

Chem 4563 Organic Qualitative Analysis

Identifications of Unknowns - Preliminary Examination

1. Preliminary examination and physical properties

The investigator should first determine that the unknown is primarily a single compound. To do this a TLC analysis of the unknown should be performed (Shriner pp 33-37). For best results, TLC analysis should be tried using three solvents of different polarity, i.e. petroleum ether, ethyl acetate and methanol. A sample that yields a single spot using three solvents of vastly different polarity will most likely be a relatively pure compound. Once the purity of the sample has been established the preliminary examination can begin.

a. Physical State (Shriner pp 31-32).

First begin by noting the physical state (i.e. solid or liquid) of the sample. Additional information such as "amorphous powder", "short needles" or "viscous liquid" often prove useful. Note also its color and any odors. The odors can be compared with odors of common compounds such as alcohols, aldehydes, ketones, esters etc. Certain compounds such as mercaptans, low molecular weight amines and isonitriles have such characteristic odor that once experience has been gained, they are seldom mistaken. NOTE OF CAUTION-*Be careful when smelling any organic compound. Carefully waft the fumes towards you nose by fanning the top of the unknown sample vial with your hand.*

b. Melting and Freezing Points (Shriner pp 37-45. Pasto 57-65)

If the sample is a solid, the *melting point* can be determined. The exact melting point can only be determined through the used of a complex apparatus. When we speak of the *melting point*, we really mean the *melting point range* (the range of temperature from when the first sign of melting begins to complete liquification). The melting point range is a useful index of the purity of a sample, impurities will lower and broaden the melting point range. A simple rule of thumb is that a melting point range of 1-2 °C represents a relatively pure compound, much broader and the sample is less pure. The melting point is a useful physical property that can aid in the identification of an unknown, but keep in mind that hundreds of different compounds can have the same melting point. Only a "mixed melting point" can be used as an absolute means of identification.

If the sample is a liquid a freezing point can be determined by cooling the liquid and measuring the temperature range of solidification. Note that the freezing point is a much less accurate determination than is the melting point

c. Boiling Point (Shriner 46-52. Pasto 66-67)

Boiling points (or once again, more correctly, boiling point ranges) can be used to aid in identifying liquid samples. Because the boiling point is dependent on atmospheric pressure, which can change from moment to moment, they are inherently less accurate than melting points. Initially, the initial liquid sample should be distilled in a small scale distillation apparatus into two fractions. The first fraction (about 20-25% of total volume) may contain water and other volatile impurities. The second fraction should be relatively pure (a rough estimate of the boiling point can be made from the distillation temperature of this fraction). Keep both fractions, but use the second fraction for a more accurate determination of boiling point via the micro capillary method. Use this fraction also for subsequent measurements of specific gravity and refractive index.

d. Specific Gravity (Shriner 55-58. Pasto 67-68)

Specific gravities of substances are determined by the direct comparison of the weights of equal volumes of sample and water at a given temperature t , and correcting to the density of water at 4°C as shown by the following equation.

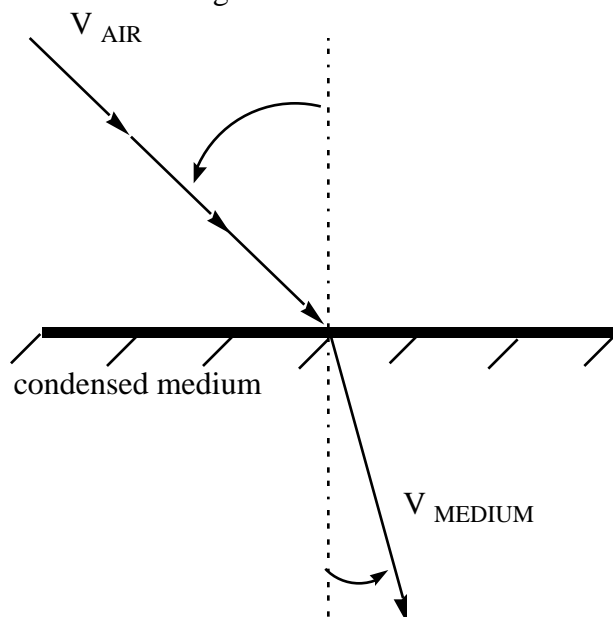
$$d = \left(\frac{\text{Wt of Sample}}{\text{Wt of Water}} \right)_t \times \text{Density of Water at } t$$

The weights of the sample and water are measured in small volumetric flasks called pycnometers. Density measurements should be carried out with as large a sample size as possible in order to minimize weighing errors. Typically, 1-2 mL volumes are used.

e. Refractive Index (Shriner 58-61 Pasto 68-71)

The refractive index derives from the fact that light travels at a different velocity in condensed phases (liquid, solid), than it does in air. The refractive index, n , is defined as the ratio of the velocity of light in air relative to the velocity in the medium being measured. The

ratio of the velocities is not difficult to measure experimentally. It corresponds to $\frac{\sin i}{\sin r}$ where i is the angle of incidence for a beam of light striking the surface of the medium, and r is the angle of refraction of the beam of light within the medium.



The instrument used to measure the refractive index is called an Abbe Refractometer. See the additional handout on operation of the Abbe Refractometer.