varieties of both engineering and operational/procedural control measures.

Hydrometer. A glass container, weighted at the bottom, having a slender stem calibrated to a standard.

Incident. A work-related occurrence during which injury, illness, or fatality happened or could have happened.

Ignition temperature. Lowest temperature at which the vapors over the surface of the liquid ignite.

Indeterminate errors. Random errors resulting from uncontrolled variables in an experiment that cannot normally be determined because they do not have a single source.

International Organization for Standardization. An international standard-setting body composed of representatives from various national standards organizations.

ISO 9001. A standard provides a model for quality assurance in the design, production, and supply of products or services.

ISO 9002. A model for quality assurance in production and installation, not however, for research and development.

ISO 9003. A model for quality assurance when only final inspection and testing are required.

ISO 9004. A model dealing with guidelines for developing quality management.

LC_{50}. The lethal concentration in air of a substance that produces death in 50% of the exposed test population within a specified time.

LD_{50}. The lethal dose required to produce death in 50% of the exposed test population within a specified time.

Liquid chromatography. A separation technique which uses two phases in contact with each other; the stationary phase can be an immiscible liquid or solid, but the mobile phase must be a liquid.

Mass percent. Grams of solute per 100 g of solution.

Mean. A technique of taking an average. Adding together the numerical values of an analysis and dividing this sum by the number *n* of measurements yields the mean.

Median. A technique that uses the same data as for calculating the mean and can be displayed in an increasing or decreasing series with the middle value simply selected as the median.

Melting point. The melting point of a crystalline solid is the temperature at which the solid substance begins to change into a liquid.

Mercury barometer. A barometer with a column of mercury whose height varies according to the atmospheric pressure.

Mode. A measurement value that appears most frequently in the series is called the mode.

Molality. Known also as molal concentration is the number of gram-molecular masses of solute per 1000 g of solvent.

Molarity. Known also as molar solution is the number of gram-molecular masses of solute per liter or 1000 mL of solution.

Normality. Normal solution has a specific number of equivalent masses of the acid or base dissolved in the solution per liter.

Pycnometer. A calibrated-volume ground, glass vessel fitted with a closure and a thermometer.

Pyrophoric chemicals. Chemicals that may spontaneously ignite upon exposure to air.

Recrystallization. A procedure whereby organic compounds which are solid at room temperature are purified by being dissolved in a hot solvent and reprecipitated by allowing the solvent to cool.

Reducing agents. Chemicals that are good sources of hydride and thus react vigorously with other chemicals or materials.

Reflux. Heating the chemical reaction or the solvent for a specific amount of time, while continually cooling the vapor produced back into liquid form, using a condenser.

Relative deviation. This measurement relates the deviation to the mean in order to indicate the magnitude of the variance. If the mean is a rather large number, then the deviation is not as critical as it would be in the case of a smaller mean.

Relative error. The absolute error (difference between the true and measured values) divided by the true value; usually expressed as a percentage.

Risk. A likelihood that the hazard will cause actual harm.

Safety. A protection or be away from danger, risk, or injury.

Safety culture. An attitude, rather than a set of rules or procedures.

Solvency. The substance to be purified should be sparingly soluble in the solvent at room temperature yet should be very soluble in the solvent at its boiling point.

Specific gravity. The mass of a substance divided by the mass of an equal volume of water.

Standard deviation. The most used of the deviation-averaging techniques because it indicates confidence limits or the confidence interval for analyzing all data.

Standard solution. A reagent of known composition used in a titration.

Steam distillation. Separating and purifying organic compounds by volatilization.

Sublimation. A phenomenon in which solids can go from the solid to the vapor state without passing through the liquid state.

Thin-layer chromatography. A simple, rapid, and inexpensive method for analyzing a wide variety of materials ranging from inorganic ions to high-molecular-weight biological compounds.

Titration. A process by which a substance to be measured is combined with a reagent and quantitatively measured.

Viscosity. The internal friction or resistance to flow that exists within a fluid.

Volume percent. Milliliters of solute per 100 mL of solution.

Volatility. The volatility of a solvent determines the ease or difficulty of removing any residual solvent from the crystals that have formed.

Abbreviations

ACS	American Chemical Society
CNS	Central nervous system
COSHH	The Control of Substances Hazardous to Health
CLP	Classification, Labelling and Packaging
CP	Chemically pure
CuCl	Copper(I) chloride or cuprous chloride
$FeSO_4$	Iron(II) sulfate or ferrous sulfate
fpm	Feet per minute
GC	Gas chromatography
GLC	Gas–liquid chromatography
GLP	Good laboratory practice
GMP	Good manufacturing practice
GSC	Gas–solid chromatography
HCl	Hydrochloric acid
HEPA	High-efficiency particulate air
HPLC	High-performance liquid chromatography
HVAC	Heating, ventilation, and air conditioning
IR	Infrared
ISO	The International Organization for Standardization
LC	Liquid chromatography
LC	Lethal concentration
LD	Lethal dose
LEV	Local exhaust ventilation
$LiAlH_4$	Lithium aluminum hydride
LLC	liquid–liquid chromatography
LSC	Liquid–solid chromatography
KI	Potassium iodide
MSDS	Material Safety Data Sheets
mps	Meter per second
NaH	Sodium hydride
$NaBH_4$	Sodium borohydride
NaOH	Sodium hydroxide
$NaHCO_3$	Sodium bicarbonate
NaCl	Sodium chloride
Na_2SO_4	Sodium sulfate
NFPA	National Fire Protection Association
NMR	Nuclear magnetic resonance
PPE	Personal protective equipment
TLC	Thin-layer chromatography
UPC	Universal Product Code
UPS	U.S. Pharmacopeia
UV	Ultraviolet
WHMIS	Workplace Hazardous Materials Information System

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Resources and Further Readings

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