

Chem 4563 Organic Qualitative Analysis

Identifications of Unknowns - Qualitative Elemental Analysis

1. Qualitative determination of elements present.

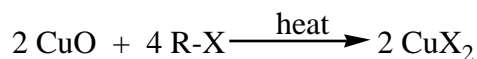
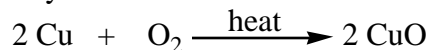
There are several quick simple tests which yield considerable useful information as to the elements that may be present in organic compounds. Remember that all organic compounds will contain C and H, other commonly found elements will be O, N, S, Halogens and various metals.

a. Ignition test (pp 32-33 od Shriner)

This simple test will indicate the presence of oxygen atoms, and also the presence of aromatic rings or metals. A small amount of the unknown is burned in the blue part of a Bunsen Burner flame. The combustion flame and residue are examined. A blue flame indicates the presence of an oxygen atom in the unknown. A yellow, sooty flame indicates the presence of aromatic rings leading to the formation of much unburned carbon as soot. Look closely at the residue of combustion...a neutral organic compound will burn completely, whereas an organic salt will leave behind the metal as a crusty residue.

b. Beilstein Test (Pasto p 319)

The presence of bromine, chlorine or iodine in organic compounds can be detected by the Beilstein Test. This test depends on the production of a volatile copper halide (CuX_2) produced when an organic halide is strongly heated with a copper oxide. The copper halide will give off blue-green light when excited in the high temperature of a burner flame. This test is extremely sensitive and a positive result should always be confirmed by other methods.

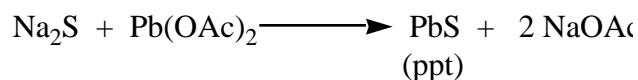


c. Sodium Fusion Test (Shriner pp78-79, Pasto pp 316-321)

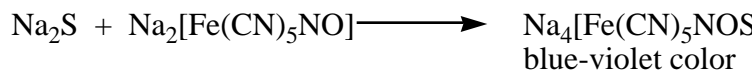
This is the most useful test for the presence of N, S, Cl, Br and I. An organic unknown is degraded under high temperature in the presence of sodium metal. Depending on the elements present the following sodium salts will be formed: Nitrogen: NaCN , Sulfur: Na_2S and halogens: NaX ($\text{X} = \text{Cl, Br, I}$). The presence of these salts is then determined by standard inorganic analysis tests.

Tests for Na_2S

i. Lead Acetate solution is added to the sodium fusion test solution. A positive test for the Sulfur is indicated by the formation of PbS as a black precipitate.

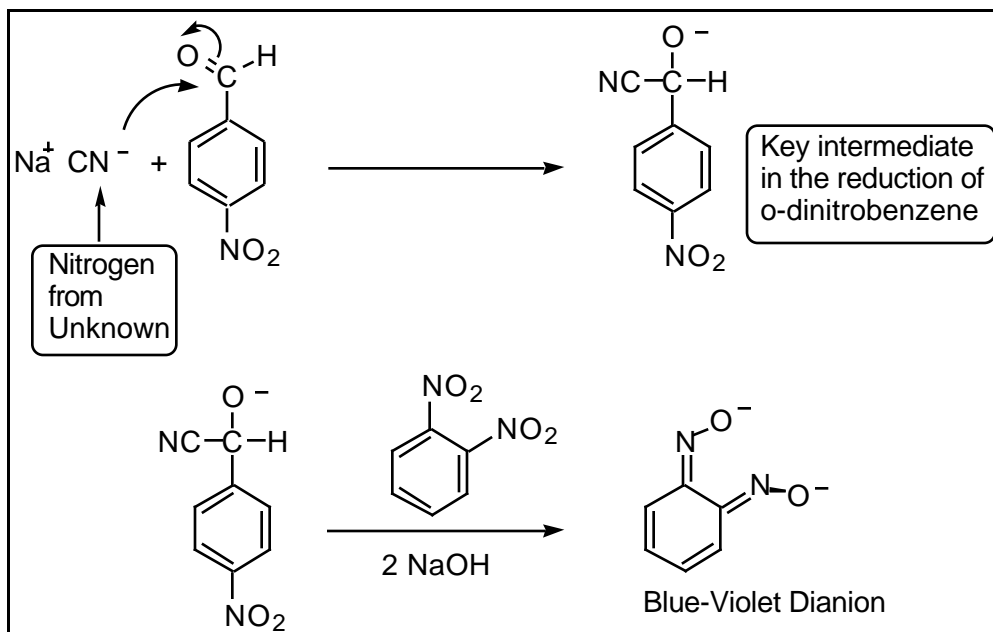


ii. Sodium nitroprusside solution is added to the sodium fusion test solution. A positive test for sulfur is the formation of a blue-violet thio-nitro complex.



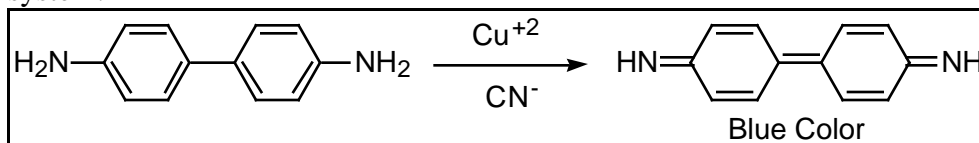
Tests for NaCN

- i. A p-nitrobenzaldehyde solution is added to the sodium fusion test solution. Then a basic solution of o-dinitro benzene is added. A positive test for nitrogen is indicated by the presence of a blue-violet color.



- ii. A second test is the classic "Prussian Blue" test. The pH of the sodium fusion test is adjusted to pH 13 by adding 10% NaOH solution. A few drops of saturated ferrous ammonium sulfate solution and a few drops of 30% sodium fluoride is added, the mixture is boiled for 30 sec, and then acidified with 30% H_2SO_4 until the brownish iron hydroxides dissolve. If nitrogen is present as CN, a dark blue precipitate of $\text{NaFe}_2(\text{CN})_6$ will form.

- iii. A third alternative test for the cyanide ion involves the oxidation of benzidine with cupric ion, a reaction that will not take place in the absence of the cyanide ion. The cyanide complexes with the cuprous ion so as to increase the oxidation potential of the system.



Tests for NaX (halides)

- i. Cyanide and sulfide anions interfere with this test. If they are present, they must be removed. To accomplish this, acidify the sodium fusion test solution with dilute nitric acid and boil for about 2-3 minutes. This will drive off any HCN or H_2S which is formed. When the solution cools, add a few drops of 5% silver nitrate solution. A voluminous precipitate indicates the presence of a halide. Silver chloride is white, silver chloride is off-white and silver iodide is yellow. Silver chloride will dissolve in conc. ammonium hydroxide, silver bromide and silver iodide are insoluble. There are further tests available to differentiate between the halides.

Read: Shriner. CH 3 pp 31-61 and CH4 pp77-83

Scheme for Qualitative Nitrogen, Halogen, and Sulfur Analysis

Step 1. Sodium Fusion. Clean ca. 0.1 g sodium (a cube 4 mm on an edge) with filter paper (use forceps), place it in a clean, dry test tube (16 × 125 mm or slightly smaller) which is mounted vertically, and melt the sodium with a small burner flame. When the sodium vapor begins to rise, drop 10–20 mg of solid or 1–2 drops of liquid unknown **directly^a** onto the sodium and heat for 30 sec (red hot). Cool, add 0.5 ml of CH₃OH and break up mass with glass rod. When any reaction with the excess sodium has ceased, add 5 ml of distilled water, heat to boiling, and filter or centrifuge while hot. Dilute filtrate or centrifugate to 20 ml with distilled water. This is the *stock solution*.

Step 2. General Test for Cyanide, Halide, Sulfide. (May be omitted.) Acidify 1 ml of stock soln with dil HNO₃. Add several drops of AgNO₃ soln. No ppt indicates absence of cyanide, halide, and sulfide. If ppt forms carry out Steps 3 through 8.

Step 3. Sulfide. Acidify 1 ml of stock soln with dil HOAc (ca. 6 M) and add a few drops of 1–5% Pb(OAc)₂ soln. A black ppt indicates sulfide.

Step 7. Bromide. Add 0.5 ml CCl₄ and 2 drops of chlorine water^d to 1 ml of the soln from Step 6. A brown color in the CCl₄ indicates bromide.

Step 8. Chloride. Dilute the remaining soln from Step 6 to 60 ml, add 2 ml of conc H₂SO₄ and 0.5 g of K₂S₂O₈, and boil for 5 min. Cool and add several drops of AgNO₃ soln. A white ppt indicates chloride.

Step 4. Cyanide. (Method A) Adjust the pH of 1 ml of stock soln to 13 (Hydrion paper) with 3 N NaOH. Add 2 drops of a fresh satur Fe(NH₄)₂(SO₄)₂ soln, 2 drops of a 30% KF soln, and 2 drops of a 5% FeCl₃ soln. Heat to boiling and acidify dropwise with 30% H₂SO₄. A Prussian blue color indicates cyanide.^b

(Method B) Acidify 1 ml of stock soln with several drops of dil HOAc in a small test tube. Carefully add a few drops of benzidine-copper acetate soln^c with a micropipette or capillary tube so that no mixing occurs. A blue color at the interface indicates cyanide.

Step 5. Halide. Acidify 10 ml of stock soln with dil H₂SO₄, boil for several min and cool.

Step 6. Iodide. Add 0.5 ml of CCl₄ to 1 ml of the soln prepared in Step 5. Add several drops of NaNO₂ soln; purple or violet color in CCl₄ indicates iodide. If iodide is present treat remaining 9 ml of above soln with NaNO₂ and extract all I₂ into CCl₄. Bring aqueous soln to a boil, cool, and proceed to Steps 7 and 8.

^aIf the unknown touches the hot sides of the tube, it may be vaporized or pyrolyzed before it has an opportunity to react with the sodium.

^bVery small amounts of cyanide may result in a green color.

^cThis reagent is actually two solutions. Solution #1 is a 1% soln of benzidine in 10% HOAc. Solution #2 is a 3% soln of Cu(OAc)₂. Store in dark bottles. Mix equal volumes of the solutions just before using. **CAUTION! Benzidine is carcinogenic.**

^dA freshly acidified soln of NaOCl or Ca(OCl)₂ or Chlorox should be used.