The Separation and Analysis of a Mixture

Background

Chemists who regularly encounter samples which must be identified have at their disposal a variety of methods, some of which date back to the very beginnings of chemistry as a science, and others which are very modern and often involve instrumentation of some sort. The fact that so many possible elements and compounds exist did not make this kind of work easy in the days before the machines entered the picture. Simply remembering possible chemical tests and their results is a feat of some magnitude. Even the experienced had to rely on a reference or two for the exotic substances they seldom encountered.

There was a time in chemical education when everyone was trained (at least in a basic way) to sort out <u>inorganic</u> materials by the ions they contained, categorizing them, sequestering them into groups by some common property (e.g., Ag^+, Pb^{2+} and Hg_2^{2+} all are insoluble with chloride and just about nothing else common is) and eventually executing more focused tests on the groups to decide what had actually been isolated (e.g., $PbCl_2$ dissolves in hot water; AgCl dissolves in aqueous NH_3 while Hg_2Cl_2 disproportionates to yield black Hg). *Qualitative analysis* has gone by the wayside in many institutions as a requirement, but there is in it a treasure trove of chemical reaction information which is still very useful in the lab for quickly identifying something by a simple test.

By contrast, the identification of *organic* compounds is more difficult by purely chemical means as there are so many compounds in any category (like alcohols, for example) and closely related substances have very similar chemical behaviors (e.g., 2-pentanol behaves much like 3-pentanol). Organic chemists have never had to deal with very many elements in most compounds so the focus in pre-instrument days was split between chemical tests that would place compounds into categories (e.g., aldehydes, ketones, alcohols) and physical tests which would distinguish among possible compounds (or derivatives of them) within a category: melting and boiling points, index of refraction, etc. Rather than an extensive memory of various tests for ions, this kind of approach required careful measurement and large reference tables.

The real challenge in working largely without instruments, however, is presented by the <u>mixture</u>. This is the way in which many substances first arrive for analysis. Not only is the substance unknown (there may be suspicions) but there is more than one substance and the pieces must be sorted out before an effective analysis can even begin. Methods of separation are important here starting with the very simple like mechanical separation and filtration to solvent extraction, fractional crystallization, distillation, and so on.

Where does it all begin? That depends on the likely ingredients in the mixture. In this experiment a *ternary* mixture consisting of one water-soluble inorganic compound, one water-<u>in</u>soluble carbonate, and one water-<u>in</u>soluble organic compound is to be analyzed. While the component mixture is artificial it affords an opportunity to examine a number of basic and useful methods for separating substances into broad categories and then narrowing down the possibilities within a known set of substances.

A little thought will lead to the "guess" that the organic compound is likely non-polar (as it would be molecular and is not water-soluble) and therefore addition of a non-polar solvent might dissolve it. Filtration could then be used to separate it from the two inorganic substances.

Assuming the non-polar solvent does not react with the organic compound, it can be removed by boiling or simple evaporation (safer in case the organic compound is temperature sensitive). One component would thus be recovered.

The remaining mixture consists of one compound which is water soluble and another which is "not" [all ionic compounds dissolve to some extent in water; here we mean "insoluble for practical purposes"]. Adding water and filtering is a simple means to separate the two inorganic compounds. Evaporation over heat is a reliable way to recover the soluble component since most ionic substances can take a fair amount of heat without decomposing.

There are three unknown ions present in the inorganic components (the insoluble compound is a <u>carbonate</u>). This is where a knowledge of simple qualitative tests is helpful. Absent interference from other substances, these tests (generally called the "confirmatory tests") often consist of a single addition of some chemical which produces a precipitate, a unique color, gas bubbles, etc. Occasionally there are more steps but that is more typical if a substance which will give an ambiguous results might be present as well--not the case in this experiment.

There are many instrumental methods which are now in use to identify inorganic substances. One fairly old one which has its origins in qualitative analysis is *atomic emission spectroscopy*. Flame tests have been used for many years to identify some ions (typically alkali metals and alkaline earth metals, but there are others). The tests are based on unique colors given off as flame-excited electrons release their excess energy and return to lower energy states in the ions. The energy released (ΔE) in the transition can be related to the frequency (ν) or wavelength (λ) of the light detected:

$$\Delta E = h\nu = \frac{hc}{\lambda}$$

where **h** is Planck's constant, 6.63×10^{-34} J·s.
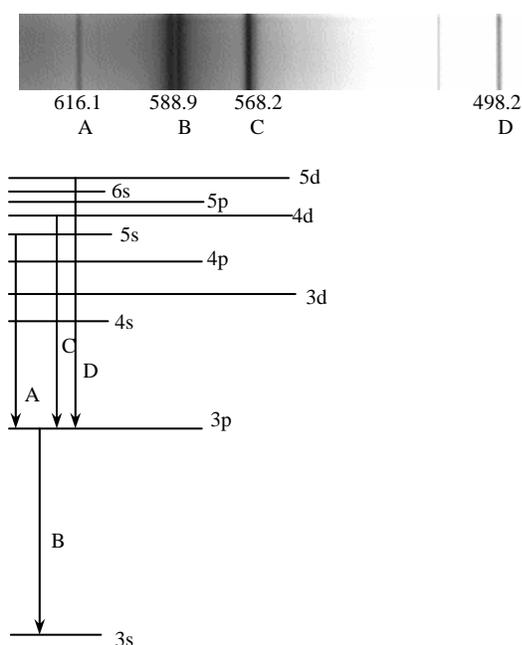
In atomic emission spectroscopy, higher energies are employed--typically from high voltage arcs or sparks--resulting in many more possible transitions. The light resulting from these transitions is analyzed by passing it through a prism or grating, separating the component wavelengths. A "fingerprint" spectrum unique to each ion results. The example above is from an actual photograph done with the instrument used in this experiment [there are more lines visible in the original film]. Although understanding an emission spectrum begins with a good grasp of the Bohr model of the atom, actual spectra are quite complex with many lines often clustered tightly together. Since the imagined "energy level" is only a high *probability* for an electron there is some variation in transition energies which generates a number of lines that might be classified as 3p→3s. Also, electron-electron interaction in all but the simplest atoms plays an important part in complicating spectra. There are many tables of emission wavelengths for elements available but even a simple visual match of spectra is sometimes sufficient if the range of possibilities has been narrowed down.

Generally only cations give arc emission spectra. Anions tend to volatilize immediately in the arc and are either destroyed or quickly ejected.

The organic components in this experiment are all related to one another and so no group separation is required [organic qualitative analysis appears in a later experiment]. Most pure organic substances have narrow melting point ranges and there are extensive tables of melting points available so this is a fairly good way to sort out possible substances within a small group of possibilities. Determining accurate melting points is tricky and patience is required to master the technique but it is an important and frequently used method.

Melting point determination can be augmented considerably if a tentative identification is made by measuring what is called a "mixed-melting point". Impurities in a sample tend to lower the melting point of a solid due to disruption of the usual intermolecular forces. When a small amount of unknown is mixed intimately with a small amount of the suspected substance (if any is available) the melting point should not change appreciably if the choice is correct. An incorrect mixture, on the other hand, should have a noticeably lower melting point.

The Experiment

There are two parts to this experiment:

- separating the mixture into three components
- determining the identity and amount of each component

The following non-locker materials will be provided:

- large sample test tube w/stopper
- petroleum ether [fume hood]
- large, numbered evaporating dish
- 2-propanone
- concentrated HCl [fume hood]
- concentrated H_2SO_4 [fume hood]
- qualitative analysis *knowns*:
  0.1 M $\underline{Co}(NO_3)_2$, 0.1 M $\underline{Cu}SO_4$, 0.1 M $\underline{Fe}(NO_3)_3$, 0.1 M $\underline{Ni}Cl_2$
  solid $\underline{Na}Cl$, $\underline{K}Cl$, $\underline{Ca}Cl_2$, 0.1 M $Na\underline{Cl}$, 0.1 M $K\underline{Br}$, 0.1 M $K\underline{I}$
  0.1 M $Na_2\underline{CO}_3$, 0.1 M $K\underline{NO}_3$, 0.1 M $Na_2\underline{SO}_4$
- analytical <u>test</u> reagents:
  1 M NH_4SCN, 4 M NH_3, 2 M HCl, 1 M KSCN, solid NaF
  1% dimethylglyoxime, 0.1 M $AgNO_3$, sat'd $Cl_{2(aq)}$, 2 M NH_3
  6 M HCl, acidified diphenylamine solution, 0.1 M $BaCl_2$, 3 M HNO_3
- flame test loop
- cobalt glass
- centrifuge w/tubes
- Thiele melting point apparatus w/capillaries, thermometer and microburner
- reference organic solids: biphenyl, naphthalene, 1,2,4,5-tetramethylbenzene

The Chemicals

2-propanone (commonly known as *acetone*) is a volatile, highly flammable liquid with a characteristic odor and sweet taste. It is completely miscible with water, forming a low boiling azeotrope which speeds evaporation and drying (hence its frequent use in rinsing wet glassware and washing precipitates). It will attack many plastics including some synthetic fabrics such as rayon.

2-propanone is used as a solvent for fats, oils, resins, waxes, lacquers, and rubber cements. It is also used in paint and varnish removers (some formulations of fingernail polish remover contain acetone). Prolonged or repeated topical exposure may cause skin dryness. Inhalation may produce headache, fatigue, and in large amounts, narcosis. Serious poisoning is rare.

Petroleum ether (which is <u>not</u> an "ether") consists of low boiling point fractions of petroleum, chiefly isomers of pentane and hexane. The liquid is clear, colorless and highly flammable with a boiling point between 35-80°C. It is insoluble in water and used as a solvent for oils, fats and waxes. Its toxicity is similar to kerosene. Skin contact should be minimized and extended periods of inhalation may cause drowsiness and coma. Ingestion causes serious GI distress.

Hydrochloric acid is also known as muriatic acid. It is the same liquid acid that is often used in controlling the pH of swimming pool water. It is sometimes colored yellow by iron impurities, traces of chlorine and organic matter. Reagent grade HCl contains about 38% hydrogen chloride gas, close to the limit of its solubility at room temperature.

Hydrochloric acid in concentrated form (12 M) has the sharp, choking odor of hydrogen chloride. It is used in the production of other chlorides and in refining some ores (tin and tantalum), cleaning metal products, removing scale from boilers and heat-exchange equipment, and as an important laboratory reagent (often in diluted form).

Concentrated solutions cause severe burns; permanent visual damage may occur. Inhalation causes coughing, choking; inflammation and ulceration of the respiratory tract may occur. Ingestion can be fatal.

Sulfuric acid is a clear, colorless, oily liquid in concentrated form (98%). It is highly corrosive and has a high affinity for water, abstracting it from wood, paper, sugar, etc., leaving a carbon residue behind. Dilution of concentrated sulfuric acid generates a tremendous amount of heat. Here in the lab your instructor prepares the dilute sulfuric acid you use by pouring the concentrated acid slowly over ICE while stirring! Even so, the resulting solution is very warm. As with all acid dilutions, acid is added to water, not the reverse, since the heat generated can boil the water at the point of contact and cause spattering.

Sulfuric acid is used to make fertilizers, explosives, dyes, parchment paper, and glue. It is used, in concentrated form, in automobile batteries as the electrolyte. It is corrosive to all body tissues and contact with eyes may result in total blindness. Ingestion may cause death. Frequent skin contact with dilute solutions may cause dermatitis.

Cobalt(II) nitrate is typically found as the hexahydrate in red, deliquescent crystals. This melts at 55°C to a red liquid which becomes green and decomposes above 74°C. It is very soluble in water and most organic solvents. Used in the manufacture of cobalt pigments and invisible inks as well as for vitamin B$_{12}$ supplements.

Copper(II) sulfate is available in both anhydrous form (pale blue to white) and the more common pentahydrate blue crystals (*blue vitriol*). It slowly effloresces in air, losing 2 waters at 30^oC, 2 more at 110^oC and becoming anhydrous at 250^oC. It is very soluble in water and methanol. The pentahydrate is used as an agricultural fungicide and bactericide as well as an herbicide (readily available at your local hardware store to kill roots in sewer pipes). It has many other uses in the dye, tanning, plating and photography industries. Copper is a trace nutrient but is toxic when ingested in sufficient quantities.

Iron(III) nitrate in hydrated form consists of pale violet to gray deliquescent crystals. Freely soluble in water, it decomposes below 100^oC. It is used as a mordant in dyeing, in tanning and as a corrosion inhibitor.

Nickel(II) chloride as a hexahydrate crystal is green and deliquescent. It is fairly soluble in both water and alcohol. It is used for plating, and in anhydrous form is an absorbent for NH_3 in gas masks.

Sodium chloride is, of course, common table salt (the non-iodized version). It occurs in nature as the mineral *halite* and is produced by mining underground deposits as well as from sea water by solar evaporation. It is white in small granular form but large crystals are translucent. The salt sold in the grocery store usually contains some calcium and magnesium chlorides which help absorb water and prevent caking.

Natural salt is the source of essentially all chlorine and sodium as well as of all, or nearly all their compounds (including HCl). It is used for preserving foods (salt curing), in the manufacture of soaps and dyes, in freezing mixtures (for making ice cream!) in dyeing and printing, and in some metallurgy.

Potassium chloride consists of white crystals which are very soluble in water. It is used in photography and in buffer solutions. Large doses by mouth can bring on acute GI irritation.

Calcium chloride is obtained as a by-product in the manufacture of sodium carbonate (the Solvay process). It is *very* hygroscopic and the anhydrous form is used as a drying agent. It is also useful for fireproofing fabrics, for melting ice and snow on the ground and roads, in concrete mixtures for greater strength, and as a brine for filling inflatable tires on tractors to provide better traction.

Potassium bromide is a white solid which is very soluble in water (1 gram dissolves in 1.5 mL of water). It is used in the manufacture of photographic papers and in some engraving processes.

Potassium iodide is a white solid, slightly deliquescent, and prone to oxidation in air. It is used in the manufacture of photographic emulsions, and in table salt and some drinking water to help prevent iodine deficiency disease.

Sodium carbonate occurs in nature in various mineral forms but much is manufactured by the Solvay process or from brines and alkali lake beds. The dry powder is slightly hygroscopic. Aqueous solutions are strongly basic. It is used in the manufacture of other sodium salts, in glass, soap, as a general cleanser ("washing soda") and in photography.

Potassium nitrate is commonly known as "saltpeter". It is a colorless, odorless solid with a saline, pungent taste. It is used in fireworks, pickling brines, the manufacture of glass, matches, gunpowder, freezing mixtures and candle wicks.

Sodium sulfate is a white powder in anhydrous form but also occurs as a decahydrate crystal (Glauber's salt). It is used to standardize dyes, in freezing mixtures and in printing on textiles.

Ammonium thiocyanate consists of deliquescent crystals which are very soluble in water and ethanol. It is used in matches, double-dyeing fabrics, photography and silk processing. Its toxicity is similar to potassium thiocyanate.

Ammonia is a gas at room temperature. Laboratory solutions of aqueous ammonia have sometimes been erroneously called "ammonium hydroxide" although there is little evidence for the existence of that compound. Aqueous solutions of ammonia are basic.

Ammonia gas can be manufactured from industrial gases associated with the processing of "coke", a spongy form of carbon obtained from processing coal and essential in steel-making. In the Haber-Bosch process nitrogen and hydrogen from these industrial gas mixtures are combined at high temperature and pressure in the presence of a catalyst to form ammonia. The gas and its aqueous solutions are colorless with a very pungent odor (lower limit of human perception: 0.04 g/m^3). Mixtures of ammonia gas and air can explode when ignited under favorable conditions. At room temperature ammonia is soluble to the extent of 31% in water, only 16% in methanol. It is used in the manufacture of nitric acid, explosives, fertilizers and in refrigeration. In anhydrous liquid form it is a good solvent for many elements and compounds, notably the alkali metals which yield blue solutions when dissolved in liquid ammonia.

Inhalation of the concentrated vapor causes swelling in the respiratory tract, spasms and asphyxia.

Potassium thiocyanate is colorless and deliquescent. When dissolved in its own weight of water, the temperature drops $30^{\circ}C$. It is used in the manufacture of artificial mustard oil, in printing and dyeing, in photography and in analytical chemistry. Extended contact may cause skin eruptions and psychosis.

Sodium fluoride is white and crystalline and of medium water solubility. Aqueous solutions will gradually etch glass but the dry solid may be stored in glass bottles. The compound is quite toxic and is used as an insecticide (must be stained with Nile Blue when sold for household use) especially for roaches and ants. It is used for disinfecting equipment in distilleries and breweries and for frosting glass. Severe symptoms results from ingesting as little as 0.25 g. Death from 4 g.

Dimethylglyoxime ($C_4H_8N_2O_2$) is a white powder with a melting point above $200^{\circ}C$. It is practically insoluble in water but soluble in alcohol and acetone. It is used in the detection of nickel and its separation from cobalt and many other metals, also to detect bismuth with which it forms a bright yellow precipitate. The structure of the compound and its nickel precipitate are shown below.

dimethylglyoxime   nickel(II) dimethylgyloxime
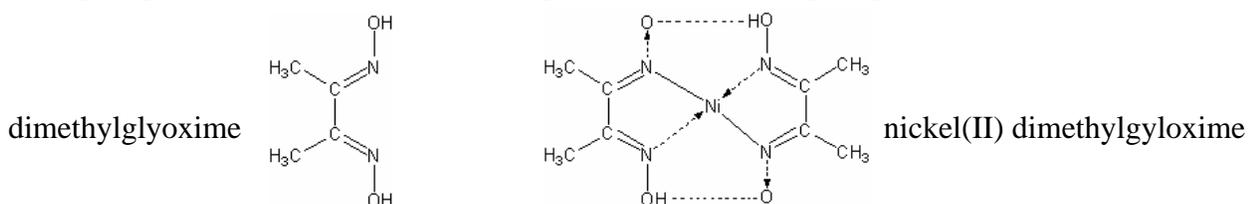
Silver nitrate forms colorless, transparent crystals. It is stable and not darkened by light in pure air but darkens in the presence of organic matter and H_2S. It decomposes at low red heat into metallic silver. It is used in photography and the manufacture of mirrors, silver plating, indelible inks, hair dyes, etching ivory and as an important reagent in analytical chemistry.

It has been used as a topical antiseptic in a 0.1 to 10% solution. However, it is caustic and irritating to skin. Silver nitrate stains skin and clothing. These stains will wear off skin in a few days to a week but clothing is generally ruined. Swallowing silver nitrate can cause severe gastroenteritis that may end fatally.

Chlorine is the eleventh most abundant element, making up about 0.19% of the earth's crust. Sea water contains nearly 3% NaCl. It is produced on a large scale by electrolysis of molten chloride or brines. Small amounts for use in the laboratory are often produced by the reaction of MnO_2 and HCl.

Chlorine is a yellowish-green diatomic gas at room temperature. In dilute water and hexane solutions it is essentially colorless. It has a suffocating odor. It forms explosive mixtures with hydrogen and many finely divided metals will burn in chlorine. It combines with all other elements except the noble gases. It is a member of the halogen family.

Chlorine is used for bleaching, purifying water, and making synthetic rubber and plastics. It is a powerful irritant and excessive exposure can cause death.

Diphenylamine ($C_6H_5NHC_6H_5$) forms salts with strong acids (like sulfuric acid) which is the form in which it is used in this experiment. The sulfate salt is practically insoluble in water but soluble in sulfuric acid. It is used in the manufacture of dyes and for stabilizing nitrocellulose explosives and celluloid. In analytical chemistry it is used for the detection of nitrates, chlorates and other oxidizing substances with which (in the presence of H_2SO_4) it gives a deep blue color.
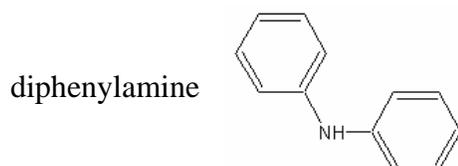
diphenylamine

In the presence of strong oxidizing agents (like nitrate ion) diphenylamine is believed to undergo the following reactions:

colorless

deep violet

55
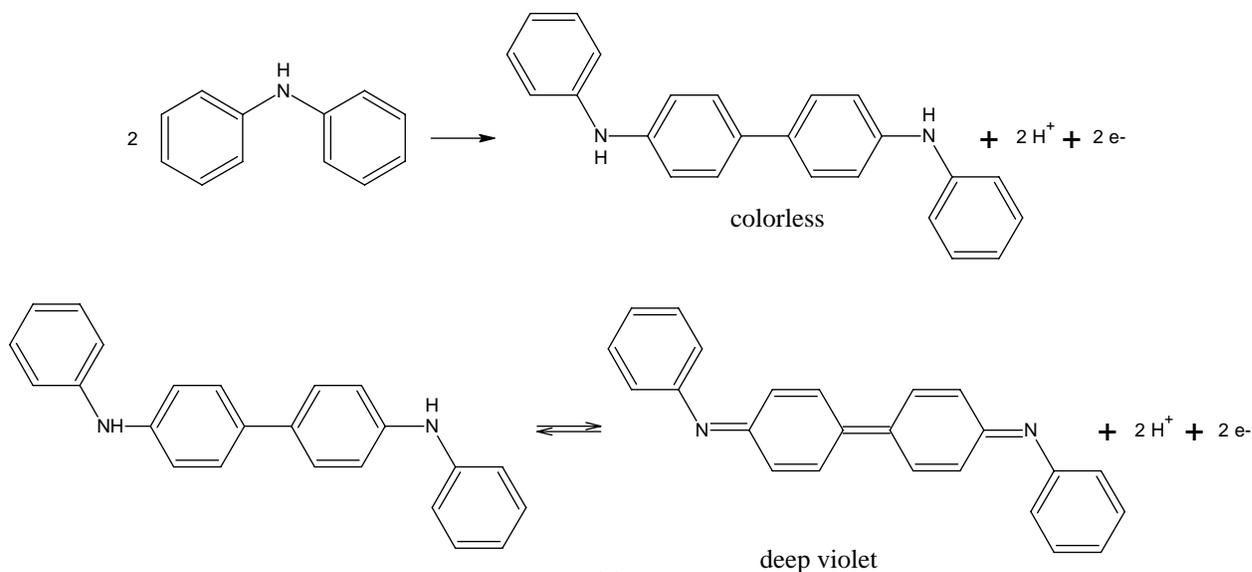
Barium chloride is most commonly obtained as dihydrate crystals. It has a bitter, salty taste. TOXIC!!! It is very soluble in water. Used in the manufacture of pigments, glass, and mordant for acid dyes.

Nitric acid has been called "aqua fortis" (strong water). It is generally produced by the oxidation of ammonia followed by reaction of the gaseous products with water. When pure it is a colorless liquid that fumes in air with a characteristic choking odor. "Concentrated" nitric acid is a water solution containing 70% HNO_3. Even dilute solutions will stain woolen fabrics and animal tissue yellow. It is a very strong oxidizing agent, reacting violently with most organic matter.

Nitric acid is used in the manufacture of fertilizers, dye intermediates and explosives.

Biphenyl (or *diphenyl*), $C_{12}H_{10}$, consists of colorless crystals with a pleasant, peculiar odor. It is insoluble in water but soluble in alcohol or ether. It is used as a fungistat for oranges (applied to the inside of packing crates or wrappers). The solid should be considered toxic.

biphenyl
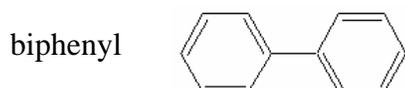
Naphthalene ($C_{10}H_8$) is the most abundant single constituent of coal tar. It consists of white crystals with the odor of moth balls (which it has been used for in the past). It has a relatively high vapor pressure as a solid even below its melting point and slowly sublimes. The solid is insoluble in water but soluble to lesser or greater degrees in various organic solvents. It is used in the manufacture of dye precursors, synthetic resins and lubricants. Its use as a moth repellant has declined since the introduction of *p*-dichlorobenzene. Poisoning may occur through the ingestion of large doses, inhalation or skin absorption.

naphthalene
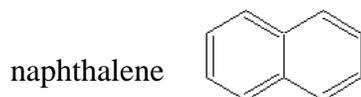
1,2,4,5-tetramethylbenzene (or *durene*), $C_{10}H_{14}$, occurs in coal tar. The solid has a camphor-like odor and is insoluble in water but freely soluble in various organic solvents.

1,2,4,5-tetramethylbenzene
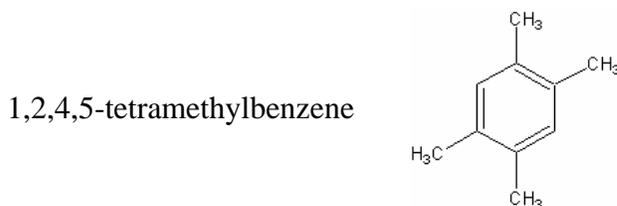
Technique Discussion

The separation of the mixture components is fairly straightforward. Two solvents are used in sequence (first slightly polar petroleum ether + 2-propanone, and then hot water). Each time the mixture is suction filtered to recover the insoluble material from the soluble. Each time BOTH the residue AND the filtrate are something you want to keep! Massing containers the components will end up in is very helpful.

The unknown should be massed (rough balance) so that you can report the composition of the mixture by mass at the end of the experiment. Petroleum ether and 2-propanone should be used with care and sparingly (all organic solvents should be used sparingly, especially those which will end up in the air like this one). About 9 mL of petroleum ether and 1 mL of 2-propanone should be added to the large test tube after the sample is transferred. A small amount of solvent mixture in the same proportion can be used to rinse the sample vial if that seems necessary. A thorough stirring is wise in case insoluble material prevents the organic material from dissolving. The boiling point of petroleum ether is fairly low but warming the mixture will speed dissolving. The safest way to do this is to place the test tube in a beaker of hot tap water. Leave the sample in the hood for a few minutes.

Suction filtration with a very volatile solvent is a little problematic. The paper dries so fast that it is difficult to achieve a good seal and solid can slip through. Since the solid at this point in the experiment needs to be further processed, it is not necessary to get it into the funnel. That means you can decant the solvent through the filter (use 2-3 circles of paper as some of the inorganic materials are very fine), transferring as little solid as possible. You can also used your stirring rod to help hold down the paper as you begin pouring, using the first little bit of liquid (which should be clear if you have allowed your sample to settle) to wet the paper. Repeat the extraction and filtering processes. Then pour the filtrate into a clean, dry beaker [your locker number should be plainly visible]. Rinse the filter flask with a small amount of petroleum ether/2-propanone, adding the rinse to the beaker. Place the beaker in the fume hood to evaporate the solvent overnight [if needed].

Because petroleum ether and 2-propanone are so flammable, no flames should be used in the lab at this point. Share a hot plate to heat approximately 30 mL of distilled water to just boiling. Add about 15 mL of the water to the test tube containing the residue. Stir for a few minutes but do not allow the mixture to settle. Seat the filter paper left from the first step with distilled water and suction filter the mixture carefully. This time you are trying to get all of the solid material out of the test tube with a minimum amount of water. Any extra water used will eventually have to be boiled away. Wash the solid in the filter bed with about 10 mL distilled water. Remember, in washing the idea is to flood the solid for a moment and then draw off the liquid. *Adding wash liquid while the suction is on does not do an effective job of washing*. Remove the filtrate to an evaporating dish, adding a small rinse of the flask. The sample should go into the oven to evaporate overnight.

The insoluble carbonate remains in the funnel at this point and it should be washed with two 5 mL portions of 2-propanone (acetone) to speed drying and aid in recovery from the paper. Continue suction until the odor of acetone is barely noticeable above the solid. Discard the acetone filtrate in the waste beaker in the fume hood. The solid can be transferred to a vial at this point and left uncapped to dry completely.

The analysis of the components can be done in any order that is convenient but there will be a schedule for using the emission spectrograph.

You should need only about 0.3 g of each solid dissolved in about 1 mL of solution to do the qualitative tests. For the soluble component, water will suffice. The carbonate can be brought into solution with 3 M HNO_3 rather than water but *recognize that in tests requiring a basic solution you may need to add somewhat more base than specified to counteract the acid*. You should, in any case, do ALL of the tests using <u>knowns</u> FIRST, recording observations carefully. When you repeat the tests on your components you can stop as soon as you have a match and it is not necessary to go through any particular sequence. It is useful to think in terms of combinations of ions which can't be soluble or insoluble as well as remembering that transition metal compounds are often highly colored while those of Groups I or II are typically white.

What follows is a summary of the qualitative chemical tests for the two inorganic components. To perform the test with your <u>unknown</u>, substitute for the *known* in the directions.

- Cobalt(II), Co^{2+}
  The pink color in water is due to $Co(H_2O)_6^{2+}$. SCN^- in a nearly neutral solution can displace water from this ion to give a dark reddish $Co(SCN)_4^{2-}$. In a less polar solvent this becomes sky blue.

  Test: 2 drops of *known* in 1 mL water. Add 5 drops 1 M NH_4SCN and 1 mL 2-propanone, more if blue color does not appear [note: Fe^{3+} forms a similar color with SCN^- but will <u>not</u> change to blue in the presence of acetone]

- Copper(II), Cu^{2+}
  The blue color in water is due to $Cu(H_2O)_6^{2+}$. Excess aqueous NH_3 initially forms a light blue precipitate of $Cu(OH)_2$ but eventually displaces the water and hydroxide to form deep blue $Cu(NH_3)_4^{2+}$.

  Test: 5 drops of *known* + 5 drops 4 M NH_3; mix well.

- Iron(III), Fe^{3+}
  Neutral solutions of iron(III) are generally yellow or orange due to the formation of small amounts of $Fe(OH)_3$ and related species. In acid solution added SCN^- will form a blood red complex often represented as $FeSCN^{2+}$ but probably consisting of several species. Unlike the similar red color produced by Co^{2+}, this color can be discharged by adding a small amount of solid NaF (forming colorless FeF_6^{3-})

  Test: 1 drop of *known* in 1 mL 2 M HCl. Add 1 drop of 1 M KSCN.

- Nickel(II), Ni^{2+}
  The $Ni(H_2O)_6^{2+}$ gives rise to the green color of nickel solutions. A bright pink/red precipitate forms when nickel hydroxide reacts with dimethylglyoxime, $Ni[C_4H_7N_2O_2]_2$

  Test: 1 drop of *known* in 1 mL 2 M NH_3. Add 5 drops 1% dimethylglyoxime. Mix well.

- Alkali metals (Na^+, K^+) and Ca^{2+}
  Flame tests are simple and effective for these ions IF the flame test loop is properly cleaned. Obtain about 3 mL of concentrated HCl from the fume hood in a dry test tube (stopper). Use this at your place to clean a flame test wire <u>until no color shows in a flame when the wire is first inserted but before it begins to glow</u>. The wire should be placed near the top of the flame and not in the lower reducing portion (blue cone).

  Test: In the order K, Ca, Na, place a <u>small</u> amount of *known* on a watch glass or scoop. Dip the wire in fresh distilled water and touch it to the solid. Test in flame. Potassium gives a pale lavender flame [tradition has it that the presence of sodium contamination can be screened out by looking at this flame through blue cobalt glass], calcium is generally described as dark orange or brick red; sodium the familiar and very persistent bright yellow. Be good and clean the wire before you put it back….

- Halide ions (Cl^-, Br^-, I^-)
  All of these ions are insoluble with Ag^+ and form precipitates that are slightly different in color. AgCl is white, AgBr is ivory or light beige, and AgI is pale yellow. The colors can be concentrated by centrifuging the precipitates. All of the solids darken gradually on exposure to light. If color discrimination is difficult, the precipitates are treated with aqueous ammonia. AgCl dissolves completely, AgBr somewhat less and AgI hardly at all.

  Bromide and iodide may also be detected by displacement with aqueous chlorine. Both impart yellow/orange colors to the solution but extraction with a small amount of petroleum ether reveals a yellow to orange color for bromine and a pink to violet color for iodine.

  Test: 5 drops of *known* in 5 mL of water (centrifuge tube). Add 10 drops of 3 M HNO_3 and 10 drops of 0.1 M $AgNO_3$. Mix well and centrifuge [you <u>must</u> use a balanced number of tubes in the centrifuge to prevent dangerous vibrations; an additional tube of distilled water will work]. Note colors. Carefully discard the supernatant liquid and add 2 mL of 2 M NH_3 to each tube, mixing well. AgCl dissolves completely forming $Ag(NH_3)_2^+$; AgBr dissolves partly in the same way and AgI hardly at all.

  <u>Alternate</u> test: 10 drops of *known* added to 10 drops of $Cl_{2(aq)}$. Add 10 drops of petroleum ether and alternately suction and expel to mix thoroughly. The characteristic colors for Br_2 (yellow/orange) and I_2 (pink/violet) form in the petroleum ether layer.

- Carbonate, CO_3^{2-}
  All carbonates react with acids to liberate CO_2. The classic test for CO_2 involves bubbling the gas through *limewater* (saturated $Ca(OH)_2$) to form insoluble $CaCO_3$. In this experiment, no other anion will produce a gas with acid.

  Test: 10 drops of the *known*. Add a roughly equal amount of 6 M HCl *all at once*. Bubbling or fizzing should be immediate and obvious.

- Nitrate, NO_3^-

  Nitrates react with strongly acidified diphenylamine to form a deep blue-violet solution. *This test is very sensitive and prone to false positives from contamination.*

  Test: 2 drops of *known* added to 2 drops of diphenylamine solution. At the fume hood carefully add 5 drops of concentrated sulfuric acid and swirl gently to mix. The color is very dark, immediate, and must be blue-violet.

- Sulfate, SO_4^{2-}

  Sulfate ion is very insoluble with barium, forming a white precipitate.

  Test: 5 drops of *known* added to 5 drops of 2 M HCl. Add 2-3 drops of 0.1 M $BaCl_2$. A white precipitate, $BaSO_4$, forms immediately.

_____

[the spectrograph and the electric arc apparatus were both constructed by Jeremy Schweitzer ('89) as part of a Senior Independent Study]

Sample preparation for the electric arc in the emission spectrograph can be a little tricky. Some samples work well "as is". Others volatilize so quickly in the heat of the arc that they are lost before sufficient emissions have been recorded. There are two possible approaches to this problem. A small amount of the solid can be made into a <u>fairly concentrated</u> *solution* by adding a drop of distilled water to some solid. In the case of an insoluble compound like your carbonate unknown, dilute HCl (2 M) may be used instead of water. This seems to slow down the burning of the sample in some cases so that a better spectrum is obtained. The solid can also be mixed with graphite powder which burns more slowly in the arc. You will use the first method in this experiment.

There are two kinds of carbon electrodes for the source. The *sample electrode* is shorter and may have a small "crater" or depression in each end. The *counter electrode* is sharpened to a point at each end. After a small amount of solution from your unknown is prepared in the spot plate provided it is dropped carefully onto one end of a *clean* sample electrode which is already positioned in the lower holder in the electric arc apparatus. The top of the sample electrode should be set at 15.5 cm above the base of the apparatus. The counter electrode is then placed in the upper holder and brought into <u>firm contact</u> with the sample electrode, not just touching the drop. *Unless there is electrical contact between the two electrodes it will be difficult to strike an arc on the first try.* Best control of the arc is achieved if the knob which moves the counter electrode is at or near the lowest position of its travel when the arc is struck

Place a loaded film holder in the spectrograph [only the side with a shutter has film in it] and/or move it to the next unexposed slot [the top of the wood frame which holds the film cassette should align with one of the marks on the right hand side]. Align the base of the arc apparatus with the mark on the spectrograph to ensure that the light from the arc passes through the slit in the spectrograph. Record the sample number and type (soluble, insoluble) in the appropriate slot on the log sheet for the film holder. This ensures that you will get the right film back after developing!

Check for clearance around the heaters and arc source and strike the arc as demonstrated. **DO NOT LOOK DIRECTLY AT THE ARC. ALWAYS LOOK THROUGH THE SHIELD WHEN ADJUSTING THE ARC**. As soon as the switch is closed the light bulb will begin to flash. This reminds means that wires are live.

Bring the electrodes apart until you have a stable arc about ¼ inch long and then remove the film shutter and count to five slowly. Replace the shutter. Extinguish the arc by moving the electrodes farther apart until the arc stops. Then **AND ONLY THEN** turn the switch off. **DO NOT USE THE SWITCH TO TURN OFF THE ARC. THE CONTACTS WILL BURN UP AFTER A FEW TIMES**.

Minor manipulations of the arc during the exposure can help to get all of the sample burning. You should be able to tell by reflected light whether or not something is burning in addition to the carbon. It is important to get a photograph of something <u>other</u> than carbon burning. If you do not think the sample has begun to burn you can delay opening the shutter but you should try to avoid overexposing the film by waiting for the "perfect burn" once the shutter is open.

Repeat the process for the other sample after inverting the electrodes [HOT!!!!]. **BE SURE TO MOVE THE FILM HOLDER TO THE NEXT POSITION!!!!** When you are finished with the electrodes place them in the beakers marked for "used" electrodes.

Technique for melting point determination for the organic component can be found in the **Introduction to the Laboratory**. *When preparing a mixed sample be sure to use no more material than is necessary to prepare one or two samples at most*. Small amounts of the two solids can be ground in the bottom of a short test tube with a stirring rod. The capillaries can be filled directly from the tube. It is possible to determine the melting points of two samples simultaneously and if you are having trouble with the technique trying a known is a good way to see if the heating rate is reasonable.

Interpreting the Emission Spectra

The electrodes used contain a sodium impurity which serves as a useful reference mark for determining the wavelengths of the lines on the film. The graph below is a calibration for the spectrograph grating based on known wavelengths of both He and H:

Spectrograph Calibration

$y = -0.4671x + 314.22$
$R^2 = 0.9998$
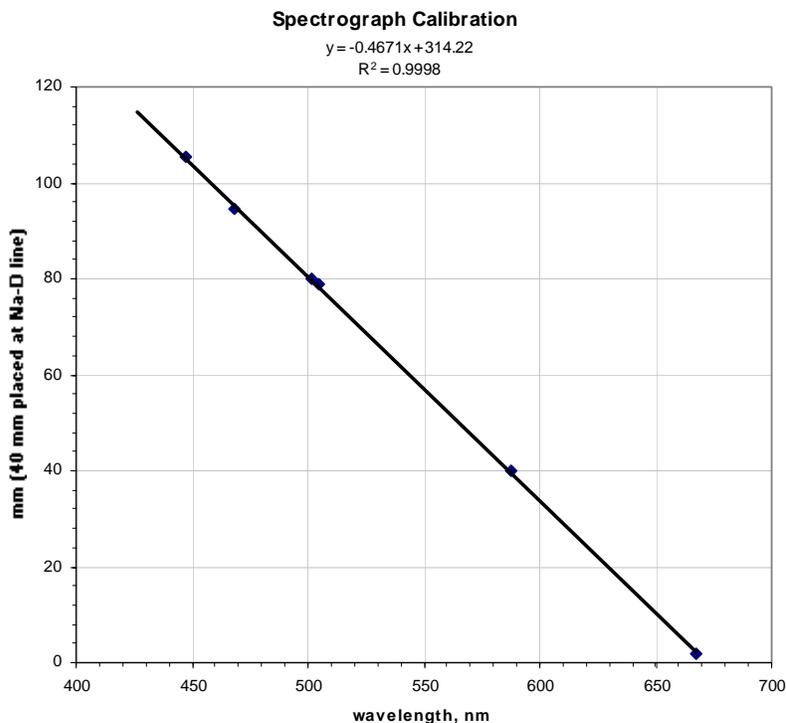
To interpret the wavelengths of the lines on the film place a mm ruler along the bottom of the film strip so that the dark Na-D line is matched with 40 mm. The wavelengths of other lines can be calculated using the equation for the calibration graph. Darker lines typically have higher "intensities" when listed in tables so selecting 3 or 4 lines (as in the sodium example in the **Background** section) is a good way to begin.

The Report

Your initial calculations should include:

1. The masses of each component recovered

Your conclusion to this experiment should include a summary of the components found (and the material lost) along with any appropriate literature references to support your determination. You should show balanced reactions for <u>all</u> the cation and anion identification tests (except nitrate, which is given in detail in the text). The emission spectra of the two cations should be matched with a reference (by wavelength). It is not necessary to match every line but 3 or 4 of the more persistent lines should be compared as well as obvious patterns or groups of lines which distinguish one spectrum from the other.