

Inorganic Synthesis

Inorganic Synthesis:

A Manual for Laboratory Experiments

By

Nikolay Gerasimchuk
and Sergiy Tyukhtenko

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DEDICATED TO THE MEMORY OF PROFESSOR ANATOLIY BRUSILOVETS –
BRILLIANT EXPERIMENTAL INORGANIC CHEMIST

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PREFACE

This laboratory manual originated from eighteen years of teaching the class *Inorganic Preparations*, which follows the *Descriptive Inorganic Chemistry* course in the Inorganic Chemistry curriculum of Missouri State University (USA). Both courses are designed for chemistry majors. They represent a logical progression and harmonic combination of theoretical background in the discipline at first, with enhancement and retention of gained knowledge during following experimental laboratory work. This course is designed for lab sessions of four hours each.

The book provides an extensive and necessary introduction for students to typical glassware and lab equipment (labware) which are normally used in the synthetic chemistry laboratory. This introduction is followed by a brief description of the main laboratory procedures and operations that are essential for safe and productive laboratory work. These were limited to: filtration, extraction, distillation and reflux, work with vacuum, anaerobic/moisture free procedures, flash column and preparative thin-layer chromatography, and products recovery from solutions. In this context it is very important to note that *this laboratory manual is neither intended to promote or advertise any of the equipment brands and their manufacturers, nor it is intended to show off, or brag about the laboratory capabilities that exist at the authors' institutions!* In fact, the glassware, apparatuses and equipment used in this book fit very well into the average teaching and research facilities typical of numerous institutions of higher education around the world. Moreover, during the description of laboratory glassware, hardware and laboratory methods at the beginning of this manual, special attention is drawn to inexpensive alternative solutions when building equipment for common procedures, as well as to cost-saving lab techniques.

All preparative experiments are designed for the synthesis of grams' quantities of compounds. This ensures students' satisfaction with the whole process of the synthesis, work-up procedures and post-lab handling of substances, many of which will be further studied. This manual is heavily illustrated with 224 figures, 12 schemes and 20 tables, to aid students in carrying out all experiments and to help them learn laboratory

techniques. The main purpose of such an illustrative approach is to go in step with a new and younger generation of *visual learners*, who, in the digital age of the internet and mobile devices, truly value the old sentiment that ‘a picture is better than a thousand words’. Almost all illustrative material was produced by the authors, taking photographs from actual lab equipment and setups, or making drawings using freely available software.

Before the description of many experiments and characterizations of the obtained compounds, there are brief and condensed sections of theoretical background information. These allow the reader to get familiar with the topic that follows. Thus, the following physical methods and techniques are presented in these short introductory sections:

- thermal analysis,
- X-ray diffraction methods,
- molecular weight determination - cryoscopic measurements,
- cyclic voltammetry measurements in solutions,
- solutions electrical conductivity measurements,
- magnetochemistry in solid state and in solution,
- spectroscopy (vibrational, electronic, ^1H and ^{13}C NMR).

The concept of indirect learning has been used by authors for many years. In our academic settings, that means splitting a class of students into two equal groups, both of which conduct the same kind of experimental preparations, but use different compounds and some alternative work-up and samples handling details. There are laboratory exercises with extensions A, B, or C. Being in the same laboratory for four hours, students, in an indirect way, learn what their peers in the other group are working on. All experiments are presented in clear, step-by-step fashion to help students to carry out particular syntheses, conduct important procedures, and accomplish necessary measurements. All sections in the book are supplied with appropriate literature references for the reader interested in further learning.

During the course of these lab experiments, suitable single crystals of several compounds were grown by students, and subsequently characterized using the X-ray analysis. The main results of this work are presented and discussed in this manual, with all CIFs for five determined structures deposited into the Cambridge Crystallographic Data Center (CCDC).

Therefore, a combination of specially selected series’ of experiments, with alternative lab work, accompanied with paragraphs of short and

concise theoretical background, and detailed examples of calculations, make this book truly unique in the modern academic environment. This book also can be a useful reference for other synthetic chemists not limited to the inorganic/coordination chemistry field, who will be interested in the *interpretation* of vibrational, electronic, and - more importantly - 1D and 2D NMR spectra.

In summary, according to numerous students' feedback and evaluations, it is engaging, very intense, and yet likeable, and is considered to be a useful class. It has been a popular laboratory course, with 120+ chemistry majors who have enjoyed taking it, thus far.

ACKNOWLEDGMENTS

This laboratory manual would not be possible without the genuine interest of graduate and undergraduate students – all chemistry majors – in learning synthetic inorganic laboratory practices. Hence, the feedback of students who took this class during their studies at Missouri State is very much appreciated. Also, many students enrolled into this laboratory course showed a great deal of dedication and persistence, especially in lengthy chromatographic separations and purifications of synthesized compounds, and patience in crystals growth. Special recognition is given to Dr. Olga Gerasimchuk, for contributing theoretical background write-up on the X-ray powder diffraction method. The electrochemical equipment for the cyclic voltammetry measurements was provided by Prof. Erich Steinle, whose time and effort is very valued. Finally, generous help from the Department of Chemistry of Missouri State University in building this course is highly acknowledged. Similarly, the authors are in debt to the Northeastern University NMR core facility for the time made available for using the instruments for recording multiple spectra for this laboratory manual.

INTRODUCTION

This laboratory course is designed to develop important practical skills for chemistry majors interested in synthetic chemistry overall, not just inorganic chemistry. Students will learn proper techniques for preparation and handling of a variety of inorganic and coordination compounds. Thus, students will conduct:

- thermal decomposition reactions,
- preparation of moderately air-sensitive compounds,
- multistep synthesis/composition reactions,
- preparation and handling of moisture-sensitive compounds,
- synthesis, isolation and purification of coordination compounds,
- characterization of the obtained metal complexes using a variety of commonly available physical methods.

This course is structured in the following way:

I) The first part, which is reflected in experiments **1 – 4**, contains preparations of typical inorganic compounds with all relevant experimental details. Characterization of these compounds includes application of thermal analysis.

II) The second part, consisting of experiments **5 – 13**, comprises the synthesis and isolation of the two specially selected coordination compounds of kinetically inert transition trivalent metal ions – Cr and Co. These complexes' purification and subsequent characterization, using several spectroscopic and physical methods such as UV-visible, IR, and NMR (^1H , ^{13}C) spectroscopy, solutions electrical conductivity, and magnetochemistry (the Evans method for solutions and the Gouy method for solid samples), takes considerable laboratory time and effort.

Both these metal centers are selected for the following reasons:

1. Co(III) complexes are intensely colored, neutral and diamagnetic, which makes them suitable for extensive studies by the NMR method, along with conventional spectroscopic methods.
2. Cr(III) complex is also colored, but represents an anionic paramagnetic compound which brings to its characterization other techniques: solutions' electrical conductivity and magnetism.

Therefore, investigations of both complexes invoke complimentary physical methods that are often used in synthetic inorganic chemistry.

Overall, the number of synthesized or studied compounds is not large – only eleven compounds: Cu_2O , $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, PbSe , PbTe , CdCO_3 , NiCl_2 , CoCl_2 , SnCl_2 including two neutral Co(III) isomeric complexes and one anionic Cr(III) complex. Two other simple inorganic compounds (KMnO_4 and $\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$), were investigated using their thermal transformations. However, for a one-semester laboratory course in preparative chemistry, it is completely sufficient, counting the time spent on chromatographic purification, obtaining what is necessary for the characterization of different spectra, thermograms, voltammograms, and powder XRD patterns.

One of the most important components of this laboratory course is not only recording, but also *interpreting*, spectra of synthesized coordination compounds. Thus, interpretation of traditional IR- and electronic spectra of complexes of Co(III) and Cr(III) is entirely delegated to students provided with respective literature citations. However, the interpretation of the NMR spectra of seemingly simple Co-complexes was *not trivial* at all. It is presented in the laboratory manual in necessary detail for educational and training purposes.

The Student's Responsibilities

- 1) Come to the laboratory session prepared. This means reading and forming a conceptual understanding of the experimental procedures before the class. An explanation of details will be provided by the class instructor in a pre-lab discussion, at the beginning of the laboratory period. Nevertheless, students must come prepared for the experiment, as an understanding of the procedures, and the concepts behind them, will extend the time actually spent in performing them, and will provide safer operations in general.
- 2) Maintain a safe environment during laboratory experiments. While in the lab, always wear approved safety goggles, rubber gloves, and lab coat. Double check that you are placing the proper waste into the proper container; mixing organic and inorganic waste can generate explosive combinations and can cause injury or even death. Above all, use common sense and caution during all lab procedures. Absolutely no goofing or horseplay is allowed.
- 3) Use chemicals, solvents, and compressed gases, wisely.

- 4) Clean the lab after the experiments. This includes washing glassware, returning all containers, vials, and bottles to their proper places, and cleaning all workspaces (bench tops, hoods, sinks, and balance room).
 - Chemicals go in the cabinets beneath the hoods.
 - Acids and bases go in their respective cabinets, below the hoods as well.
 - Non-flammable solvents belong in the cabinet to the left of the chemicals.
 - Flammable solvents go in the yellow, flammable cabinet at the front of the room.
- 5) Students are expected to actively participate in data collection, recording spectra, and their understanding and interpretation, following detailed examples provided in the laboratory manual.
- 6) Compose and submit, in a timely manner, lab reports that include all details of the work performed: specifics of the procedure (including any deviations from the directions contained herein); chemical equations; quantities of the compounds used, in grams and moles; observations made during the course of the experiment; yield of the desired compound; and some plausible sources of its loss.
- 7) Stock all the obtained compounds in ampoules, or tightly closed and parafilm vials, in a dedicated safe place. Attach a label to an ampoule, or vial and write the compound's formula, amount, date, and the author's name.
- 8) Segregate waste (organic *vs* inorganic), and properly dispose of used chemicals and solvents.

CHAPTER 1

EXPERIMENTAL METHODS AND LABWARE IN INORGANIC SYNTHESIS

1.1. Commonly Used Glassware and Hardware

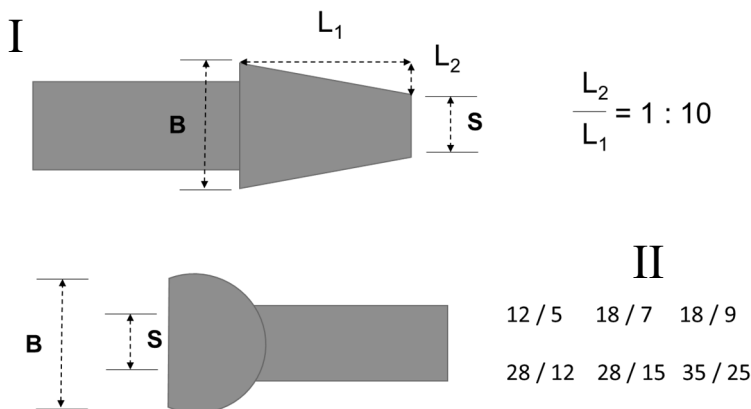
1.1.1 Types of laboratory glass, glass joints, greases

Glass is an amorphous solid material, obtained in an oven at a high temperature. Different oxides, such as SiO_2 , Na_2O , B_2O_3 and others, being melted and thoroughly homogenized, form glass for variable applications depending on the purpose. Laboratory glassware is made of four different types of glass: 1) fused silica, or quartz, SiO_2 ; 2) borosilicate Pyrex®-type/Kimax, etc.; 3) ‘molybdenum glass’; and 4) soda-lime green glass. There is a very significant difference in their thermal expansion coefficients and chemical composition. The most thermally stable (with the lowest expansion coefficient) is quartz; pure SiO_2 . ‘Molybdenum glass’ is indispensable when an electric feed through is required; the Mo-wire has the same thermal expansion coefficient and the glass-metal junction is vacuum-tight. However, the need for such a specific type of glass is far less common in synthetic chemical laboratory use, as opposed to electrochemical, physical chemistry, or physical laboratories. Therefore, in this manual we will focus on only three types of glass, the physical properties of which are summarized in Table 1.

Glass joints are used for the quick, tight, and convenient connection of different pieces of glassware during a variety of laboratory operations. Glass joints are conical (tapered), spherical, and flat O-ring, as displayed in Figures 1–5. Among tapered joints, there are clear, non-ground joints (made by pressing hot glass into high precision molds), and ground joints. Spherical joints are always ground, while flat O-ring joints are always clear. Tapered and spherical joints have two distinctive parts; inner (*F*, female type), and outer (*M*, male type), which, being connected, provide secure junctions of different pieces of glassware. In order to provide continuous connection of joints during work, plastic clips are used (Figure

Table 1. The most commonly used types of laboratory glass and their physical and chemical properties.

Glass type	Quartz	Borosilicate	Soda-lime (green)
Property			
Point of annealing, °C	~1120	~550	~520
Softening, °C	1710	820	700
Working T, °C	1850	1240	1050
Coeff. expansion, ppm	0.6	3.3	9.3
Density, g/cm ³	2.65	2.23	2.51
Chemical stability	unstable to bases	medium	relatively stable

**Figure 1.** **I:** Tapered/conical glass joints were standardized to have 1:10 conicity (the cone angle) regardless of the joint's length. The *M* type of joint (outer) is shown as an example. **II:** Spherical ground glass joint, and the most commonly used sizes in chemical laboratories'. The *F* type (inner) is shown.

8), while for spherical and flat O-ring joints, metal clamps are used (Figures 4, 5). The diameters of portions of the joint are labeled B (big) and S (small), respectively, and used for the joints' size marking. An adoption of the same set of standard sizes throughout the scientific community around the world has allowed joints to be mutually interchangeable and replaceable, independent of the state or method of their manufacturing (Figure 1). For spherical joints, their size is determined by the diameter of ball size and the inside diameter of the joint (glass tube part), with all numbers being in millimeters.

Thus, a tapered joint #24/40 reads as largest diameter of 24mm, and the length is 40mm. For a spherical joint #28/15, the reading is ball diameter 28mm, while the opening, the tube diameter, is 15mm.

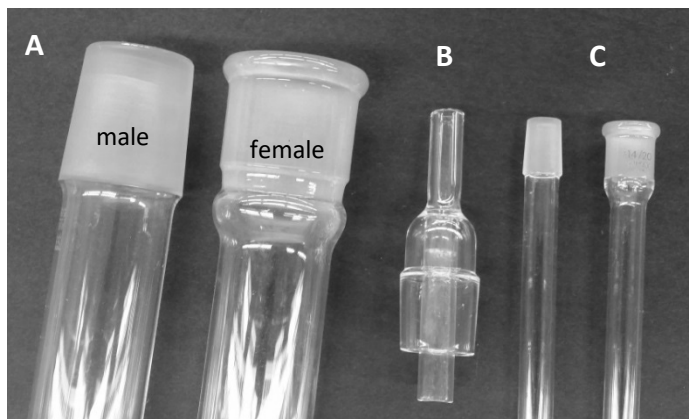


Figure 2. Unlubricated tapered ‘short’ glass joints; grounded Pyrex joints (A,C), and hot-pressed clear glass joint (B, by Vicor®).

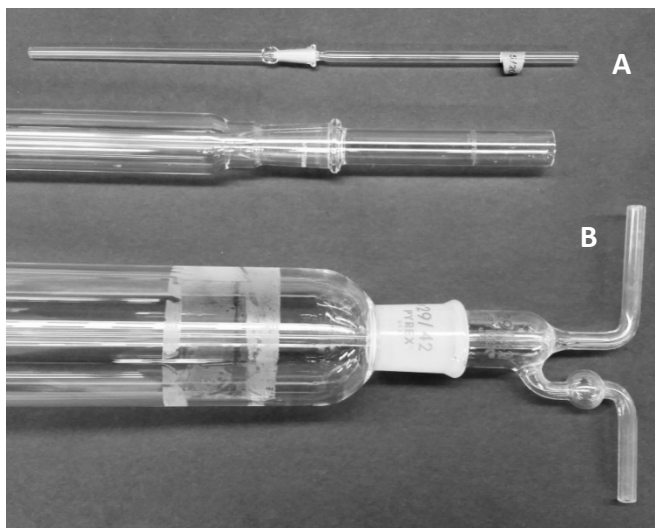


Figure 3. Unlubricated tapered full-length glass joints; grounded Pyrex joints (5/20 - A, and 29/42 - C), and hot-pressed clear glass joint (19/38 - B, by Vicor®).

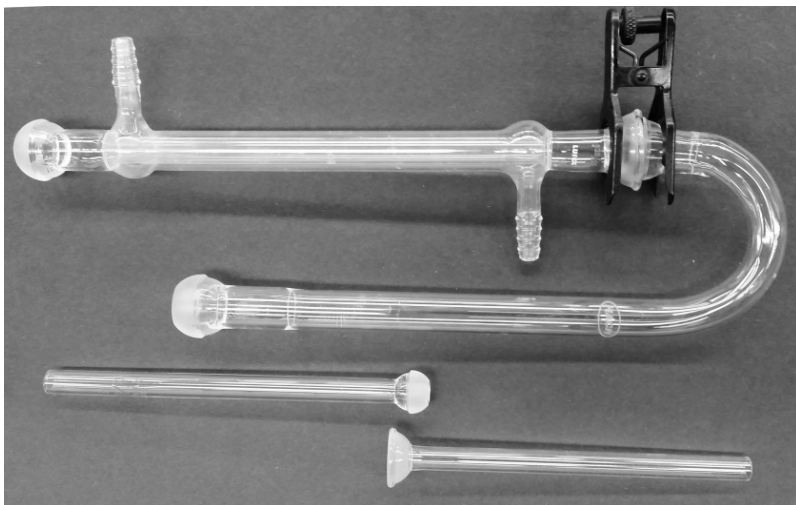


Figure 4. Unlubricated spherical grounded glass joints of different sizes. A small amount of grease and a metal clamp are required to keep joints tight.

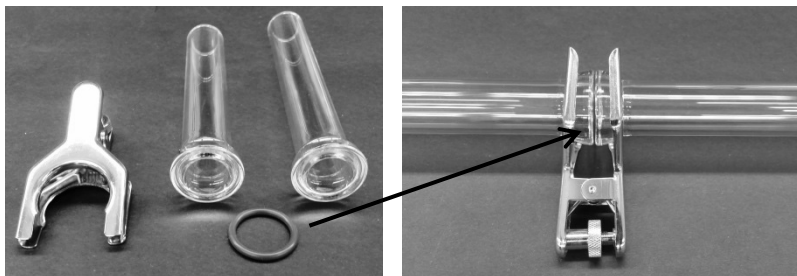


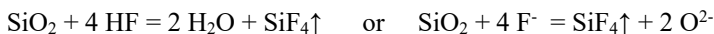
Figure 5. Flat, polished, clear, O-ring glass joints. A metal clamp is required to keep joints tight. No grease is necessary to provide vacuum-tight connection.

Quartz is the least chemically stable glass, but has excellent thermal stability. A great variety of test tubes, flasks, beakers, and evaporating dishes are made from quartz. Because of its intrinsic chemical purity (just SiO_2), quartzware is widely used in analytical chemistry for the analysis of special purity materials, used for instance, in electronics, when possible leaching of boron, as well as Ca, Mg and Na ions, is undesirable. Quartz is also transparent for the visible and NIR regions of the electromagnetic spectrum, and for UV-radiation down to 190nm. Thus, it

is used in windows' materials and cuvettes for numerous photochemical and optical spectroscopy applications.

Pyrex/Kimax/Duran borosilicate glass is the dominant material for the manufacturing of modern laboratory glassware. It is also relatively stable to temperature gradients of almost 250°C without cracking, whereas 'green glass' is the most stable to etching by bases in solutions, but has very low tolerance for heat shock.

All types of glass, and glassware made from it, are highly sensitive to fluoride anion, because of the fast formation of gaseous SiF₄, which leaves the system and etches, or weakens, the glass:



Therefore, special care should be taken to avoid even short contact of any glass with HF, its solutions and salts, even those not soluble in water. Plastic bottles and plastic-ware are necessary for the work and handling of fluorine-containing ionic inorganic compounds.

Tapered joints in common laboratory settings can be easily connected and held in place by color-coded plastic clamps (Figures 8, 9).

Table 2. The most common tapered joint sizes used in synthetic laboratories. All sizes are in mm; the small end diameter is notated in parenthesis as Θ.

'Shorty' (Θ)		Medium length (Θ)		Full length (Θ)	
14/10	(13.5)	14/20	(12.5)	14/35	(11.0)
19/10	(17.8)	19/22	(16.6)	19/38	(15.0)
24/12	(22.8)	24/25	(21.5)	24/40	(20.0)
29/12	(28.0)	29/26	(26.6)	29/42	(25.0)
34/12	(33.3)	34/28	(31.7)	34/45	(30.0)
45/12	(43.8)	n/a		45/50	(40.0)

Threaded glass items are a recent addition to the ways of connecting different glass pieces. One of the methods is to make a thread on a glass by stamping molten glass into the cast form, as introduced by some companies making laboratory glassware (Aldrich, Figure 6), and stopcocks (Kontes, Ace, Figure 7). Stopcock plugs are commonly made of highly chemically-resistant Teflon, and silicon rubber O-rings, making a tight fit which does not require lubrication. The latter makes stopcocks very suitable for both vacuum applications, and in addition of chemicals in

laboratory procedures, makes funnels that are capable of controlled delivery of very aggressive liquids and solutions such as nitric acid, bromine, *etc.*

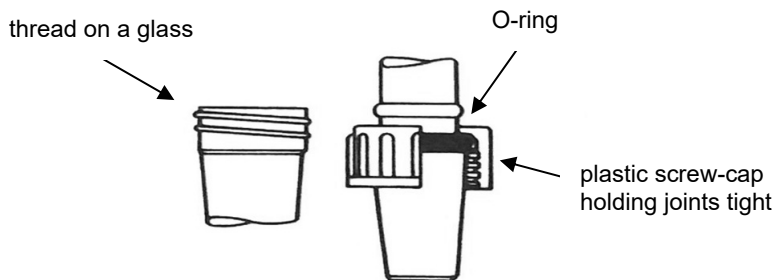


Figure 6. Two lines outer thread on a tapered glass joint designed by Aldrich.

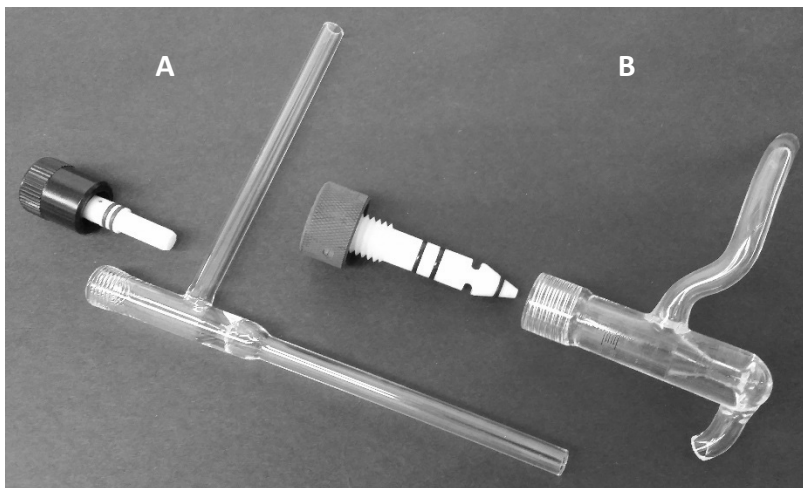


Figure 7. Two vacuum stopcocks with threads on glass: *outer*, **A** (manufactured by Kontes, ChemGlass and others), and *inner*, **B** (pioneered by Ace Glass Inc.).

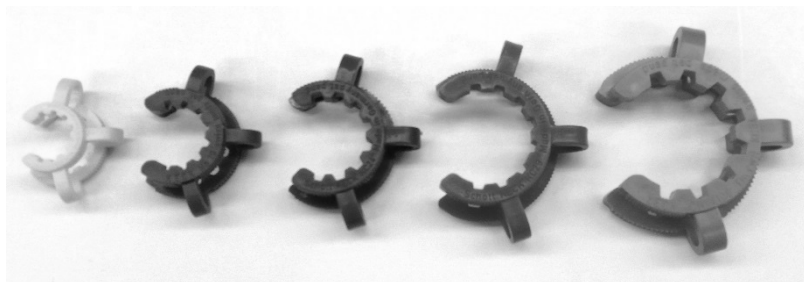


Figure 8. Plastic clamps (Keck clips) for the secure connection of the most common joints from left to right: #14 (yellow), #19 (blue), #24 (green), #29 (red), and #34 (orange).

Greases. All joints are made to fit the purpose which is to provide the tight connection of different pieces of glassware during a variety of laboratory procedures. One of the most important properties is vacuum tightness, followed by solvent/solution tightness. Normal ground joints (both tapered and spherical) are not tight or leaking, unless grease is used to lubricate both *F* and *M* type of joints (Figures 2, 4). Vacuum-tight yellow color greases are made of petroleum products (Apiezon-type) and are readily available, albeit pricy. More economical versions are clear silicon greases. Both can be applied on joints, as a thin layer at room temperature or, slightly heated, which is better for providing complete lubrication; an air/vacuum-tight pair of joints is transparent and has no streaks or discontinuity (Figure 9). Both of these greases can be safely used during work with aqueous solutions, alcohols, acetonitrile, and acetic acid.

Both petroleum and silicon greases should be removed prior to glassware storage and cleaning using hydrocarbons, such as heptane or hexanes soaked into a cotton ball. All these procedures must be conducted wearing protective gloves (to avoid skin damage), under the ventilation hood, and in complete absence of an open flame to avoid fire. Clear glass joints do not require lubrication for normal operations, because of their intrinsic tightness achieved during manufacturing, but these joints are considerably pricier and rarely used in chemical laboratories.

Because of the solubility of petroleum-based greases in hydrocarbons, other types of starch-glycerol based greases, which are not soluble in the former, are used [1,2].

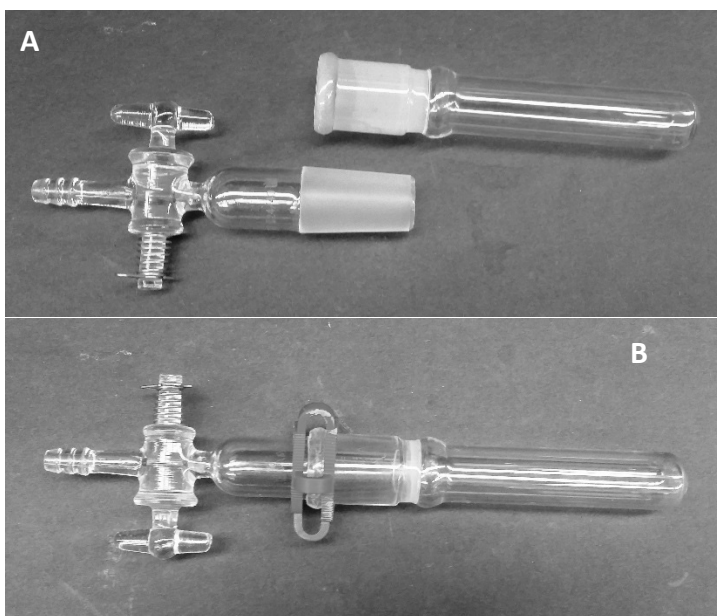


Figure 9. A pair of full length #24/40 tapered joints: **A** – un lubricated, and **B** – greased with Apiezon M, and secured together with Keck plastic clamps.



Figure 10. Petroleum-based vacuum greases in aluminum foil tubes.

1.1.2 Glassware for common laboratory procedures and operations

Vessels for carrying out chemical reactions in open air

These pieces of glassware are beakers, flasks, and test-tubes. They all exist in a great variety of sizes. Below, you may find pictures and short descriptions of all these items with some comments.



Figure 11. Pyrex beakers of variable sizes (A), and jacketed beaker (B).

Beakers are known to be made of flint glass (green glass), Pyrex/Kimax glass, and quartz, all in variable sizes (Figure 11 A). A set of the most usual volumes of beaker ranges from 10mL to 2L capacity. Marks indicate approximate volume and can't be used for accurate measurements. A special kind of beaker – a jacketed one – is used for carrying chemical reactions, or crystallizations at controlled temperatures by circulating hot (or cold) fluid from the thermostat (Figure 11 B)[see Section 1.1.3 below].

Flasks can be round-bottomed, or flat-bottomed, with the latter group providing the convenience of being able to stand unsupported on level flat surfaces, such as benchtops, hotplates, and ventilation hoods (Figure 12). The top end of a flask can be just fire-polished, or with a tapered ground joint. Also, flasks can have more than one end (called a *neck* in this category of glassware). Two or three-neck round flasks are widely used in the lab (Figure 13), although four and five-neck flasks are known, but rare, and mostly used in laboratories carrying out chemistry procedures in the field of natural products synthesis, medicinal chemistry, organic/heterocyclic chemistry, and polymers chemistry. These flasks are commonly named as *reactors*. As beakers, flasks have a variety of sizes, and in the chemical laboratory, the most useful volumes range from 25mL to 2L. All the flasks

mentioned here are made of thermally stable glass, such as Pyrex/Kimax, or quartz (single neck only), because their main purpose is to carry out reactions which, most of the time, involve heating.



Figure 12. Flasks: round flat-bottomed, round, and pear-shaped.

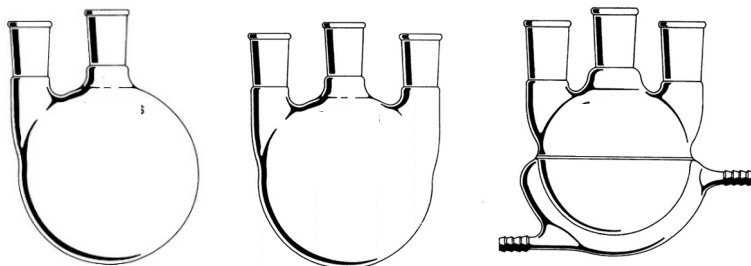


Figure 13. Two-neck reaction flask, and three-neck reaction flasks, including jacketed flask.

The extra necks are there to accommodate connection to additional funnels, such as gas tubes to deliver gases, reflux condensers, or thermometers, which are needed to carry out certain chemical reactions. Jacketed reactors are very convenient for low-temperature procedures, or in conditions when heating of the vessel should be confined into a small place, and the use of a hot plate is not desirable, or possible.

Another type of flask widely used in the synthetic laboratory is the flat-bottomed conical flask – Erlenmeyer flask – which is made in a large variety of sizes and types of glass. There are flint glass, Pyrex/Kimax, and quartz flasks, with volumes for the first two types of glass ranging from 10mL to 4L. Typical sets of these flasks are shown in Figure 14.

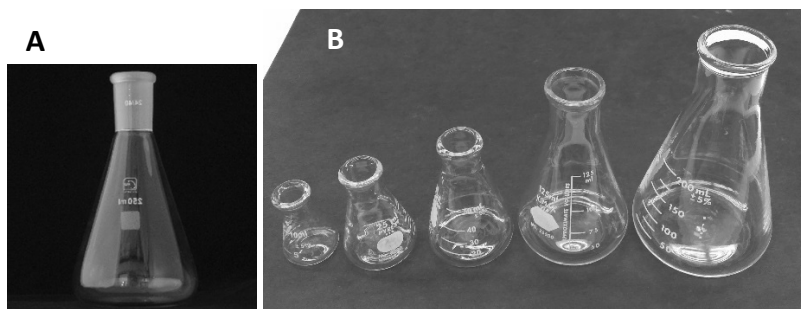


Figure 14. Conical (Erlenmeyer) flasks with ground taper joint (A), and with fire-polished rim end (B).

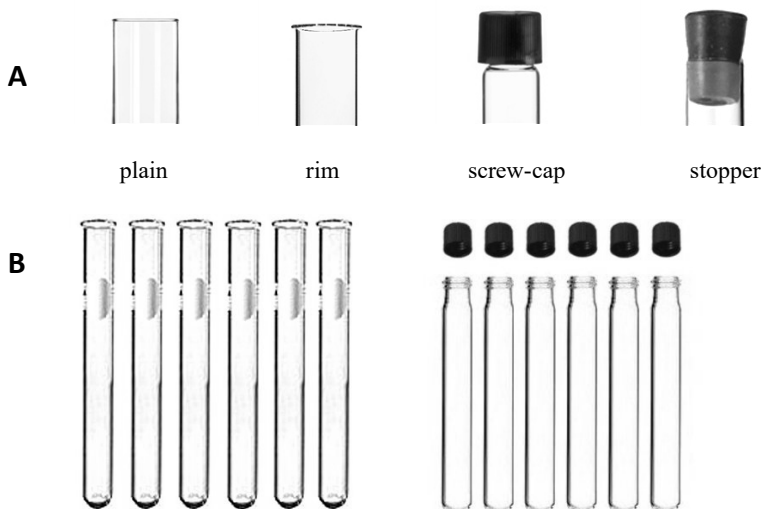


Figure 15. Types of test tubes' ends (A), and sets of the most commonly used test tubes in the laboratory (B).

Test tubes. Large varieties are available for common laboratory work, both by size/diameter, and by the type of test tube end, as shown in Figure 15. Depending on the type of laboratory work, test tubes can be made of plastic or glass of different kinds; green borosilicate, Pyrex/Kimax, or quartz. Typical glass-made representatives are shown here.

Glassware for laboratory processes

Addition of gases to the reaction mixture can be achieved by direct bubbling using a gas conditioning bottle (Figure 16A), or via adapters, either straight, or angled, with multiple ports, when more than one gas is needed (Figure 16B). For example, the washing bottle allows drying of the gas, or monitoring the rate of gas addition by counting bubbles. When the number of inlets into the reaction vessel is limited, a multiple port adaptor is a convenient piece of glassware, where, for instance, an inert gas and a gas for the reaction (H_2S , CO_2 , NH_3 , etc.) can be added simultaneously, at different rates (Figure 16B).

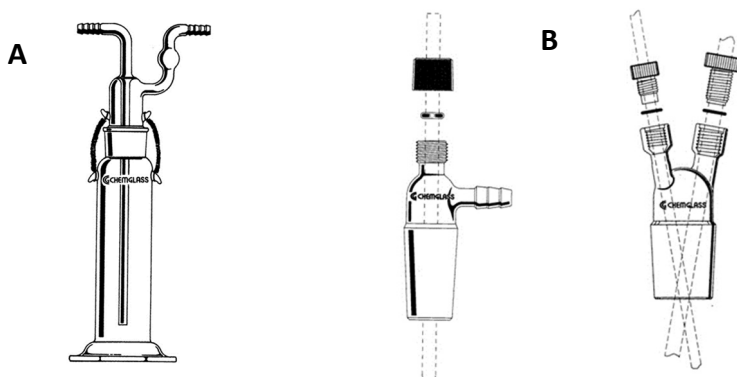


Figure 16. Bottle that allows gas conditioning and monitoring (A) and straight, single tube, single and multiple port adapters (B).

Adding liquids and solids to the reaction mixture (or transfer of these materials) can be accomplished using additional glassware funnels, shown in Figure 17. Fast, unregulated addition/mixing can be achieved using these funnels.

As depicted in Figure 18, the addition of liquids (A), or solids (B), can be done in a dropwise or stepwise fashion, over a controlled, prolonged time. In all these cases, ingredients can be added under vacuum, or an inert gas blanket, due to the side bypass tube indicated by the arrow. The tube allows for keeping the same pressure above and below the stopcock. As shown in Figure 18, funnels are available in a variety of sizes, but made exclusively from thermally stable Pyrex/Kimax glass.

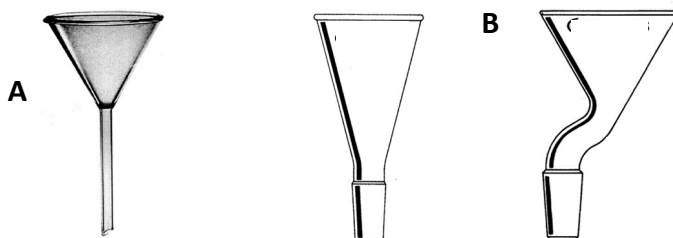


Figure 17. Transfer of liquids (A) and addition of solids using straight or curved adapters for the reactors with multiple necks, when space around them is often limited (B).

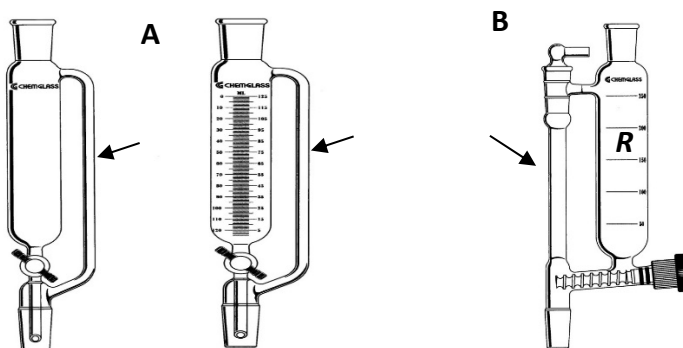


Figure 18. Funnels for regulated addition of liquids (A) and solids (B) to the reaction mixture. The latter funnel has a Teflon-made screw turning, which allows advancing of solid material from the main reservoir *R* to the vessel below.

Addition of small quantities of liquids by pipettes. For qualitative, quick, and convenient addition of solutions and solvents, two types of pipette are widely used in the synthetic chemical laboratory; disposable variable length glass pipettes, and disposable plastic pipettes (Figure 19).

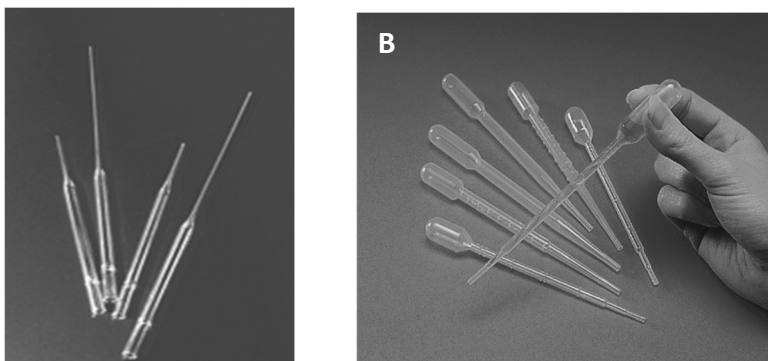


Figure 19. Disposable glass (A) and plastic pipettes (B).

Glass pipettes are made of flint (green) glass, and require a small rubber bulb for use. Their total capacity is $\sim 3\text{mL}$, and they are only for delivery/transfer of liquids, since they don't have graduated marks. Plastic pipettes are made of thin polyethylene or polypropylene, appear as translucent devices in several sizes, and can deliver from 5mL to 25mL of liquid. Marks on plastic pipettes are not very accurate, and these pipettes are only for delivery/transfer of approximate ($\pm 5\%$) quantities. Both types of pipette are resistant to corrosive substances in ambient conditions such as acids and bases (for several minutes at least), work well with the majority of common organic solvents/solutions, and, therefore, have gained popularity in laboratory practice over the last two decades.

Compounds' storage

Chemical compounds that require storage without contact with moisture or air can be kept in vacuumed desiccators charged with drying agents. These are typically P_2O_5 in a porcelain or glass dish, activated (preheated under vacuum – see Figure 35 in the next section) with granulated silicagel, anhydrous salts such as CaCl_2 , CaSO_4 , or concentrated H_2SO_4 , placed inside the Erlenmeyer flask inside the desiccator (Figure 20). Most desiccators these days are equipped with stopcocks, to provide a vacuum which can be pumped within a minute or two, to speed up the drying of material in these very useful pieces of glassware. Glass desiccators (Figure 20A) require a thin layer of lubricating grease to keep the vacuum inside, while plastic desiccators need to have a soft rubber O-ring for the same purpose (Figure 20C). In desiccators, compounds can be stored in vials of different kinds, beakers, flasks, or bottles made of clear or amber glass, or

plastic. If dryness is a concern, then the most convenient way of storage is the use of dry cabinets (Figure 20B) filled with solid absorbents; drierite®, or blue, indicating silicagel (with CoCl_2 as the color-changing ingredient).

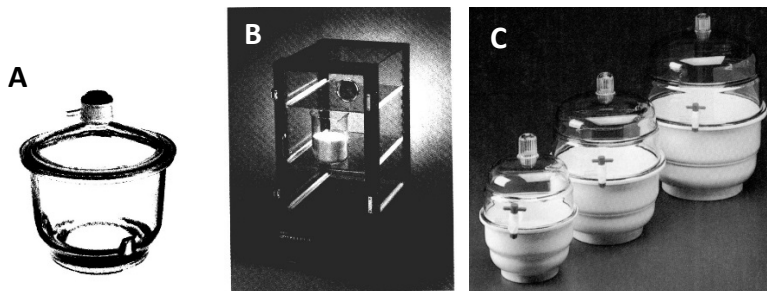


Figure 20. Desiccator (A), plastic dry cabinet (B), and plastic vacuum desiccators (C).

Important auxiliary glassware: gas washing bottles, drying tubes, gas drying towers, and porcelain-ware

Typical examples of these pieces are presented in Figures 21-23. The **gas washing bottles** have a fritted (coarse grade) ending at the end of the inner tube, which provides much larger numbers of small bubbles coming through the washing liquid, for better efficiency. Often, this is concentrated H_2SO_4 or H_3PO_4 used for gas drying, but frequently, concentrated solutions of baking soda, or bases, are used to trap acidic impurities, such as gaseous HCl or mist of the acids above. The layer of liquid inside the bottle is normally kept $\sim 2\text{cm}$ above the upper end of the frit to avoid a significant inner pressure build-up. Plastic clips or metal springs are often used to keep both parts of washing bottles tight, because of the presence of some small extra pressure normally encountered during work with these devices.

Drying towers are normally filled with blue-indicating SiO_2 , granulated anhydrous CaCl_2 , glass/ceramic/porcelain beads, mixed with P_2O_5 . The first agent has a very large static capacity to absorb moisture, while the last agent is the most efficient, albeit messy, during its replacing. Two cotton balls (or compacted glass-wool balls) on the top and the bottom of the tower are necessary to contain the drying content inside.

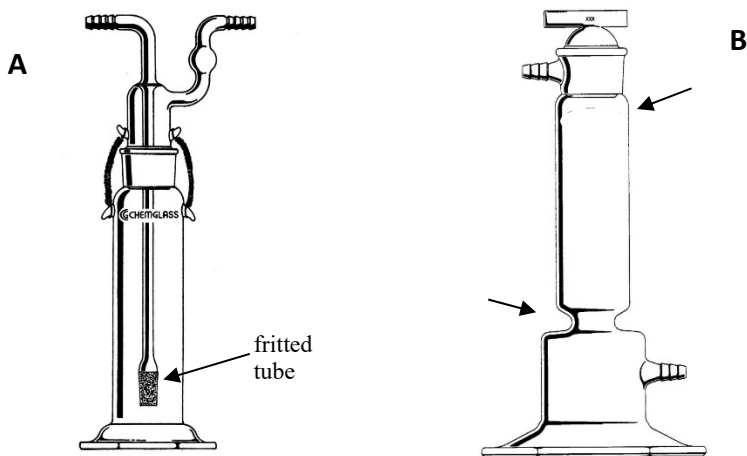


Figure 21. The washing bottle with a fused coarse glass frit (A), and the drying tower (B). Arrows indicate where cotton/glass-wool balls should be placed to prevent motion of drying agents during work or handling the tower in the lab.

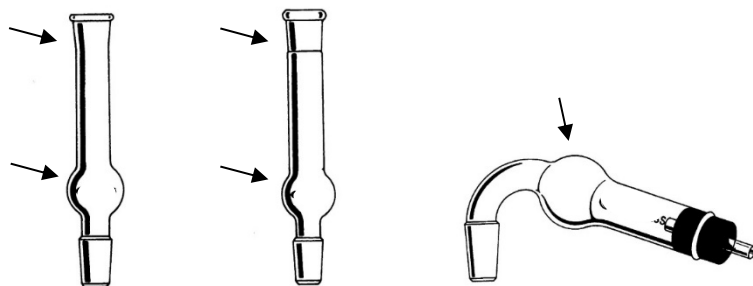


Figure 22. Drying tubes (to be filled with a desiccant) to prevent moisture entering distillation equipment, or freshly distilled solvents, or reaction mixtures. Arrows indicate where cotton/glass-wool balls should be placed to keep drying agents in place.

Drying tubes normally have tapered joints for connection with the condenser, or other parts of distillation equipment, to which they are attached by plastic clamps (Figure 22). It is very important to keep free passage of air through these tubes and avoid clogging, because of the absorbed moisture! Failure to maintain this working condition may lead to whole reflux or distillation equipment breakdown, due to pressure buildup.