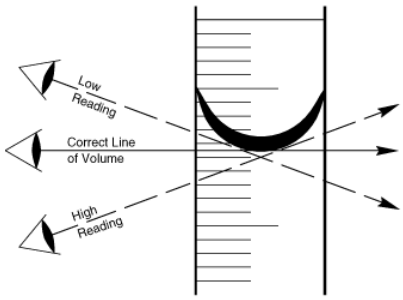
Chapter 6 Volumetric Analysis

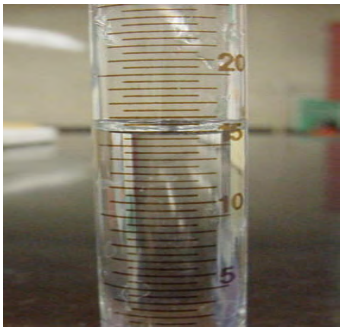
Volumetric analysis involves the measurement of liquids. Since water and wastewater laboratories deal mostly with liquids, it is easier to measure liquids as volumes rather than weigh them. Typical activities of the lab technician would involve measuring volumes and transferring liquids, preparing standard solutions and analysis by methods such as titration and spectrophotometry

When water is placed in a container, there is a chemical attraction between the water and its container. Water tends to adhere to the sides of the container and "climb" the sides. The stronger the attraction, the higher the water will climb. Glass has a stronger adhesive attraction than plastic. This climbing liquid gives a curved and distorted surface called a meniscus.

The water level is measured at the bottom of the meniscus. When measuring liquids, it is important to read the water level at a 90° angle to avoid parallax error. Parallax error occurs when the technician looks at the meniscus incorrectly.



Read the meniscus of the graduated cylinder below. You read _____ ml

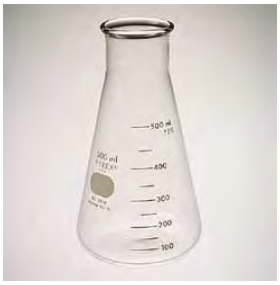


(15 ml)

Glassware manufacturers etch the volume marks on the glassware. Different types of glassware have different calibration marks and accuracy. Glassware can be divided into two general categories - general glassware and measuring glassware.

General Glassware

The two most widely used pieces of general glassware are beakers and erlenmeyer flasks.



They are used to mix and heat solutions, to hold samples and to provide a container for chemical reactions such as titrations. Many beakers and flasks have graduation markings, however, the markings are only approximate readings, usually within 5%. This inaccuracy delegates these pieces of glassware to measurement of non-critical volumes. Beakers and erlenmeyer flasks can be heated and cooled without concern for distortion of the graduation marks. Glassware marked **Pyrex®** or **Kimax®** can be heated and cooled without regard to temperature shock and resultant glassware breakage.

Measurement Glassware

All glassware designed for volumetric measurement are labeled either TD or TC. TD glassware is used "To Deliver" while TC glassware is used "To Contain".

"To Deliver" (TD) Glassware

Glassware used "to deliver" consists of:

1. Graduated Cylinders
2. Burets
3. Pipets

Graduated Cylinders

Graduated cylinders are used to deliver low accuracy volumes. Graduated cylinders are found in volumes of 10, 25, 50, 100, 250, 500, and 1000 milliliters.

In wastewater analysis, graduated cylinders are useful for total solids and total suspended solids measurement because the solids may clog other higher accuracy glassware.

When using a graduated cylinder, select a size closest to the volume needed to reduce the error involved. For instance, if you need to measure 40 ml, use a 50 ml graduated cylinder rather than a 100 ml cylinder. Graduated cylinders are made of high quality borosilicate glass or plastic such as polypropylene. Both polypropylene plastic and glass graduated cylinders can be autoclaved as necessary.

Burets

Burets are designed "to deliver" variable volumes. They are made from accurate bore glass tubing with glass or teflon stopcocks and capillary tips. The stopcock is a valve used to regulate the flow of liquid from the buret and with a little practice can deliver 1 drop at a time. Stopcocks are made from either glass or Teflon. Teflon stopcocks are more expensive than glass but eliminate binding problems and contamination from stopcock grease. Cheaper burets still use glass stopcocks and must be lubricated with stopcock grease. When using stopcock grease, only use a very thin layer as the grease will work its way into the bore and plug or restrict the flow of liquid from the buret.

Burets are marked on the side in various graduations. The most common sizes are 25 and 50 mls with graduations divided into 0.1 ml increments. Buret readings can be interpolated to the nearest 0.01 ml but for most analysis, only 0.1 ml accuracy is needed.

Filling a Buret

Burets are primarily used for titrations. Titrations require the addition of a controlled and measurable amount of liquid. To accurately measure this volume, the buret must be clean, uncontaminated, and used correctly. To fill a buret correctly and avoid contamination:

1. Close the stopcock

2. Pour approximately 10 ml of the solution to be used into the buret.
3. Drain some of the solution through the buret tip and pour out the remainder to drain.
4. Repeat these steps 3 to 4 times
5. Fill the buret above the zero line, and check for bubbles clinging to the walls of the buret. If possible fill the buret from the original reagent bottle; otherwise, transfer a small amount to a dry, clean beaker. Bubbles on the side of the buret can be released by gently tapping with your finger.

Safety: Fill the buret over the sink and below eye level.

6. Withdraw the excess liquid through the tip to remove any air bubbles in the stopcock or capillary tip. A bubble in the tip is an error.

7. Adjust the meniscus to zero by opening the stopcock.
8. Remove any drops clinging to the tip by touching the buret tip to the wall of a waste solution beaker (not the original beaker to avoid contamination). Residual drops on the outside of the buret will give inaccurate results.
9. Place the buret in the buret stand, making sure it is clamped vertically and clamped tightly.

Care of Buret
Poor rinsing or cleaning may cause solids to dry on the inside of the buret. A clean buret should produce a smooth sheet of water. If drops of liquid adhere to the inside of the buret, it is dirty and must be cleaned. Small volumes of liquid adhering to the inner glass wall make it impossible to accurately determine the amount of liquid delivered. Wash dirty burets with hot water, soap, and a buret brush. Rinse 10 times with large volumes of tap water, then rinse 5 times with small volumes of distilled water. Wash the buret immediately after use and store inverted on the buret stand with the stopcock open.

Burets should not be used for storage. Always throw the buret contents away when finished for the day and never return them to the original container. If the solution is to be left in the buret for a few hours, cover the buret top with a beaker or cap to prevent dust contamination and liquid evaporation. Never store bases in a buret for any length of time. Bases will cause glass stopcocks to freeze and can etch the glass walls thus altering the buret's capacity.

Use of a Buret
To use a buret, simply make sure it is clamped vertically and the stopcock is closed. After filling correctly, turn the stopcock to zero the buret. Record the initial buret reading. To deliver correctly, turn the stopcock slowly to dispense the desired volume. A good technician will be able to control the buret such that only one drop can be delivered if desired. When delivery is completed, record the final buret reading. To determine the volume delivered, subtract the initial reading from the final reading. Be careful to avoid parallax errors.

Pipets
The third piece of glassware used "to deliver" various volumes of liquid is called a pipet. There are 2 major categories.

1. Measuring (Mohr and Serological) pipets
2. Volumetric (Transfer) Pipets

Filling any pipet requires suction. All pipets should be filled using a pipet bulb to provide the necessary suction. A pipet bulb is a mandatory safety device and must be insisted upon in all lab work. Pipet bulbs eliminate contact between the analyst's mouth and the pipet, thereby preventing accidental ingestion or inhalation. Pipet bulbs are often contaminated, so they must be handled carefully and cleaned when a solution has accidentally been sucked into the bulb. Clean the pipet bulbs promptly to avoid corroding the internal check valves.

Pipets are used both for measuring and transferring volumes. One major problem encountered with pipets used to measure

wastewater is the presence of large particulate matter. The pipet tip may be too small to allow some solids in and thus filters the sample or the tip may clog when letting liquids/solids out. This will also act as a filter and alter the actual sample concentration.

Measuring Pipets

Measuring pipets fall into 2 types:

1. Mohr Pipets
2. Serological pipets

The top pipet below is called a Mohr pipet. Mohr pipets are graduated in various divisions almost to the end of the pipet. No liquid should be delivered past the last graduation. They have very narrow diameter tips and are not very useful in wastewater analysis if suspended solids are present.

Figure: Mohr pipet

Serological pipets are graduated in various divisions all the way to the end of the pipet. These are often called blowout pipets. They have a large bore and work well with most wastewater samples. If solids interfere, the sample can often be homogenized to minimize plugging.

Figure: Serological pipet

Safety: Serological pipets should be blown out using a pipet bulb not your mouth.

Using Mohr and Serological Pipets

1. Select a dry, clean pipet of appropriate size. If clean, dry pipets are unavailable, rinse with the solution to be used. Avoid contaminating or diluting the solution by dipping a dirty or wet pipet into the original solution. Pour some of the solution into a clean beaker, and then discard after rinsing the pipet.
2. Use a pipet bulb. First squeeze the bulb to remove air, immerse the pipet tip into the reagent then fill the pipet above the calibration mark.

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3. Remove the pipet bulb and place your index finger over the pipet end. These pipet bulbs are not designed to be inserted into the pipet, only set on the top to create a suction.

4. Wipe the pipet tip with a clean cloth or Kimwipe® to remove any drops clinging to the outside of the pipet.
5. Hold the pipet vertically and gradually drain the excess solution into a waste beaker until the meniscus is exactly on the desired mark, usually zero. Never put the excess solution back into the original reagent bottle. If there is a drop still hanging on the tip, gently touch the tip to the side of a waste beaker.

6. To deliver, allow the reagent to drain vertically into the desired receiving container. By gently twisting the pipet, the rate of withdrawal can be controlled. If using the full volume, blow out the last remaining drop in serological pipets but do not go below the last line on Mohr pipets.
7. Discard any excess solution remaining in the pipet.

Volumetric Pipets
Volumetric pipets or transfer pipets are special pipets used for accurate work. They have a smaller measurement error than Mohr or serological pipets. Volumetric pipets differ from serological pipets in that they have only one calibration mark. Volumetric pipets come in standard sizes of 1.0, 2.0, 3.0, 4.0, 5.0, 10.0, 15.0, 20.0, 25.0, 50.0, and 100.0 milliliters.

Figure: Volumetric pipet

Most procedures requiring high accuracy use volumetric pipets. If the procedure specifically requires a volumetric pipet, it is implied by using the decimal point in the notation. For instance, if the procedure calls for 5 ml of solution, a serological pipet could be used. However, if the procedure calls for 5.0 ml, a volumetric pipet should be used. Volumetric pipets are commonly used to prepare working standards from stock solutions.

Using Volumetric Pipets
1. Use a pipet bulb, suck a few milliliters of the chemical reagent into the pipet to rinse the pipet. Hold the pipet horizontal and turn the pipet to rinse the insides. Drain and discard the solution.
2. Squeeze the pipet bulb to remove air, place the bulb on the end of the pipet, immerse the pipet tip into the reagent then fill the pipet above the calibration mark.
3. Quickly remove the pipet bulb and place your index finger over the pipet.
4. Dry the outside of the pipet tip with a paper towel or kimwipe.
5. Hold the pipet vertically and gradually drain the excess solution until the bottom of the meniscus is on the calibration mark. Do not drain the excess solution back into the original solution.
6. To deliver, allow the reagent to drain vertically into the desired container. Allow the liquid to drain for 5 to 10 seconds after the liquid is dispensed. **Do not blow out.** Touch the pipet tip to the side of the receiving container. There should be a small volume of liquid left in the tip. The presence of this drop is accounted for in the calibration of the pipet and must not be blown out.

Cleaning Pipets
1. Store dirty pipets upside down in a pipet basket in soapy water.
2. When full, rinse for 1 to 2 hours in the pipet rinser.

3. Remove and rinse in a distilled water bath 3 times.
4. Let dry. Pipets that do not drain smoothly or leave residual drops inside the pipet are dirty and need more aggressive cleaning with acid.

"To Contain" (TC) Glassware

Volumetric flasks
Volumetric flasks like volumetric pipets are specially calibrated flasks with a single calibration mark on the neck. Volumetric flasks are used only "to contain" a specific volume, not

to deliver the volume. A 100 ml volumetric flask filled to the mark will **contain** 100 ml but will not **deliver** 100 ml if it is inverted and drained. Commonly available sizes of volumetric flasks are 25, 50, 100, 250, 500, 1000 and 2000 milliliters. Volumetric flasks are used to make reagents and standard solutions. Volumetric glassware is usually calibrated at 20°C. Hot liquids should never be added to volumetric flasks and the flask itself should never be heated. Heating will "melt" the glass. While this melting will not be visible it will change the flask's calibration.

Figure: Volumetric flask

Using a Volumetric Flask

1. Carefully transfer a known volume or weight to the flask. Volumetric pipets should be used to transfer known volumes. If the substance is a powder, transfer using a funnel. Rinse the powder from the funnel and neck of the volumetric flask several times using distilled water.
2. Fill the flask approximately 3/4 full, stopper, and thoroughly mix. Continue mixing until all the powder has dissolved.
3. Fill to the calibrated mark with distilled water.
4. Stopper and mix by inverting again. Invert a minimum of 10 times to make sure the liquid in the neck gets mixed. Each time allow the trapped air to move through the solution completely. Shaking or twirling is ineffective. Magnetic stirrers are OK but the magnet should be added after filling to the calibration mark. Be careful the magnet does not displace water out the top of the flask.

Glassware Cleaning

If handled promptly, most dirty glassware can be cleaned with soap and water. Cleaning should be done as soon as possible to avoid drying solids on the side of the glassware. The standard procedure for glassware cleaning is:

1. Add a ***pinch*** of laboratory detergent to the glassware.
2. Add hot tap water.
3. Scrub the glassware using an appropriate size brush. Avoid scratching the glass. As brushes become used, the metal if often exposed and can easily scratch the glass. Dispose of bad brushes.
4. Rinse ***10 to 20 times with tap water*** to remove the detergent. Allow the water to drain each time.
5. Rinse ***5 times with small amounts of distilled water***. At this point the glassware is clean but has residual tap water that needs to be removed. Distilled or deionized water has few impurities and is used as a final rinse. The glassware does not need to be filled completely when using distilled water. Five to ten precent of the bottle volume is adequate. Again allow time for the glassware to drain between successive rinses.
6. Dry the outside of the glassware and store in a dust free environment.

For more stubborn films or residues such as iron stains, or grease accumulations, stronger cleaning solutions may be necessary. The most common is chromic acid cleaning solution. To prepare this solution, slowly add l liter of concentrated sulfuric acid, with stirring, to 35 ml of saturated sodium dichromate solution. Be sure to use safety goggles, gloves, and an apron when using chromic acid. This solution is very dangerous, requiring special handling and disposal.