

TREATMENT OF EXPERIMENTAL DATA

I. PRECISION AND ACCURACY

The only kind of physical quantity that can be measured with perfect accuracy is a tally of discrete objects, for example, dollars and cents or the number of objects in a museum case. In measuring a quantity capable of continuous variation such as mass or length there always is some uncertainty because the answer, like an irrational number such as π , cannot be expressed by any finite number of digits. The volume of liquid in a buret, for example, is capable of continuous variation and can only be estimated because obtaining a measurement requires guessing just where the liquid level lies between marked volume divisions on the buret wall. The precision of the volume estimate depends on the quality of the buret and the skill of the experimenter. In addition to errors which result from difficulties of constructing and using measuring devices, other errors over which the experimenter has no control are inherent in measurements. Therefore, at least two, preferably three or more, determinations of any quantity should be made for comparison purposes. After making several measurements of some quantity, the best value to use generally is the average of all the measurements. The "true" value—more correctly, the "accepted" value—of important quantities such as physical constants listed in a handbook (for example, the velocity of light in a vacuum), is chosen by some competent group of experts who critically examine all the available data to select the most probable value.

It is important to distinguish between the **precision** and the **accuracy** of a series of measurements.

The precision indicates how reproducible the measurements are.

Measurements whose values scatter widely are less precise than measurements whose values lie close together, even though the average value of the two sets of data might be exactly the same. Measurements of the diameter of a solid cylinder made with a micrometer will be more precise than the same measurements made with a meter stick because the meter stick is more coarsely graduated.

The accuracy indicates how well the measurement agrees with an accepted value.

The accuracy of a measurement is unrelated to its precision. Accuracy depends on how well the measuring device is calibrated with respect to some accepted standard, such as the international reference meter length at the National Bureau of Standards. If a precise micrometer reads 1.50 mm when it actually should measure 1.75 mm, then the average value of a very precise series of measurements will be in error by 0.25 mm, inaccurate by: $(0.25/1.75)(100\%) = 14.3\%$.

One can only judge the accuracy of a measurement by comparing it with an accepted value. If no accepted value can be found, the accuracy cannot be ascertained.

II. DETERMINING PRECISION:

The precision of an experimental determination may be taken to be a statement about how widely the individual values of a series of measurements deviate from the average value. The arithmetic average of a series of measurements is usually taken to be the "best" value, but the average value gives no information about the precision, or "scatter", of the separate measurements. The most common ways to express experimental precision are by the **average deviation**, **relative average deviation**, and **standard deviation**.

1. Average Deviation

The simplest measure of precision is the **average deviation**, which is determined as follows:

1. Calculate the average value of all the of measurements
2. Subtract the average value from each individually measured value; this quantity is called the **deviation**,
3. Sum the deviations (treat each deviation, whether positive or negative, as a positive quantity) and calculate their average.

Written as an equation, the average deviation \bar{d} is:

$$\bar{d} = \frac{\sum_{i=1}^n |x_i - \bar{x}|}{n}$$

where n is the total number of measurements, the summation goes from $i=1$ (the value of x for the first measurement) to $i=n$ (the value of x for the n th measurement), x_i is the value of the i th measurement, and \bar{x} is the average value of all the measurements. The vertical lines on each side of the parenthesis in the numerator are an **absolute value** symbol. They indicate that the quantity between them is to be regarded as a positive quantity.

Using the absolute value of a number simply means always treating the number as a positive quantity, regardless of whether the true value is positive or negative.

The numerator, then, is the sum of the absolute values of all the deviations.

EXAMPLE 1:

In a series of measurements, the following values for the molarity of a potassium permanganate solution were obtained: 0.1010, 0.1020, 0.1012, 0.1015 mol L⁻¹ (moles per liter). Calculate the average deviation.

ANSWER:

Individual measurements	Individual deviations from the average (absolute value)
0.1010	0.1014 - 0.1010 = 0.0004
0.1020	0.1014 - 0.1020 = 0.0006
0.1012	0.1014 - 0.1012 = 0.0002
<u>0.1015</u>	0.1014 - 0.1015 = <u>0.0001</u>
$\Sigma x_i = 0.4057$	$\Sigma d_i = 0.0013$

$$\text{Average } x = \bar{x} = \frac{0.4057}{4} = 0.1014 \text{ mol/L}$$

$$\text{Average deviation} = \bar{d} = \frac{0.0013}{4} = 0.0003 \text{ mol/L}$$

These results would be reported as: **0.1014 ± 0.0003 mol/L.**

2. Relative Average Deviation

Precision also may be expressed as the **relative average deviation (r.a.d.)**, defined as *the average deviation divided by the average value*.

EXAMPLE 2:

The r.a.d. for the measurements in Example 1 is:

$$\text{r.a.d.} = \frac{\text{av. deviation}}{\text{av. measured value}} = \frac{\bar{d}}{\bar{x}} = \frac{0.0003}{0.1014} = 0.003 \text{ (dimensionless)}$$

(Only one significant figure is valid.) The percent r.a.d. is an often used variation. It is obtained by multiplying the r.a.d. by 100%:

$$\text{r.a.d.} = \frac{0.0003}{0.1014} \times 100\% = 0.3\%$$

The precision of an experiment varies with the method and apparatus used. An experienced chemist using equipment commonly available for routine analytical work should be able to determine the chloride concentration in a solution with a precision of 0.1% r.a.d. The average inexperienced student is more likely to obtain a precision around 1.0% r.a.d.

3. Standard Deviation

The **standard deviation** has greater theoretical validity than the average deviation. The average deviation is popular because of its simplicity but is reliable only if the number of measurements is very large, around 10 or more. For smaller sets of data, the standard deviation gives a much better indication of

measuring precision. Both methods indicate the same precision for random errors in a very large number of measurements.

The standard deviation is determined as follows:

1. Calculate the average of a series of measurements.
2. Determine the deviation of each measurement from the average.
3. Square the deviations and add up their squares.
4. Divide the sum of the squares of the deviations by $(n - 1)$, where n is the total number of measurements.
5. Take the square root of the result from step 4.

Let x_1 be the value of the first measurement, x_2 the value of the second, and so forth. Let \bar{x} be the average value of all the measurements. Then the deviations in step 2 above are found as in the average deviation, by subtracting the average value from each measured value. Let the deviation of measurement 1 be d_1 , of measurement 2 be d_2 , etc. Then:

$$\begin{aligned}d_1 &= x_1 - \bar{x} \\d_2 &= x_2 - \bar{x} \\d_3 &= x_3 - \bar{x} \\&\text{etc.}\end{aligned}$$

Written as an equation, the standard deviation σ is:

$$\sigma = \left(\frac{d_1^2 + d_2^2 + d_3^2 + \dots + d_n^2}{n - 1} \right)^{1/2} = \left(\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n - 1} \right)^{1/2}$$

where n is the total number of measurements, the summation goes from $i = 1$ (the value of x for the first measurement) to $i = n$ (the value of x for the n th measurement), x_i is the value of the i th measurement, and \bar{x} is the average value of all the measurements. Example 3 illustrates how to determine the standard deviation of a series of measurements.

EXAMPLE 3:

Calculate the standard deviation of the measurements in Example 1 of the molarity of a potassium permanganate solution.

ANSWER:

Measurement number	Measured molarity (mol/L)	Individual deviations from the average	Deviations squared
1	0.1010	$0.1010 - 0.1014 = -0.0004$	$(-0.0004)^2 = 1.6 \times 10^{-7}$
2	0.1020	$0.1020 - 0.1014 = +0.0006$	$(+0.0006)^2 = 3.6 \times 10^{-7}$
3	0.1012	$0.1012 - 0.1014 = -0.0002$	$(-0.0002)^2 = 0.4 \times 10^{-7}$
4	<u>0.1015</u>	$0.1015 - 0.1014 = +0.0001$	$(+0.0001)^2 = 0.1 \times 10^{-7}$
	$\Sigma x_i = 0.4057$		$\Sigma d_i^2 = 6.6 \times 10^{-7}$

$$\text{Average molarity} = \frac{0.4057}{4} = 0.1014 \text{ mol/L}$$

$$\text{std. dev.} = \sigma = \left(\frac{6.6 \times 10^{-7}}{4 - 1} \right)^{1/2} = 0.00047 \text{ mol/L}$$

These results would be reported as:

molarity of potassium permanganate solution = 0.1014 ± 0.0005 mol/L (std. dev.).

Notice that in this case, with only a few measurements, the standard deviation more realistically indicates less precision in the measurements than did the average deviation.

The standard deviation has a precise theoretical meaning.

If the deviations from one measurement to another are perfectly random, the magnitude of the standard deviation gives the range of spread from the average value within which 68% of all repeated measurements are expected to fall.

For example, if you make 100 duplicate measurements of the mass of a sample, 68 of these measurements should fall within plus or minus one standard deviation of the average value. Ninety-five percent of all duplicate measurements should lie within two standard deviations¹ (2σ : std. dev. multiplied by two). Two standard deviations ($2s$) is said to represent the 95% confidence level. Testing these statements on an actual sample can be a useful way of determining whether or not the errors in a given measurement are truly random or not. If some systematic error is present, such as a steady drift in an instrument calibration due to a changing temperature, the precision predictions of the standard deviation will not hold true.

Like the average deviation, use of the standard deviation is strictly valid only for an infinite number of measurements. When the total number of replicate measurements is quite small, perhaps four or five, the standard deviation should be regarded only as a rough estimate, but it is better than the average deviation and is the most useful indication of measurement uncertainty for finite data sets.

III. DETERMINING ACCURACY:

Precise measurements are not necessarily accurate. The **accuracy** expresses the agreement of the measurement with an accepted value for the quantity. If no accepted value is known, the accuracy cannot be ascertained. When a quantity is measured for which a "true" or accepted value is known, it is usual to express the accuracy in terms of the **absolute error** and **relative error**, both of which compare the measured value with the accepted value.

The absolute error (also called just the error), is the experimentally determined value minus the accepted value.

The relative error is the absolute error divided by the accepted value.

EXAMPLE 4:

Suppose that the accepted value for the normality of the permanganate solution in Example 1 is 0.1024 mol/L, as measured by the instructor of the course. What are the absolute error and relative error for the determination of the normality in Example 1?

ANSWER:

$$\begin{array}{ll} 0.1014 \text{ mol/L} & \text{the determined average value} \\ - 0.1024 \text{ mol/L} & \text{the accepted value} \\ \hline -0.0010 \text{ mol/L} & \text{the absolute error} \end{array}$$

from which the relative error is -0.0098 , obtained as follows:

$$\frac{-0.0010}{0.1024} = -0.0098$$

Notice that there are no units for the relative error.

Other ways to express relative error are by **percent relative error (%)**, **parts per thousand (ppt)**, and **parts per million (ppm)**. The relative error from above may also be expressed as:

$$\begin{array}{ll} -0.0098 \times 100\% & = -0.98\% \\ -0.0098 \times 1000 \text{ ppt} & = -9.8 \text{ ppt} \\ -0.0098 \times 1,000,000 \text{ ppm} & = -9800 \text{ ppm} \end{array}$$

IV. PROPAGATION OF ERRORS:

Often, several different measured quantities are used to calculate another quantity, as when the density of an object is found by dividing its measured mass by its measured volume. Uncertainties in the measured quantities naturally will result in an uncertainty in the calculated quantity. If the uncertainties in the measured quantities have been determined, the most probable, or **statistical uncertainty**, in a calculated quantity can be found by using the following rules.

¹ Actually, 95% of the measurements should lie within 1.96 standard deviations. Using a value of 2σ is close enough and, in any case, it errs on the safe side.

1. Statistical uncertainty in sums and differences

Suppose a calculated quantity is $F = x \pm y$. Let U_F , U_x , and U_y be the statistical uncertainties in F , x , and y , respectively.

The statistical uncertainty in F equals the square root of the sum of the squares of the uncertainties in x and y .

In equation form: $U_F = (U_x^2 + U_y^2)^{1/2}$.

EXAMPLE 5:

The mass of water in a beaker is found by weighing the dry beaker empty and then weighing it with the water in it. The mass of the water is the difference between these two masses. Each mass is weighed four times. The results, with the calculated average deviations, are:

mass of beaker when empty (m_b): 9.8264 ± 0.0005 g

mass of beaker with water in it (m_{b+w}): 16.7193 ± 0.0005 g

mass of water (without uncertainties): $m_w = m_{b+w} - m_b = 16.7193 - 9.8264 = 6.8929$ g

statistical uncertainty in mass of water: $U_w = (0.0005^2 + 0.0005^2)^{1/2} = (5 \times 10^{-7})^{1/2}$

$U_w = \pm 0.0007$ g (rounded to one significant figure)

The measured mass of water is expressed correctly as: $m_w = 6.8929 \pm 0.0007$ g

2. Statistical uncertainty in products and quotients

Suppose a calculated quantity is $F = (xy)/z$. Let U_F , U_x , and U_y be the statistical uncertainties in F , x , and y , respectively. The statistical uncertainty in F is:

$$U_F = F \left\{ \left(\frac{U_x}{x} \right)^2 + \left(\frac{U_y}{y} \right)^2 + \left(\frac{U_z}{z} \right)^2 \right\}^{1/2}$$

EXAMPLE 6:

The density of an object is found by dividing its measured mass by its measured volume. The volume and mass each are measured seven times, the mass on an analytical balance and the volume by displacing water in a graduated cylinder. The results, with their calculated standard deviations, are:

mass of object: $m = 9.2152 \pm 0.0003$ g

volume of object: $V = 8.74 \pm 0.07$ mL

density of object (without uncertainties): $r = 9.2152/8.74 = 1.05$ g/mL

statistical uncertainty in density: $U_d = (1.05) \left\{ \left(\frac{0.0003}{9.2152} \right)^2 + \left(\frac{0.07}{8.74} \right)^2 \right\}^{1/2} = \pm 0.008$ g/mL

The measured density is correctly expressed as: $r = 1.05 \pm 0.01$ g/mL (rounded to 2 decimal places)

This example illustrates a very important point.

The precision of a result calculated by multiplication and/or division can be no greater than the precision of the least precise quantity used in the calculation.

When different measurements are combined in a calculation to obtain a new quantity, such as dividing mass by volume to get density, the precisions of the different measurements will, in general, be different. It can be seen that the uncertainty in the density measurement is dominated by the uncertainty of the volume measurement, which is known only to three significant figures. A less precise balance could have been used without decreasing the precision of the measurement at all. If a more precise density measurement is needed, the precision of the volume measurement must be improved first. There is no point in improving the mass measurement alone because it would make no difference in the final uncertainty of the density value.

V. SIGNIFICANT FIGURES:

Whenever a measured value is given, the number should be expressed in a manner that makes the degree of uncertainty perfectly clear. This is done by writing a value so that it contains only those digits that are known with certainty (have not been estimated), plus one more figure (the first estimated figure). The last figure in the number is always one that requires some degree of estimation and, therefore, it serves as an indication of the precision of the value.

Significant figures are the number of digits necessary to express a measurement or calculation to the precision with which it was made.

It is important to remember that the number of significant figures is unrelated to the position of the decimal point. The numbers 1056, 105.6, 1.056, 0.1056, 0.001056, and 1.056×10^7 all are written with just four significant figures. Zeroes which serve only to locate the decimal point, as the first two zeroes in 0.001056, and powers of ten which are needed to express the magnitude of a value, do not count as significant figures.

Usually, there is no problem in reporting the correct number of significant figures to express the result of a direct measurement because the measuring instrument simply does not give extra meaningless figures. However, when calculations are performed to obtain some desired quantity, extra numbers often appear that have no experimental validity. This is especially true when using an electronic calculator. Extra meaningless figures always should be eliminated by rounding off the calculated value to the correct number of significant figures.

Rules for Rounding Off to the Correct Significant Figures

1. When the first digit after the last significant figure is less than 5, simply cut off all extra figures without changing the last significant figure.

Example:

A calculation gives the number 3.9634263 for a value that should have four significant figures. The fifth digit (which is the first nonsignificant figure) is 4, which is less than 5. Therefore, the value is correctly given as **3.963**.

2. When the first digit after the last significant figure is greater than 5, add 1 to the last significant figure and drop all following digits.

Example:

A calculation gives the number 0.0462733 for a value that should have three significant figures. The first nonsignificant figure is 7 (the zeroes in front of the 4 serve only to locate the decimal point and do not count as significant figures), which is greater than 5. Therefore, the value is correctly given as **0.0463**.

3. When the first digit after the last significant figure is equal to 5, the situation is ambiguous and there is no universally accepted way to handle this case. A good guide to follow is:

- a.** Look at the *second* digit after the last significant figure. If it is larger than 5, round the last significant figure upward by adding 1 to it. If it is 5 or smaller, or if there is no second nonsignificant figure, go to step **b**.
- b.** When the first digit after the last significant figure is equal to 5, and the second digit after the last significant figure offers no basis for rounding upward, as explained in **a**, always round the last significant figure to the nearest *even* number. This offsets any psychological bias for rounding in a non-random manner, since there is an equal probability that choosing the next nearest even number results in rounding up or down.

Example:

a. A calculation gives the number 123.6257 for a value that should have five significant figures. The first non-significant figure is 5, which is ambiguous with respect to rounding up or down. Because the second non-significant figure is 7, which is larger than 5, the last significant figure should be rounded upward by adding 1. The value is correctly given as **123.63**.

b. A calculation gives the number 3.775 for a value that should have three significant figures. The correct value could be either 3.77 or 3.78, since 3.775 is exactly in the middle between them. By choosing the closest *even* number, the value is correctly given as **3.78**.

Rules for Finding the Correct Number of Significant Figures

An exact treatment for finding the correct number of significant figures is more complicated than necessary for most situations. If you remember that **no mathematical operation can increase the precision of an experimental result**, you can use three simple rules for determining the correct number of significant figures.

1. When the precision of a number has been determined, as the standard or average deviation, the average value of a series of measurements should have the same number of decimal places as the \pm value of the deviation.

Example:

The molarity of permanganate solution in Example 1 has an average deviation of ± 0.0003 . Therefore, the average value of the molarity should contain four figures after the decimal point. In calculating the average, the calculator result of

$$0.4057/4 = 0.101425000 \text{ mol/L}$$

must be rounded to **0.1014 mol/L** in order to use significant figures correctly.

2. If a value is calculated using multiplication and/or division, the value should be rounded off to have the same number of significant figures (regardless of the position of the decimal point) as the quantity used in the calculation that has the least number of significant figures.

Example:

The velocity of a rolling ball is determined by observing that it rolls 135.6 cm in 12.1 seconds. Using a calculator, the velocity found to be:

$$(135.6 \text{ cm})/(12.1 \text{ s}) = 11.20661157 \text{ cm/s}$$

Because the time measurement, 12.1 seconds, has only three significant figures, the answer is limited to three significant figures. The answer is expressed correctly as **11.2 cm/s**.

3. If a value is calculated using addition and/or subtraction, the value should be rounded off to have the same number of *digits after the decimal point* as the quantity used in the calculation that has the least number of digits after its decimal point.

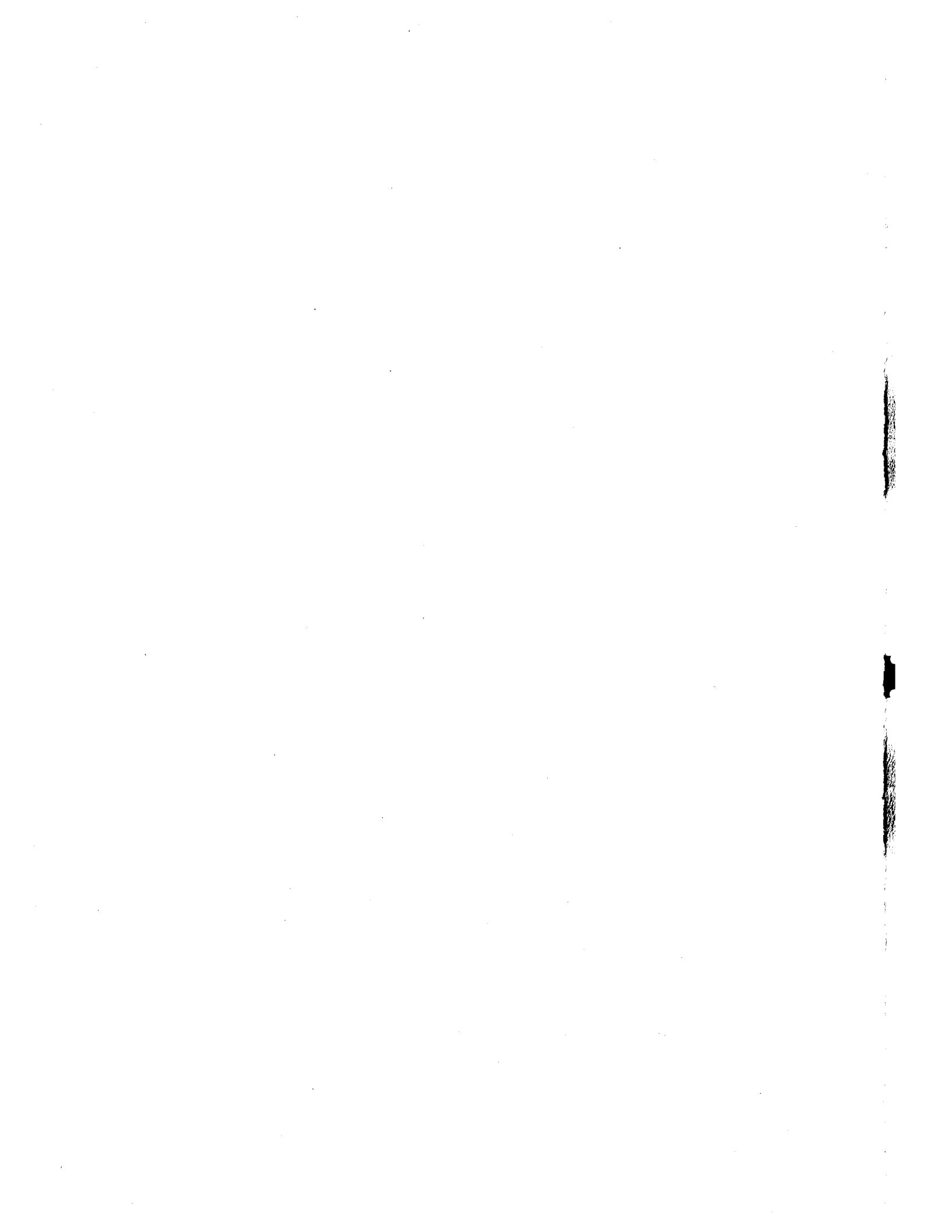
Example:

$$\begin{array}{r} 265.3 \\ 33.67 \\ 1.0983 \\ \hline 300.0683 \end{array}$$

Because 265.3 has only one digit after the decimal point, the answer must be rounded off to just one decimal place, as indicated by the vertical line. The answer is correctly given as **300.1**.

$$\begin{array}{r} 34.694 \\ -34.63 \\ \hline 0.064 \end{array}$$

Because 34.63 has only two digits after the decimal point, the answer must be rounded off to two decimal places. The answer is correctly given as **0.06**.



I. POURING LIQUIDS

SAFETY

1. Check whether bottles are wet on the outside. If so, clean with wet sponge before handling.
2. Keep fingers out of path of flowing liquid. Rinse hands with water after operation.

Methods

Pour from a spout when possible. A funnel or glass rod (see Figure xx) may be used as a pouring aid. Lay only flat-top stoppers on the table with the sealing surface pointing up to avoid accidental contamination from contact with the table surface. Hold "pennyhead" stoppers and other types between the index and middle fingers, and hold the bottle with all fingers of the same hand, as illustrated in Figure 0.3. When removing these stoppers it is best to approach them with your palm up in order to grasp the stopper between your fingers from the back of your hand.

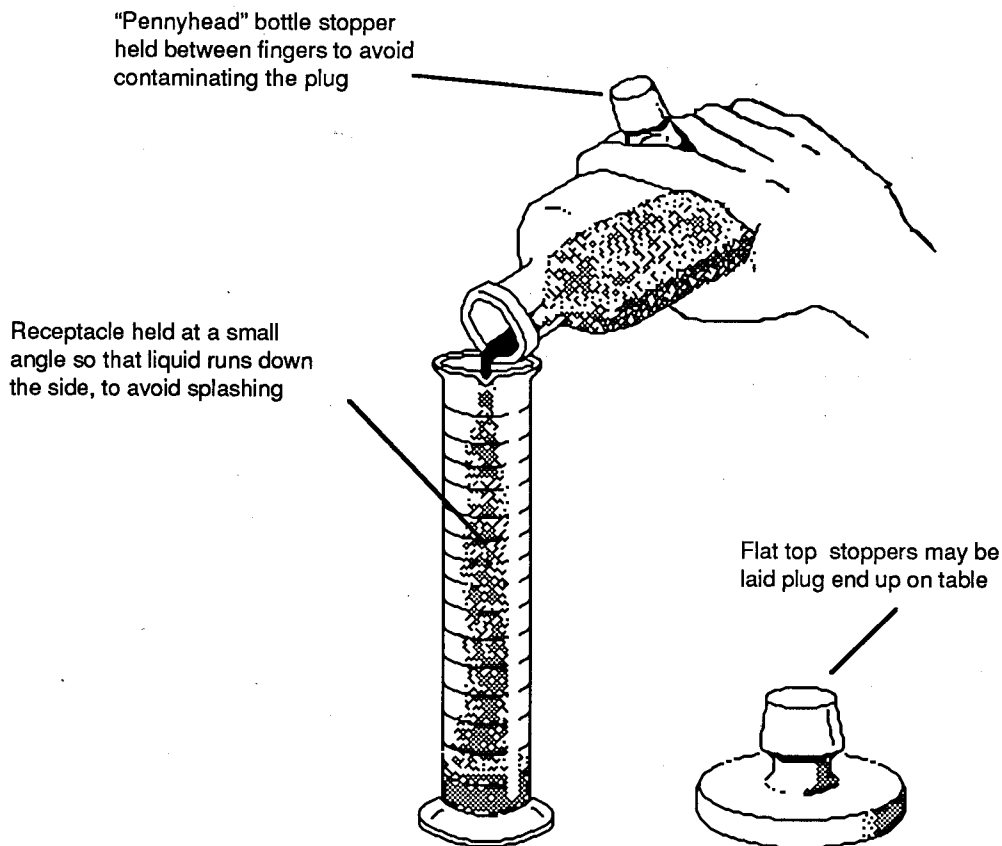


Figure 0.3. Pouring liquids.

Never pour directly from a 2 L or larger container into a narrow-mouthed vessel; pour into a beaker and then from the beaker into the final container.

Pour concentrated sulfuric acid into cold water (*never water into the acid*) slowly, with stirring. Use a vessel designed to withstand thermal shock (for example, a beaker or flask), not a bottle or graduated cylinder.

If too much is taken, discard the excess; never put anything back into a reagent bottle.

II. TRANSFERRING POWDERS

SAFETY

Many solid chemicals are corrosive and will damage skin and clothing. Many solids are poisonous.

Do not touch solid chemicals.

Methods

Use a disposable plastic weighing dish or place the powder on weighing paper or other smooth paper. Curl the paper into a chute and use it as a funnel for pouring. Do not try to pour powder directly from a container into anything that does not have a very wide mouth. With small-mouthed containers, use a **clean** spoon or spatula. If too much is taken from the reagent bottle, discard the excess. Reagent chemicals must be kept pure.

Never put anything back into a reagent bottle.

III. WEIGHING:

The Laboratory Triple-Beam Balance

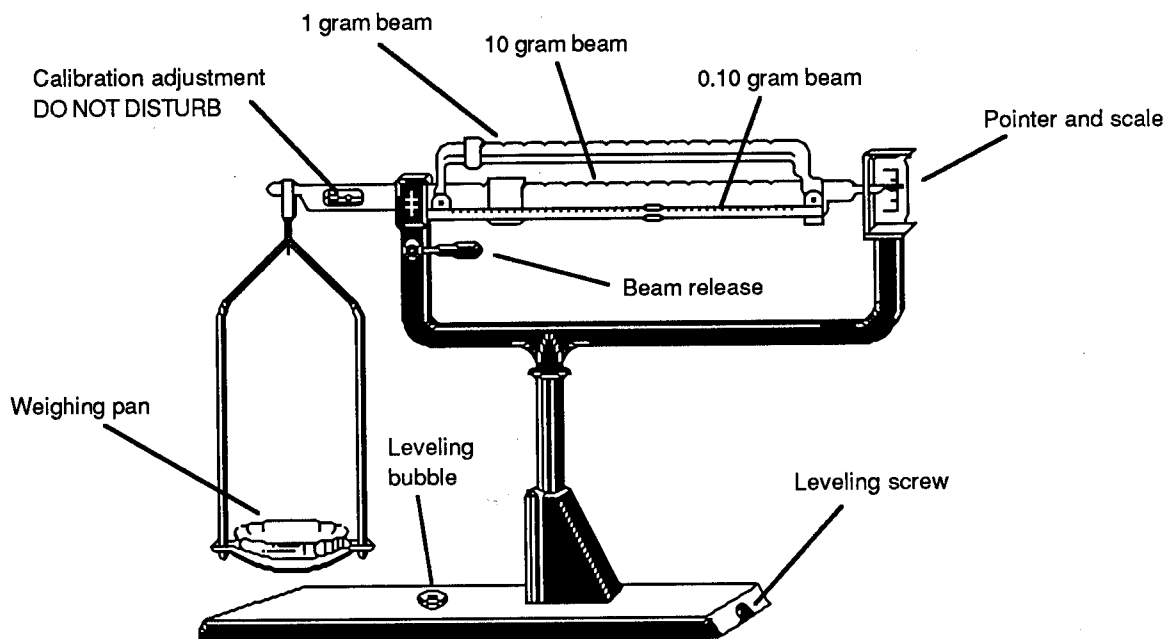


Figure 0.4. An agate or stainless steel knife-edge triple-beam balance (accuracy 0.01g).

Methods

This is the balance to use when a sensitivity of ± 0.1 g is satisfactory. Set all rider weights to zero. Avoid drafts. Set balance swinging slightly (pointer should move two to five divisions away from center). Average one reading above center with one reading below center. If average (called "zero point") falls outside the range of -1 to +1, move the small screw at the calibration adjustment (ask instructor first) until the average falls within this range.

If the material to be weighed is a clean solid (metal bar, dry beaker, etc.) at room temperature, set it on the platform. If the material is a powder or liquid, use an appropriate **previously weighed (tared)** container (weighing paper, weighing bottle, watch glass, beaker, etc.). Never place a powder directly on the platform. Now move the rider weights until the swings of the pointer again average between -1 and +1. This is the "rest point." Read the values where the rider indices point and record the total weight.

Protect the balance from corrosive chemicals by keeping it clean at all times. Dust the pan before and after use.

The Single-Pan Analytical Balance

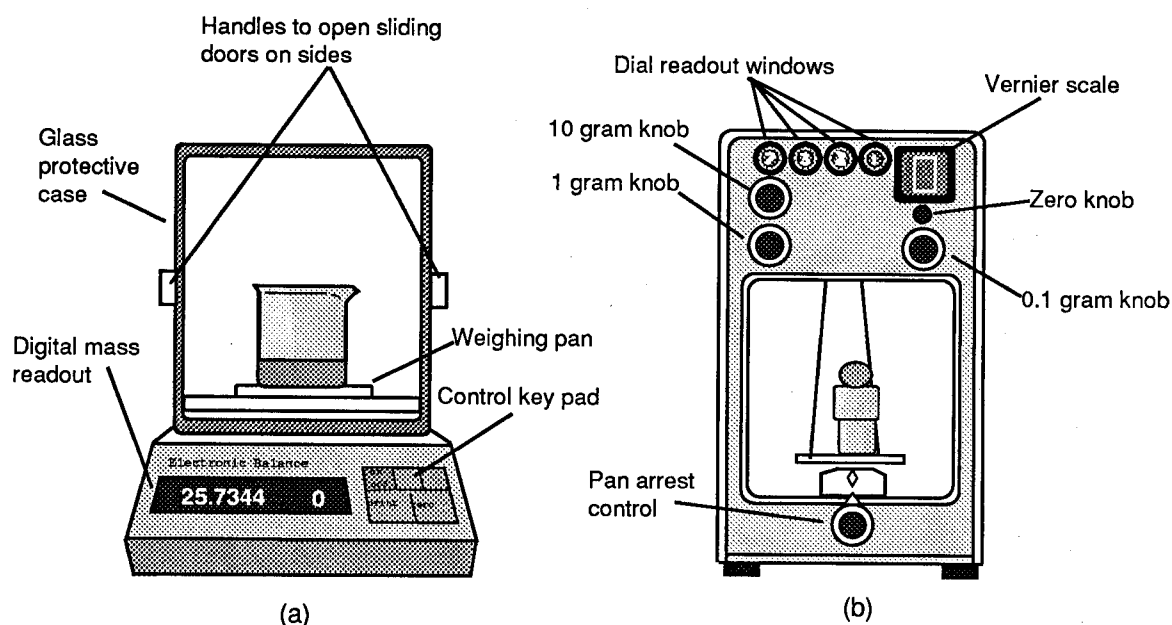


Figure 0.5. Typical single-pan analytical balances with weighing accuracy of ± 0.0001 g:

- (a) An electronic balance detects the small downward motion caused by a mass on the weighing pan by its disturbance of a magnetic field.
- (b) A mechanical balance weighs by substituting weights on a single beam arm to balance the mass on the weighing pan.

Methods

The single-pan analytical balance is one of the chemist's most important tools. The analytical balance you will use is a sensitive instrument that has a precision of approximately ± 0.0001 g. You must treat it with courtesy and respect, for it does endure abuse very well. There are too many different models in use to give detailed operating instructions here. Two commonly used types, electronic and mechanical, are illustrated in Figure 0.5.

With an electronic balance, a mass on the weighing pan causes the pan to press a small metal mass downward, into a magnetic field. The disturbance of the field is sensed by an electronic circuit that activates an opposing electromagnet and measures the current required to force the pan back to its original position.

With mechanical balances, a mass on the balance pan causes the deflection of the beam from which it hangs. The deflection movement is optically measured with a system of mirrors and lenses. By turning the weight knobs, you can place appropriate counter-weights on the beam to balance out the mass on the weighing pan and restore the beam to its original position.

Your instructor will demonstrate how to weigh samples on your particular models.

Do not attempt to operate an analytical balance until your instructor has demonstrated the correct procedure and has approved your use of the instrument.

GENERAL PRECAUTIONS FOR USING AN ANALYTICAL BALANCE

1. An analytical balance is a delicate instrument and should not be treated roughly. Handle all controls gently. With mechanical balances, rapid turning of the knobs will throw the weights off of their rests. Never force a knob to turn. Protect the balance from corrosive chemicals by dusting before and after use.

If the balance does not work, notify the instructor. Do not try to fix it.

2. Keep the door to the weighing pan closed at all times except when placing or removing objects on the pan. Air drafts will change your mass readings, and dust and fumes should be prevented from entering at all times.

3. The balance pan and floor must be kept very clean. If you find them dirty, clean them up. If you spill anything, clean it up right away. Always brush off the pan with the small brush provided just before you load anything onto it.

4. Before weighing any glassware, wipe it off with a towel to remove moisture and grease. Do not handle anything to be weighed with your fingers to avoid moisture and grease. Use tweezers, forceps, clean gloves, or toweling to handle samples. Never handle standard weights with your fingers, for the subsequent corrosion can ruin them.

5. **With mechanical balances, never load or unload the pan unless the balance is "arrested."** When "arrested," a support protects the delicate pivots against excessive loads, like accidentally dropping something on the pan. (This is not a problem with electronic balances.) A good practice is never to open the balance door without arresting the balance and never release the arrest unless the door is closed.

6. Never weigh anything that is not at room temperature. The analytical balance is much more sensitive than the triple beam balance and is affected by air currents created by thermal convection from hot objects. Atmospheric moisture may condense on cold objects.

7. Only hard bulky objects, such as an aluminum bar, may be placed directly on the pan for weighing. Liquids and powdered, granulated, or pelleted solids must be held in a previously weighed (tared) dry container at room temperature. If the material may interact with the atmosphere (evaporate, fume, adsorb moisture, or oxidize) during weighing, the container must be closed. For solids that do not require protection from the atmosphere, it is permissible to use chemical weighing paper. Weigh the empty paper first and subtract its weight from the total weight of sample and paper.

8. During the final part of the weighing, keep the balance door closed.

9. Keep your hands, arms, and feet off of the balance table to avoid vibration.

10. When you are finished weighing, leave the balance leveled, zeroed, clean, arrested (for mechanical balances), and closed.

The Top-Loading Balance

Another type of balance that might be available is the top-loading kind. These are intermediate in sensitivity between the analytical single-pan balance and the triple-beam balance, usually having a sensitivity of $\pm 0.001\text{g}$. They are very convenient and easy to use. Like the more sensitive analytical balance, both electronic and mechanical versions are available, although electronic top loaders have largely replaced the mechanical ones. The operating principles are similar to the analytical balance.

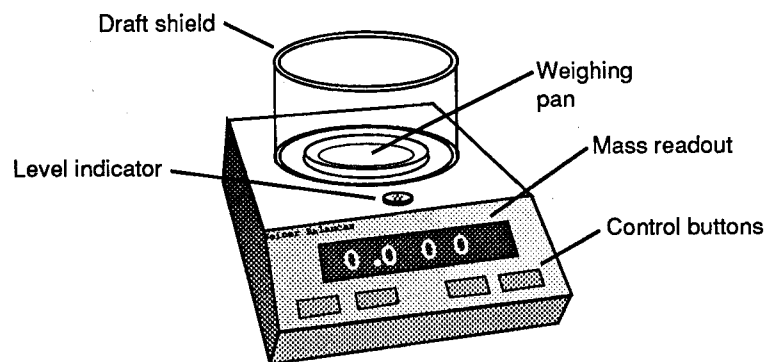


Figure 0.6. An electronic top-loading single-pan balance (accuracy $\pm 0.001\text{g}$).

GENERAL PROCEDURES FOR WEIGHING SAMPLES ON ALL BALANCES

1. **Know the mass limit of your balance.**
2. Be sure the weighing pan is clean and empty.
3. Check the balance level and adjust if necessary.
4. Check readout zero and adjust if necessary.
5. Place sample in center of weighing pan. Always use a container or weighing paper.
6. Operate the controls as instructed to obtain an accurate measurement.
7. Read the mass value and write it down.
8. After weighing, arrest the pan if necessary, remove your sample, and return all controls to zero.
9. **Leave the balance in a clean condition.**

Weighing a Predetermined Quantity of Solid Sample

First, weigh the empty container. This is called the **tare mass**. This tare mass is recorded and then subtracted from the final mass to obtain the mass of the sample.

Electronic balances generally subtract the tare mass automatically and read the sample mass directly.

Transfer the sample with utmost care to the container in which it is to be used, using a camel's hair brush for the last few particles. A powder funnel (short, wide neck) or chute made of weighing paper may be used to transfer a sample into a flask. If you plan to dissolve the weighed sample, the last portion should be transferred by rinsing all containers and funnels several times with the solvent, adding the rinse liquid to the sample container. If the material to be weighed interacts with the atmosphere, put a little more than the desired amount quickly into a closed weighing bottle. Portions are removed in rapid operations, with minimal openings of the container, until the amount of sample remaining is close to the desired quantity.

One can never obtain a predetermined mass with maximum accuracy and the use of predetermined masses should be avoided whenever possible.

Weighing a Sample Whose Mass Is Not Decided in Advance

This is more accurate than trying to obtain a predetermined mass. In this case, one makes a rough estimate of a suitable quantity of sample, weighs it accurately, and then works with whatever accurately determined mass is obtained. A solid sample is often weighed out from a small test tube or weighing bottle into a larger beaker or flask. In such cases, it will be preferable to weigh the sample in its lighter container, then pour a portion into the beaker or flask and reweigh the original container with the remaining sample. When a sample is issued in a corked, labeled tube, transfer it before weighing to a clean, dry weighing bottle with no paper label, to avoid gross errors such as the transfer of cork particles and weight changes from variations of moisture content in the label and its adhesive.

Heating to a Constant Mass

To get a reproducible mass free from error caused by unknown amounts of moisture and other variable volatile impurities in the sample, it is necessary that empty crucibles and crucibles with contents be heated to constant mass. To accomplish this, heat the crucible for a minimum of 15 minutes at the required temperature. Cool the crucible to room temperature, in a desiccator if necessary to keep it dry, and then weigh it.

Allow 15-20 min for cooling; the crucible must be at room temperature before weighing (see item 2 under "General Precautions for Using an Analytical Balance," page 15.

Reheat for about 5-10 min, cool, and reweigh. Repeat the process until the mass remains constant within 0.1 to 0.3 mg, depending upon the precision required. The use of crucible tongs is recommended.

A desiccator is a container that provides a comparatively dry atmosphere in which crucibles and other materials may be stored. The lower portion of the desiccator contains a desiccant, usually anhydrous calcium chloride or silica gel.

IV. LIQUID MEASURE

The Graduated Cylinder

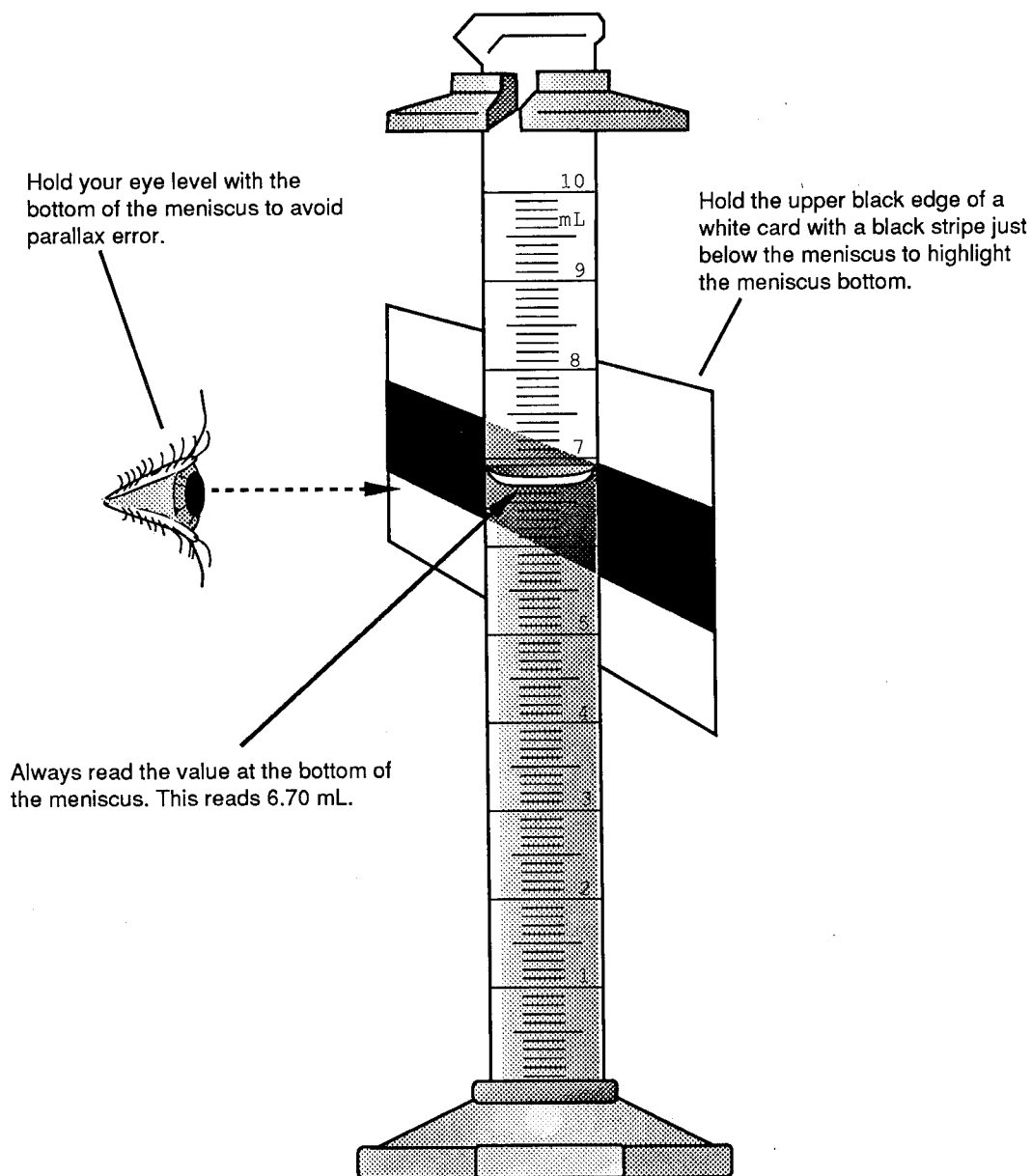


Figure 0.7. Reading a graduated cylinder. A white card with a black rectangle held with the upper black edge just below the meniscus will highlight the meniscus bottom and aid reading. Pipets, burets, and volumetric flasks are read in a similar manner.

SAFETY

1. See Section I., page 11, for filling a graduated cylinder .
2. Do not put hot liquid into a graduated cylinder.

Methods

Read the **bottom** of the meniscus (see Figure 0.7; instructor will demonstrate). Be certain your eye is level with the meniscus bottom to avoid parallax. Note that the lowest division on the graduate cylinder may be missing because of the curvature of the bottom of the cylinder.

The Pipet**SAFETY**

1. Always use a rubber-bulb pipeting device to draw the liquid up into the pipet. Your instructor will demonstrate how to adjust the liquid level by controlling the entrance of air.
Do not pipet any liquids with your mouth.
2. Be careful to always keep the pipet tip well below the surface of the liquid from which you are filling. If the surface drops below the pipet tip during the filling operation, air will enter the pipet rapidly, bubbling up through the liquid and pushing liquid high into the pipet. This can contaminate the liquid by bringing it into contact with the rubber bulb.
3. **Never insert the pipet into a reagent bottle.**
Instead, pour some of the liquid into your own container before pipetting it.

Methods

Practice filling the pipet with water. Submerge the tip well below the liquid level, then draw up the water until the level in the pipet rises above the upper graduation mark. Control delivery with your forefinger. Practice control. Note and understand the calibration marks on your pipet before you use it. Now draw in some of the liquid to be measured, rinse the pipet, and discard rinsing liquid (see page 18 for pipet rinsing technique). The pipet is now ready for use. Rinse it well with water when you are finished.

The Buret**SAFETY**

1. Use a funnel or small beaker for filling the buret.

Methods

To fill the buret, support it vertically in a buret holder with a small funnel in its top and pour directly from the reagent bottle through the funnel.

The funnel must be rinsed with water and dried before being used again for refilling the buret.

If the bottle is too large to be held comfortably or its mouth is constructed so that liquid cannot safely be poured from it into the funnel, the buret may be filled from a small beaker. However, any solution left in the beaker will dry out, and the beaker must be rinsed with distilled water and dried before each use.

Before using it, rinse the buret with water. Remove the stopcock plug (remove retaining ring first if it is present). Clean the plug and the inside of the barrel by wiping and drying carefully with cloth or soft paper. Make sure the hole in the plug is clean. If the plug is glass, smear one thin line of grease along the length of the plug between (and away from) the hole openings. (Teflon plugs do not require grease.) Smear another thin line on the other side. Insert the plug into the barrel in the open position (hole aligned vertically) and press firmly for a few moments while the grease spreads under the pressure. Do not twist. The grease should spread sufficiently to seal without clogging the passage hole. Save the retaining ring; do not replace it until you have finished with the buret. Now close the stopcock and support the buret with a ringstand and buret clamp.

Fill the buret to about one-fifth of its volume with the liquid to be used. Rinse the stopcock by letting liquid flow through it into the sink or a waste beaker; repeat the rinsing. Then, fill the buret above the zero mark and discharge the first portion of solution rapidly to remove any bubbles from the tip.

Close the stopcock and fill the buret above the zero mark again. Allow liquid to be discarded through the stopcock until the upper level reaches the zero mark or slightly below. Check the following:

- a. none of the liquid must be on the **outside** of the buret due to gross carelessness in filling;
- b. the stopcock and tip must be full of liquid (no air bubbles);
- c. when handling the stopcock, always maintain a slight positive (inward) pressure on it to avoid the possibility of a leak.

The buret is now ready to deliver the required liquid volume.

Adding a measured volume of one solution to another solution to complete a reaction is known as titration.

When you have finished with the buret, drain the liquid completely, then rinse three times with water.

Summary of Buret and Pipet Cleaning Technique

Before a buret or pipet is used, it must be rinsed with several small portions of the solution that it will contain, so that this solution will not be diluted by the water remaining on the walls.

A buret can be rinsed by pouring the solution slowly down the walls, rotating to insure that no part of the surface is missed.

This rinsing must be performed at least three times.

To rinse a pipet, draw a small amount of the solution into the glass bulb portion and, by shaking and tilting, bring it into contact with the entire glass surface of the bulb portion and of the upper stem, as far up as the mark. Rinse three or more times.

A buret or pipet measures the volume of liquid that is to be delivered to another container.

To insure reproducible delivery, the inner wall of the buret or pipet should be clean enough to leave an *unbroken* film of water after drainage.

Sufficient time should be allowed for drainage, about 10-20 seconds, before a buret reading is made or a pipet is considered to be empty.

The tip of a buret or pipet should be touched to the inner wall of the receiving vessel to transfer any hanging partial droplet. Any liquid that remains in the pipet tip should *not* be blown out.

Most pipets are not "calibrated for blowout." All measurements are made by reading the liquid level at the lowest point of the meniscus. Your eye should be level with the meniscus to avoid parallax error. The meniscus can be highlighted conveniently by a white card containing a black rectangle. The card is held in position with the top edge of the black rectangle directly below the meniscus (see Figure 0.7, page 16).

The Volumetric Flask

SAFETY

1. Fill the flask with a funnel or from a small beaker.
2. Never put a hot liquid into a volumetric flask.

Methods

The volumetric flask is made so that it contains an accurately known volume of liquid, at a certain temperature, when it is filled to a calibration mark on the neck.

The neck must be clean so that water drains in an unbroken film.

To prepare a solution containing a known weight of a solid solute in a known volume of solvent, either of the following two procedures should be used:

1. Weigh the solid into a beaker and add enough water (or other solvent) to dissolve it. Stir as needed. If heating is necessary, be careful not to lose any material by spattering; if the solution must be boiled, keep the beaker covered with a watch glass and then rinse the condensate on the underside of the watch glass into the beaker.

Let the solution cool to room temperature before adding it to the volumetric flask.

Introduce the solution into the volumetric flask with the aid of a funnel, using a stirring rod to guide the flow. Rinse the beaker (including the outside of the lip), the stirring rod, and the funnel (including the outside of the stem) several times with water from a wash bottle. When all of the sample is in the flask, add distilled water nearly up to the bottom of the stem.

2. If the solid is finely divided (no lumps), flows freely, and dissolves easily without pronounced evolution of heat or gas, it may be weighed directly into the volumetric flask, with the aid of a **dry** powder funnel (a funnel with a **short, wide** stem). After all the solid has passed through the funnel, rinse the funnel (including the outside of the stem) with water from a wash bottle. When all of the sample is in the flask, add water nearly up to the bottom of the stem and let stand, with occasional swirling, until the solid is dissolved.

Now add water carefully until the **bottom** of the meniscus is just at the mark on the neck.

Use a medicine dropper to add the last few drops.

Let the water run down the neck and allow time for drainage after each drop. Stopper the flask with a rubber or a glass stopper (not a cork) and mix by inverting at least twenty times.

V. CLEANING VOLUMETRIC GLASSWARE

SAFETY

1. Some cleaning solutions for volumetric glassware are extremely corrosive. Handle them with great care.
2. Draw cleaning solution up into a buret by suction from an aspirator *through a safety bottle*.

The standard of cleanliness demanded for burets, pipets, and the necks of volumetric flasks is much higher than for other glassware because water hangs in drops on even a slightly greasy surface.

Solution that sticks to the glass surface without draining is not measured properly and is not reproducible, causing measuring errors.

After washing with soap and water and thorough rinsing, the last traces of grease can usually be removed with a strong laboratory detergent. Sometimes, however, it is necessary to use a strong oxidizing solution of $K_2Cr_2O_7$ in H_2SO_4 , commonly called "cleaning solution."

This solution is extremely corrosive, especially when hot, and must be handled with great care. DO NOT USE THIS CLEANING SOLUTION WITHOUT PERMISSION FROM YOUR INSTRUCTOR.

VI. BORING CORKS AND RUBBER STOPPERS

SAFETY

1. The boring tool used for making holes through corks and rubber stoppers must be regarded as a dangerous cutting tool, like a knife or ice pick.

Never use your hand as the support for a stopper being bored.

Methods

Holes often must be made in corks and stoppers so that glass tubes and thermometers can be passed through the stopper into a container.

For corks, first soften them by rolling in a cork softener, a wheel that turns in an off-center track so that the cork is squeezed into an ever-smaller space. If a softening wheel is not available, roll the cork on a tabletop under pressure, using a board or heavy book as the rolling device.

Remember that rolling to soften a cork also will reduce its diameter.

A borer tube is selected so that its outside diameter is a trifle less than that of the glass tubing to be inserted.

1. Sharpen the borer with a borer sharpener (a knife blade resting in a metal cone; your instructor will demonstrate its use).
2. Place the cork or stopper on a solid, relatively soft surface that you can afford to damage (e.g., wooden board, heavy cardboard, or paper pad), and proceed to bore through from one side by simultaneously pushing and twisting the borer into it. After penetrating about half-way, withdraw the borer and press out any material in the tube with the metal rod that is provided.
3. For small corks and stoppers, continue cutting until the borer emerges from the other side. For large corks and stoppers, invert the plug and complete the hole from the other side.

VII. FITTING GLASS TUBING INTO CORKS, RUBBER STOPPERS, AND RUBBER TUBING

SAFETY

Jamming the jagged end of a piece of fractured glass tubing into your hand while trying to force the tubing through a rubber stopper may be the most common injury-causing accident in student chemistry laboratories. The strong pressures exerted just before the tubing breaks make it almost impossible to avoid hurting yourself. Such accidents can be avoided, however, by following the recommended procedure.

ALWAYS follow these rules:

1. Be certain the glass tip is fire polished.
2. Use a lubricant (glycerin, soapy water, or stopcock grease) in the hole of the stopper AND on the glass tip.
3. Grip the glass with your finger tips very close to the entry into the stopper so that the the glass has less tendency to flex when pushed.
4. Use a towel to protect your hands.
5. In the early stage, before the glass has come through the other side of the stopper, **DO NOT HOLD YOUR HAND FLAT AGAINST THE STOPPER SURFACE AS A SUPPORT.**
6. *Rotate* the stopper onto the glass. Do not force the glass into the stopper with straight pushing.
7. When removing glass from stoppers, observe precaution 3. **A cork borer lubricated with glycerin is a handy tool for removing glass from a stopper.**
8. If the glass becomes stuck at any time, do not try to remove it. See your instructor.

VIII. DECANTATION AND GRAVITY FILTRATION

Methods

Decantation and filtration are two common methods for separating solid material from a liquid.

Decantation: Allow the sample to stand undisturbed for a time so that the solid material can settle to the bottom. Then, carefully pour off the liquid leaving the settled solid undisturbed. Use a glass rod as a pouring aid (see Figure 0.8). A **centrifuge** is an instrument for speeding the settling of solids in liquids by rapidly spinning the sample container so that centrifugal force acts to drive the solid toward the container bottom.

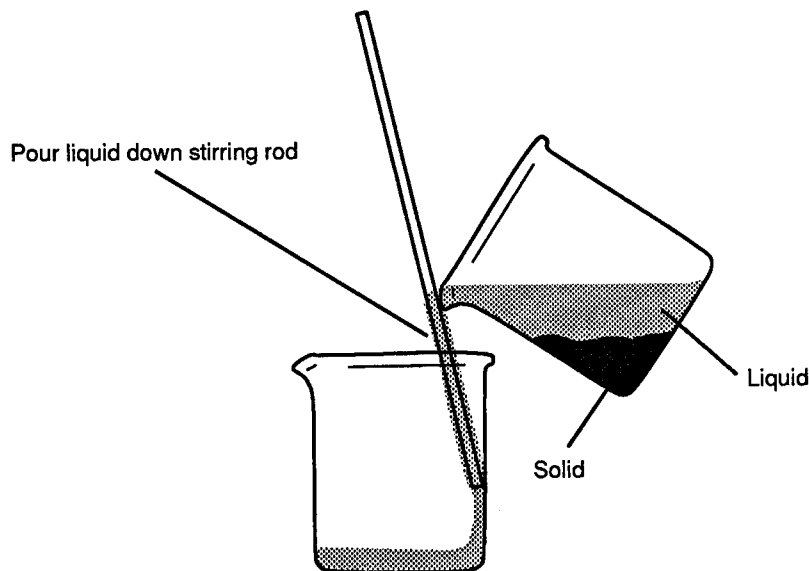
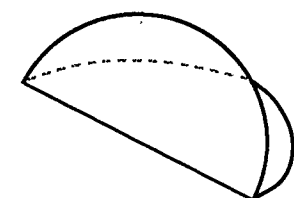


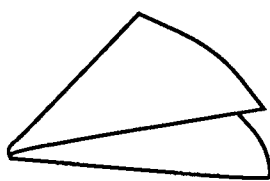
Figure 0.8. Decantation, using a glass rod as a pouring aid

Filtration: Fold a circle of filter paper sharply in half to give a half-circle. Then fold it in half again to give a quarter-circle. Shape the paper into a cone by separating one thickness from the other three (see Figure 0.9). Insert this filter paper cone into a funnel cone. Use a little water² to make the cone fit snugly in the funnel: wet the paper thoroughly and press the paper against the funnel wall with your finger or a glass rod, carefully pressing out any air pockets between the paper and the glass.

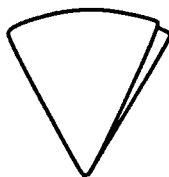
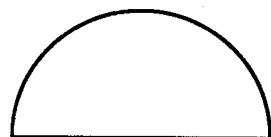
A glass rod or any other tool used to press the filter paper into the funnel must be blunt and smooth, to avoid tearing the wet paper.



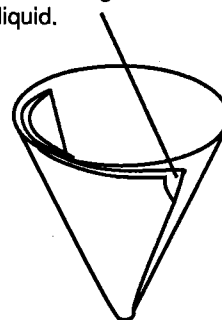
Fold filter paper circle evenly in half.



Fold again, leaving the top quarter section a little short.



Tear off this outer corner so that the torn edges cannot press together. This torn corner allows both sides of the fold to seal against the funnel wall to prevent air from entering and breaking the suction created by flowing liquid.



Open out the larger quarter section and insert into funnel. Moisten with distilled water and seal against funnel wall with finger pressure.

Figure 0.9. Preparation of a filter paper cone.

Pour the mixture to be filtered directly into the filter cone, not down the side of the funnel. Use a glass rod as a pouring aid (see Figure 0.10).

The liquid level in the funnel must never rise above the top of the filter paper.

The tip of the funnel stem should touch the side wall of the receiving container, to avoid splashing.

The funnel should be supported in a ring attached to a ring stand or in an arm support for funnels. The liquid part of the sample is called the **supernatant**. The liquid collected after it has passed through the filter is called the **filtrate**. The solid that is retained on the filter is called the **residue**.

² If the sample contains a liquid other than water, that liquid should be substituted for water in this procedure.

Washing a Solid by Decanting through a Filter

Decant the supernatant liquid through the filter. Add about 25 mL of water or wash solution to the solid, stir with a clean rod to thoroughly mix the solid and wash water, and allow the solid to settle. Then decant the wash water. Repeat the washing three or four times.

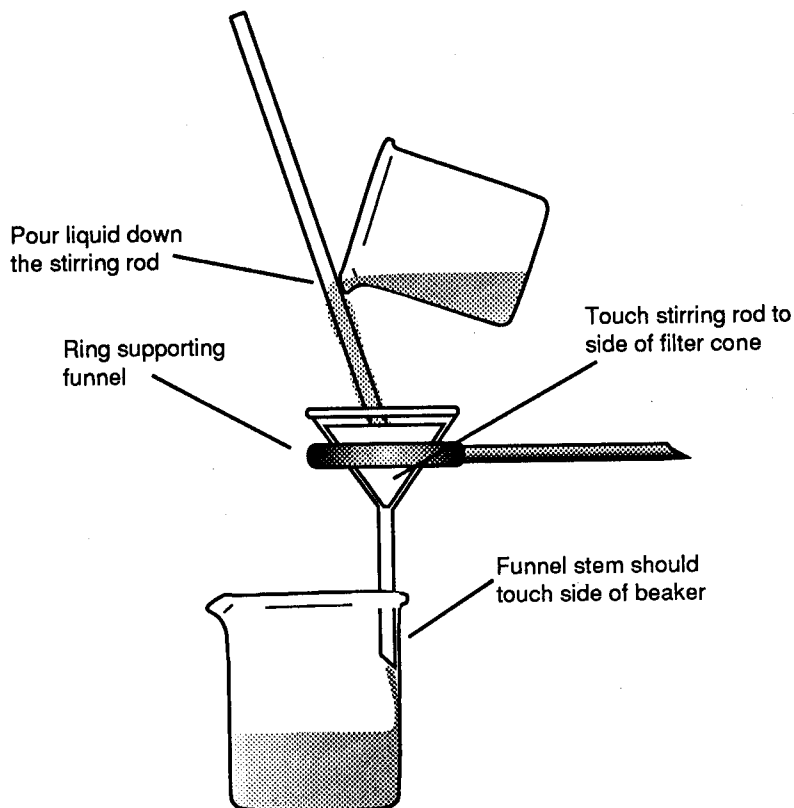


Figure 0.10. Gravity filtering, using a glass rod as a pouring aid

Transferring the Precipitate

After washing, it frequently is necessary to completely transfer all of the solid to the filter. Most of the solid can be transferred during the last decantation. To complete the transfer, hold the stirring rod across the top of the beaker firmly with your forefinger, holding the beaker with your remaining fingers (see Figure 0.10). Tilt the beaker so that its bottom is above its pouring spout and the glass rod runs from the spout into the filter. Use a wash bottle to direct a stream of water to flush the solid with the water down the glass rod into the filter. Then, place the beaker on the desk and flush any particles adhering to the wall back into the bottom of the beaker, using as little water as possible. Then flush the solid into the filter as before.

A **policeman**, which is a rubber tip fitted onto one end of a glass rod, may be used to scrub the remaining traces of solid from the beaker walls. Use a wash bottle to rinse the solid from the policeman directly into the filter.

IX. VACUUM (SUCTION) FILTRATION

SAFETY

Use thick-walled glassware to prevent implosion.

Methods

A water aspirator or vacuum line is used to provide the suction. A Buchner funnel is inserted through a rubber stopper into the filter flask and a safety bottle should be inserted in the suction line between the vacuum source and filter flask (see Figure 0.11a). All connections are made with thick-walled rubber or plastic vacuum tubing and rubber stoppers. The filter paper should be just large enough to cover all the holes in the flat-bottomed portion of the funnel, but not so large that it has to be wrinkled to make it fit. Wet the paper with the same solvent as is in the sample to be filtered.

Support the flask and filter with a ring or clamp to prevent the apparatus from tipping over.

Porcelain filter crucibles with permanent porous beds also are commonly used. These require a special rubber holder to attach the crucible to the filter flask (see Figure 0.11b).

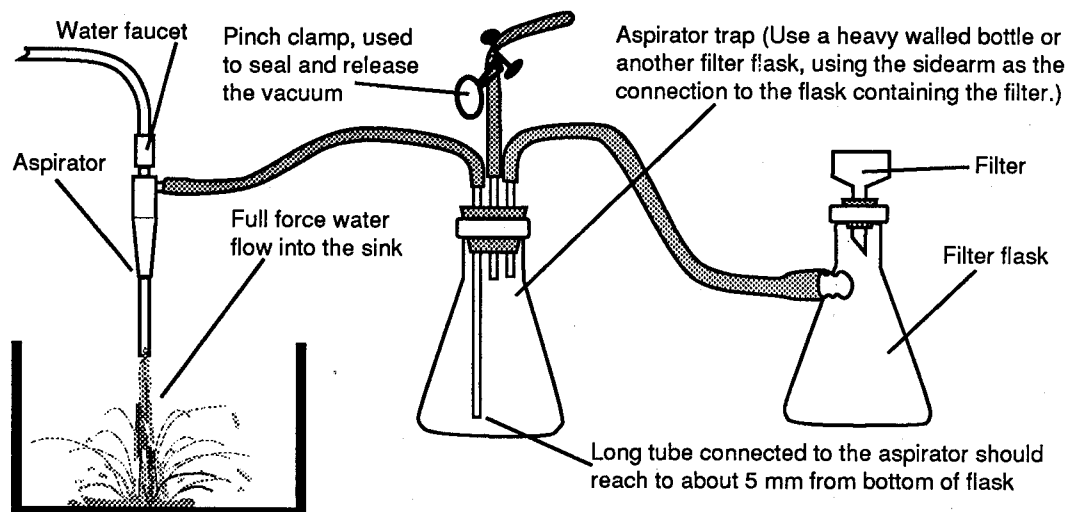


Figure 0.11a. Suction filtering setup with aspirator, aspirator trap (safety bottle), and filter in filter flask.

Keep the aspirator faucet turned on to its fullest extent to obtain maximum suction and to prevent aspirator water from backing-up into your filtering apparatus.

Never not turn off the water during a filtering or washing operation. Turn the suction off and on by opening and closing the pinch clamp.

Always add sample to the filter with the pinch clamp open. Then close the pinch clamp to draw the solvent through the filter.

This procedure is especially important when washing the product. Adding the washing solvent to the filter with the suction off insures that the washing solvent remains in contact with the solid sample long enough for efficient washing. Close the pinch clamp to turn on the suction after insuring that all the solid has been covered with washing solvent.

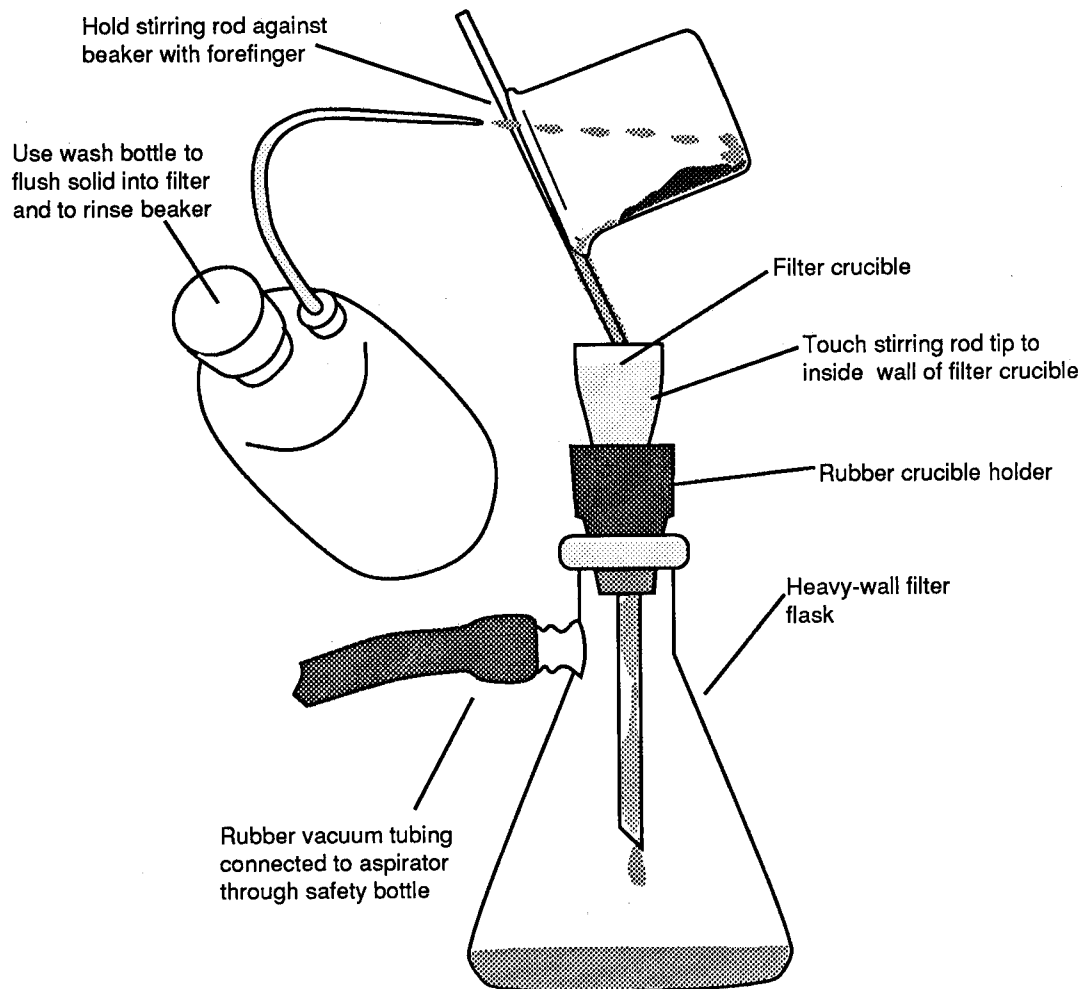


Figure 0.11b. Transferring solid to a porcelain filter in a suction filtering apparatus

X. SETTING UP AND USING GLASS EQUIPMENT

SAFETY

1. Clamp glass parts very carefully to avoid causing stress and strains.
2. Never heat a "closed" system — one which is tightly sealed from the atmosphere.
3. Never heat flammable liquids with an open flame.
4. Never point the open end of a test tube being heated toward anyone, including yourself.
5. Understand the functions of all the parts of your equipment.

Methods

General principles to keep in mind:

1. Glassware larger than test tubes usually should be supported from below in addition to being clamped. A ring or tripod with a wire gauze square makes a good support for heating beakers and flasks.
2. When heating, observe the following precautions:
 - a. Use a wire gauze to distribute the heat more evenly when heating beakers, flasks and evaporating dishes.

- b. Test tubes may be heated directly in a flame.
Never heat a test tube strongly above the liquid level nor at the very bottom of the tube. Heat the tube at one side near the bottom.
Heating above the liquid level may overheat the glass and crack it. Heating at the bottom may cause a large vapor bubble which could blow the contents right out of the mouth of the tube.
- c. Crucibles should be supported in a clay or wire triangle and heated directly with a flame.
- d. Clamp flasks and test tubes very close to their open ends. Clamp just firmly enough to prevent motion; excessive pressure may break the glass.
- e. The wire-spring test tube holder should be used only to hold small test tubes. It will not hold heavy objects securely.
- f. Never heat graduated cylinders or other volume calibrated glassware with a flame. These items can, however, be dried in an electric oven.
- g. Do not use a compressed air jet for drying. The air often is contaminated with oil and water from the compressor.
- h. Do not heat equipment at or near the point where they are supported by a clamp or near cork or rubber parts.
- i. When heating a solid that may melt, be sure the container tilts upward enough to insure the melt does not run out.

XI. DISTILLATION

SAFETY

When setting up and using a distilling apparatus, observe all the safety precautions listed above in Section X.

Liquid solutions and mixtures often are separated and purified by **distillation**, a process which vaporizes the most volatile components and condenses them into a separate container. Condensation of hot vapors is accomplished with a flowing-water condenser. The vapor system makes contact with the atmosphere at the receiving flask after all vapor has condensed so that evaporation losses are minimal. The liquid formed by condensation is called the **distillate** and the liquid remaining in the distilling flask is called the **residue**. A typical apparatus is illustrated in Figure 0.12. For safe and efficient operation of the distilling apparatus, you must observe the following precautions:

1. Cooling water must flow through the condenser from bottom to top, to insure uniform contact with the inner cooling wall.
2. The condenser must not be sealed to the receiving flask, to prevent any pressure build-up.
3. The distilling flask should not be more than half-full at the start of distillation, to prevent any liquid splashing over into the condenser during boiling.
4. Add several boiling chips at the beginning to prevent liquid "bumping". NEVER add boiling chips to a hot liquid sample.
5. Never heat the distilling flask or residue to dryness. With no liquid in the flask, the temperature can rise high enough to crack the glass or decompose the residue, sometimes with violent results.

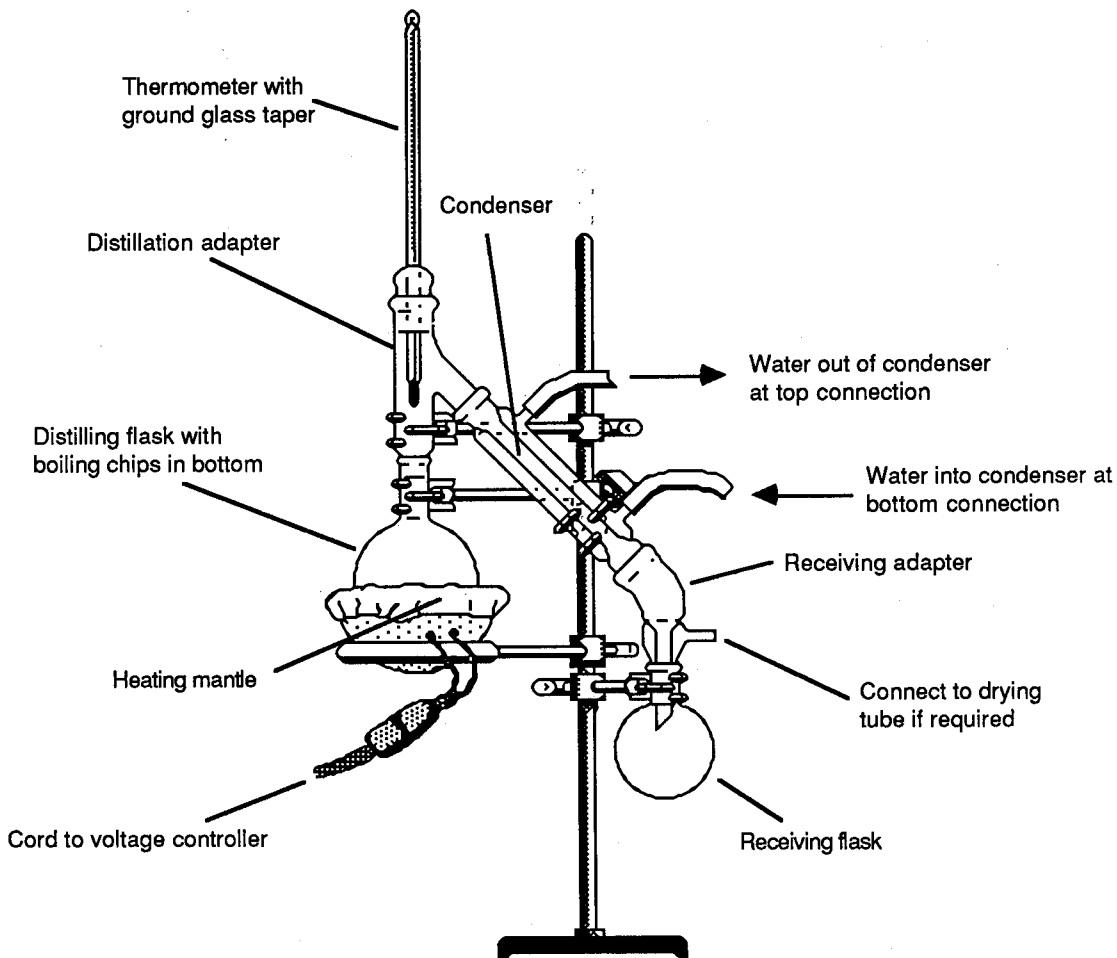


Figure 0.12. Distillation apparatus.

XII. THE pH METER

A pH meter is an electronic instrument for directly and continuously measuring the hydrogen ion concentration of solutions. A sensing electrode and a reference electrode are immersed in the sample solution, generating a voltage that is proportional to the solution pH. The results are displayed on a meter or chart recorder as the pH value. The sensing and reference electrodes may be two separated units or they may be combined into a single electrode structure. A typical pH meter is illustrated in Figure 0.13.

pH electrodes are very delicate and easily damaged. They must be handled with care. Avoid bumping them against any solid surfaces, such as beaker walls or bottoms.

Procedure for Using a pH Meter

1. The electrodes must be hydrated. They should have been soaking in distilled water overnight.
2. Some meters require one-half to one hour warm-up time for maximum stability. Be certain warm-up has been sufficient and do not turn the meter off between measurements. Use the "standby" switch position during warm-up and between measurements.

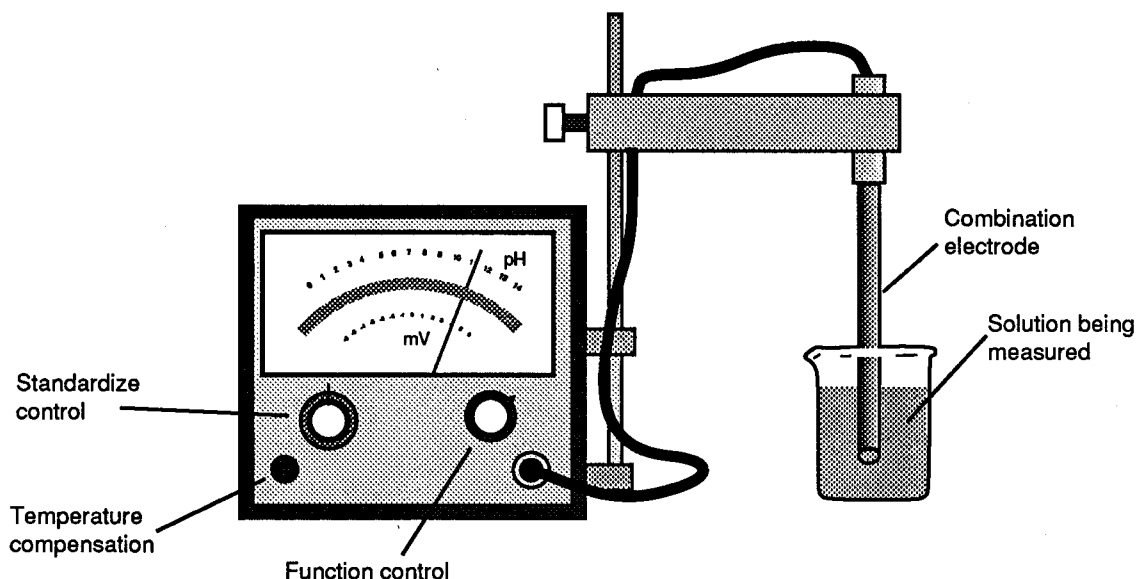


Figure 0.14. pH meter with combination electrode that combines both the sensing and reference electrodes.

3. Raise the electrodes out of their soaking bath, rinse them thoroughly with distilled water from a squeeze bottle, and dry them carefully with soft tissue.
Well-soaked electrodes can be left in the air for 10-20 minutes without losing their water of hydration.
4. If your meter does not have automatic temperature correction, you must set the proper control to correct for the temperature of the solution you are measuring. pH electrodes are temperature sensitive. Measure the solution temperature with a thermometer.
Samples may be measured conveniently in 150-250 mL beakers.
5. Lower the electrodes into the buffer solutions to be used for calibration. Wait about two minutes before reading to allow the electrodes to reach thermal equilibrium. It is best to use at least two calibration buffers, about 3 pH units apart. If only one buffer is used, its pH should be near the pH to be measured.
6. Switch from "standby" to the "measure pH" position and adjust the meter to read the known buffer pH.
7. Turn back to "standby," raise the electrodes from the buffer solution, and rinse and dry them carefully as before.
8. Measure and record the sample volume.
9. Immerse the electrodes in the sample solution. The electrodes should be covered with solution but should not be in danger of bumping into the beaker bottom.
10. Read and record the sample pH. After the measurement, switch the meter to "standby," raise the electrode carefully out of the sample solution, and rinse them well. When not in use for longer than 10-15 minutes, leave the electrodes soaking in distilled water.
Always rinse and wipe dry the electrodes between immersions in different solutions.

XIII. CHEMICAL ANALYSIS WITH AN ABSORPTION SPECTROMETER

Absorption spectrometry can be used to identify components of a solution and measure their concentrations. The amount of light absorbed by a compound at different wavelengths is a characteristic of the compound and the pattern of light absorption, called a **spectrum**, can serve as an identifying "fingerprint." The higher the concentration of the compound, the stronger the absorptions at each wavelength, allowing the magnitude of absorption to be used to measure the sample concentration (see Figure 0.15a, b).

A compound is identified by comparing its spectral "fingerprint" with spectra of known compounds, using a dictionary of standard spectra.

To find the concentration of a compound:

1. **Calibrate the sample by measuring the amount of light absorbed at a particular wavelength by the compound at several known concentrations.**
2. **Make a graph of absorbance vs. sample concentration (see Figure 0.15b)**
3. **Measure the absorbance of the unknown sample at the same wavelength and read the sample concentration from the calibration graph.**

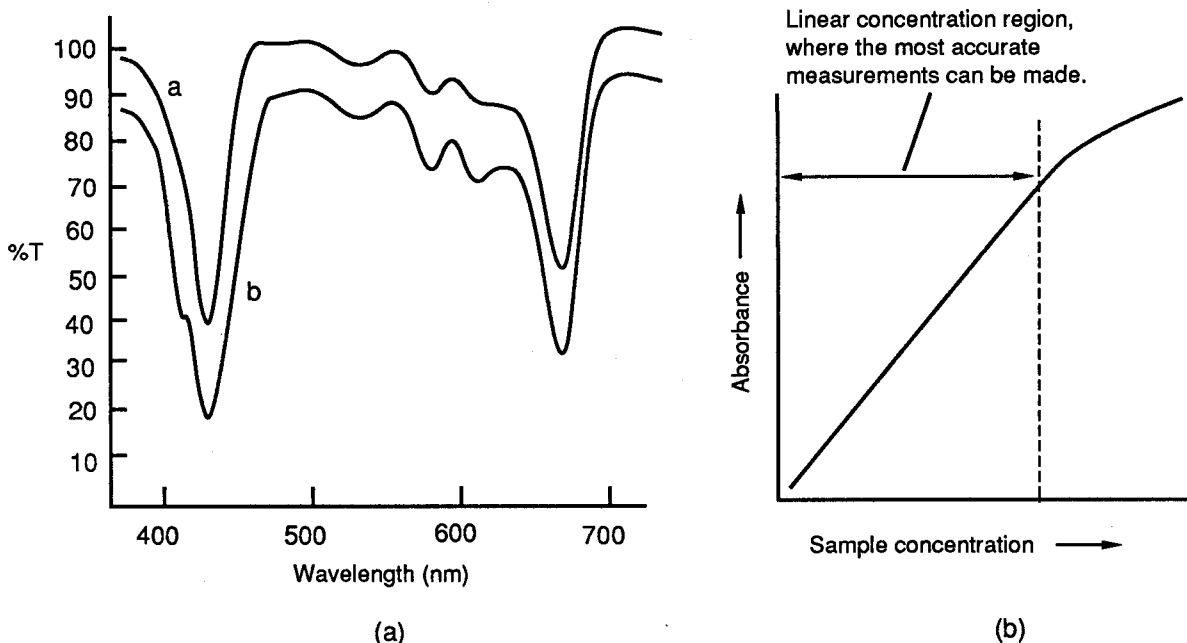


Figure 0.15. Chlorophyll-*a* spectra and a characteristic absorbance graph, showing how sample absorbance increases with concentration.

- (a) Transmission spectrum of a solution of chlorophyll. Curve *b* is at a higher concentration than curve *a*, and the spectrum shows that the *b* sample absorbs more light than the *a* sample.
- (b) Typical plot of sample absorbance at a single wavelength vs. sample concentration. If the sample concentration is too high, the plot becomes nonlinear.

The spectrometer contains a light source, optical components to disperse the light and pass the separated wavelengths through the sample, and a detector that measures how much light passes through the sample at each wavelength. Your instructor will explain the specific operating procedure for the particular instruments that are in your laboratory. Some general principles are presented below.

Principles and Procedure

For accurate analyses, it is necessary to distinguish between light absorbed by the solute sample and light lost in unrelated ways, such as by reflections and scattering from the sample holder (called a **cell** or **cuvette**) and absorption by the solvent. In addition, the light source and detector have their own characteristic spectral output and response. For these reasons, it is necessary to make two measurements, one using a cell containing only the solvent with no sample dissolved in it (called the **blank**), and another

using a different cell with both solvent and sample. It is important that the two cells be as identical as possible, so that their light-loss characteristics are the same. When the spectra from the blank and sample are compared, their differences are due only to light absorption by the sample, since other light losses are the same in both measurements.

Some instruments, called **double-beam spectrometers**, can accommodate both the blank and sample cells simultaneously and measure both at the same time, presenting only the desired difference signal. With a **single-beam spectrometer**, two separate measurements must be made of the blank and sample and the difference signal calculated by hand.

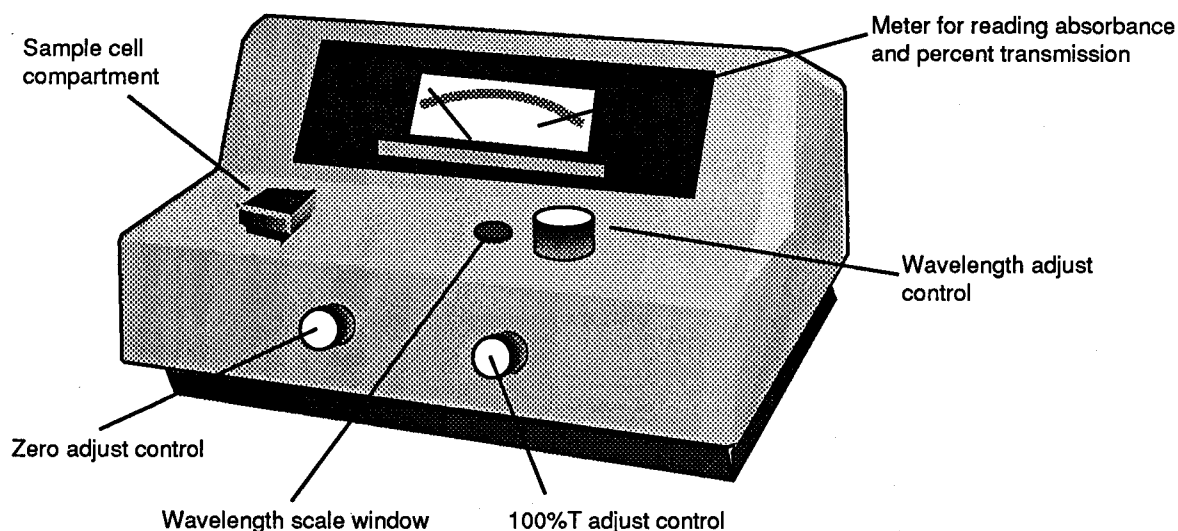


Figure 0.16. Typical spectrometer for routine analysis.

Light Measurements

Spectrometers measure the light reaching the detector in terms of the light *transmitted* by the sample or the light *absorbed* by the sample.

The **percent transmission** through the sample is defined as:

$$\%T = \text{percent transmission at a particular wavelength} = \frac{\text{light intensity measured with sample cell}}{\text{light intensity measured with no cell}} \times 100$$

The **absorbance** of the sample is defined as:

$$A = \text{absorbance} = \log_{10} \frac{100}{(\%T)} = 2 - \log_{10} (\%T)$$

Each of the measurement quantities has different advantages. $\%T$ has a linear scale on the spectrophotometer meter, making it easier to read than *absorbance*, which has a logarithmic scale. However, the relationship between sample concentration and *absorbance* is frequently linear, whereas sample concentration and $\%T$ are related in a non-linear manner. A graph of sample concentration versus absorbance is frequently a straight line and allows easy interpolation between calibration point when measuring unknowns.

Calibration graphs should always be made by plotting *absorbance* on the vertical axis and *sample concentration* on the horizontal axis.

Stepwise Procedure for Spectrometer Analysis

1. Most instruments require one-half to one hour warm-up time to insure light source and detector stability. Be certain warm-up has been sufficient and do not turn the instrument off between measurements.
2. Clean the outside of your cells by wiping them carefully with lab tissue.
Do not wipe the cells with paper towels, which might cause tiny scratches.
Any lint or scratches will scatter light and cause errors. If the inside of the cell is dirty, ask your instructor for guidance. Always use the same cell for the blank and the same cell for the sample.
Do not touch the lower three-fourths of the cell with your fingers.
The light passes through this part and any smudges or oil on the surface will alter the absorbance.
3. Rinse each cell with distilled water to remove any traces of previous samples. Shake out the rinse water as completely as possible.
4. Rinse each cell three or four times with small amounts of the solution to be measured, to prevent any dilution of the solution by residual water.
Use pure solvent in the blank cell and sample solution in the sample cell.
Then dry the outside of the cell carefully with lab tissue.
5. Fill the cells to the proper level with the liquids to be measured (usually one-half to two-thirds full, sometimes indicated by an index mark).
Be sure there are no small air bubbles attached to the inner surface and no dirt or lint on the outer surface.
6. Adjust the spectrometer:
 - a. **Turn the wavelength control to the desired setting.**
 - b. Adjust the zero control with the sample compartment empty and its cover closed. Under these conditions, a shutter blocks the light beam from the detector, so that the correct reading on the meter is 0.0% transmission (infinite absorbance).
Turn the zero adjustment until the meter reads 0.0% transmission.
This adjustment should be checked and reset from time to time.
 - c. Insert the cell containing the blank.
Adjust the 100% T control until the meter reads 100% transmission (or zero absorbance).
Inserting the cell automatically opens the light shutter and allows the light beam to pass through the cell to the detector. Adjusting the blank cell to 100% T compensates for all instrument factors and light losses other than sample absorption. Remove the blank.
 - d. Insert the sample cell.
Read the transmission and absorbance values from the meter.
7. If necessary, run a series of calibration measurements all at the same wavelength, obtaining the absorbance of several samples with known concentrations. You can use a graph of absorbance versus known concentrations to find unknown concentrations from their measured absorbances. It is wise to check the instrument zero and 100% T setting occasionally.