

# THE CHEMICAL CHARACTERIZATION OF ORGANIC FUNCTIONAL GROUPS: AN EXPERIMENT FOR THE ADVANCED HIGH SCHOOL CHEMISTRY LABORATORY

John A. Ricketts  
Department of Chemistry  
DePauw University  
Greencastle, Indiana 46135

**ABSTRACT:** The time limitation placed on laboratory activities, the use of flammable solvents and corrosive chemicals, and the need for expensive glassware precludes the use of extensive organic synthesis in the high school laboratory. A scheme is presented in this paper to identify chemically whether a pure organic, mono-functional compound is a carboxylic acid, acid anhydride, alcohol, aldehyde, amide, amine, ester, ether, ketone, phenol, or hydrocarbon. The classification reactions are performed on a semimicro scale using inexpensive reagents. The experiment is written as an "open-ended" project that requires each student to make decisions that are based upon individual observations.

**KEYWORDS:** Organic chemistry, laboratory experiments, functional groups, chemical characterization.

## INTRODUCTION

An introduction to organic functional group chemistry is now a part of many college-level, introductory chemistry courses, especially the course for the non-science major and, to a lesser extent, the chemistry course for the science major. Therefore, units emphasizing organic chemistry have a place within the advanced high school chemistry course.

Many of the organic syntheses that are done at the college level require the use of corrosive reagents, appreciable amounts of starting materials, flammable and toxic solvents, and expensive glassware. Furthermore, their completion requires longer than 50 minutes. Such constraints limit the number of organic synthesis experiments, in which products are isolated, purified, and characterized, that are amenable for use in high school.

The student's laboratory experience should introduce organic reactions and serve as a pedagogical adjunct to the lecture in the organic chemistry unit of study. Laboratory exercises that establish chemically the presence of a particular functional group in an organic compound meet these criteria. The experimental test procedures should require simple equipment, use minimum amounts of inexpensive and non-corrosive chemicals, be capable of rapid completion, and allow the differentiation between various functional groups. A set of test procedures that are performed on a semimicro scale satisfy these constraints.

Two examples of organic functional group analysis experiments are worth citing. They are easily adaptable for use in the high school laboratory. Silvert (1987) describes an exercise in which organic compounds can be identified as alcohols, aldehydes, or ketones. The test reagents are acidified sodium dichromate solution, iodine dissolved in potassium iodide solution, 10% sodium



Table 1. Equipment and reagents required at a student workstation.

Equipment	Reagents
6 - 3" test tubes with corks	6 M hydrochloric acid (HCl)
3 - 4" test tubes with corks	6 M sodium hydroxide (NaOH)
1 - 10 mL graduate	15 M ammonium hydroxide (NH <sub>4</sub> OH)
2 - 5" glass stirring rods	5% ferric chloride (FeCl <sub>3</sub> )
2 - medicine droppers with bulbs	2% potassium permanganate (KMnO <sub>4</sub> )
1 - 50 mL beaker	ceric nitrate reagent (dissolve 40 g
1 - 100 mL beaker	(NH <sub>4</sub> ) <sub>2</sub> Ce(NO <sub>3</sub> ) <sub>6</sub> in 100 mL of 2 M HNO <sub>3</sub> )
1 - micro metal spatula	chromic acid reagent (dissolve 25 g CrO <sub>3</sub> in
1 - 125 mL plastic wash bottle	25 mL of conc. H <sub>2</sub> SO <sub>4</sub> ; cautiously add to 75
1 - centrifuge test tube brush	mL of distilled water with vigorous stirring)
1 - wooden clothespin-type test	2,4-dinitrophenylhydrazine reagent (dissolve
tube holder	3 g 2,4-dinitrophenylhydrazine in 15 mL of
1 - test tube block	conc. H <sub>2</sub> SO <sub>4</sub> ; cautiously pour with stirring
	into a mixture of 70 mL of 95% ethanol and
	20 mL of distilled water)
	95% ethanol (the denatured alcohol from the
	drugstore is suitable as a solvent)
	acetone (the acetone from the drugstore is
	suitable as a solvent)
	tetrahydrofuran

hydroxide solution, and 2,4-dinitrophenylhydrazine (DNPH) solution. Griswold and Rauner (1991) outline a procedure to differentiate between primary, secondary, and tertiary alcohols, aldehydes, ketones, phenols, alkenes, and ethers. Their scheme employs nine separate tests: a water solubility test, an ignition test, the Baeyer test, the iodoform test, the Lucas test, the ferric chloride test, the ceric nitrate test, the reaction with DNPH solution, and the reaction with a solution of bromine dissolved in carbon tetrachloride.

The experiment presented here is an open-ended exercise that deals with the identification of the following functional groups: alcohols (primary, secondary, or tertiary), aldehydes, amides, amines (primary aliphatic or aromatic, secondary aliphatic or aromatic, or tertiary), carboxylic acids, acid anhydrides, esters, ethers, hydrocarbons (saturated, unsaturated, or aromatic), ketones, and phenols. The inclusion of a larger number of functional groups introduces more organic reactions and affords a broader view of the subject. Salts of amines and carboxylic acids are excluded as possibilities in the identification procedures.

The chemical principles of the tests are outlined within the experiment; consequently, the laboratory experience can provide the basis for further discussion during formal class time. The student soon appreciates that qualitative organic functional group analysis is not as formalized as is qualitative inorganic ionic analysis. The tests in organic functional group analysis are not as sensitive as those in inorganic ionic analysis, and in many instances, no single test is specific for a particular functional group. Several functional groups may react differently with the same reagent. Impurities in the sample can lead to an incorrect interpretation of experimental observations.



Table 2. Special reagents and test compounds for the side shelf.

Special Reagents	Test Compounds
<b>Solids</b>	
ferric ammonium sulfate ( $\text{Fe}(\text{NH}_4)(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ )	primary alcohol (1-butanol)
potassium thiocyanate (KCNS)	secondary alcohol (2-butanol)
anhydrous aluminum chloride ( $\text{AlCl}_3$ )	tertiary alcohol (2-methyl-2-propanol)
2-naphthol ( $\text{C}_{10}\text{H}_7\text{OH}$ )	aldehyde (butanal)
citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ )	amide (acetamide)
	primary aliphatic amine (benzylamine)
	primary aromatic amine (2,5-dichloroaniline)
<b>Liquids</b>	
acetic anhydride ( $\text{C}_4\text{H}_6\text{O}_3$ )	secondary amine (dibutylamine)
chloroform ( $\text{CHCl}_3$ )	tertiary amine (tributylamine)
	anhydride (propionic anhydride)
	carboxylic acid (benzoic acid)
	ester (propyl acetate)
<b>Solutions</b>	
1% sodium nitroprusside ( $\text{Na}_2\text{Fe}(\text{CN})_5(\text{NO}) \cdot 2\text{H}_2\text{O}$ )	ether (tetrahydrofuran)
1% sodium nitrite ( $\text{NaNO}_2$ )	saturated hydrocarbon (cyclohexane)
4% potassium iodate ( $\text{KIO}_3$ )	unsaturated hydrocarbon (cyclohexene)
0.1% soluble starch	aromatic hydrocarbon (benzene)
2% potassium iodide (KI)	ketone (2-butanone)
0.5% nickel chloride ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ )	phenol (phenol)
saturated with carbon disulfide ( $\text{CS}_2$ )	
1M hydroxylamine hydrochloride ( $\text{NH}_2\text{OH} \cdot \text{HCl}$ ) in 95% ethanol	
Lucas reagent (dissolve 160 g anhydrous $\text{ZnCl}_2$ in 100 mL of conc. $\text{HCl}$ )	

## THE CLASSIFICATION TESTS

An analytical scheme cannot easily be written for qualitative organic functional group analysis. The student performs ten Exploration Activities on a set of known organic compounds prior to identifying an unknown compound. The procedures are carried out on a semimicro scale, using 10-50 mg samples of compound dissolved in a suitable solvent. Each classification reaction normally requires no more than a total volume of 1-2 mL of solution. The procedures have been adapted from journal articles and qualitative organic analysis texts. The test procedures were verified using organic chemicals that were found in the chemical storeroom at DePauw University. A listing of the compounds that were used to verify the test procedures appears as part of each Exploration Activity.

Table 1 lists the equipment and the set of reagents available at each student workstation. The reagents are conveniently stored in 30 mL dropping bottles equipped with dropping pipets. The bottles can be collectively organized in a plastic tray and shared with neighboring students in the class. Table 2 lists those special reagents that are necessary for some of the procedures and lists a set of



mono-functional organic compounds, which can be used to illustrate the interaction of the various reagents with specific functional groups. The representative compounds are stored in appropriate containers on a laboratory side shelf. Students may not remove these substances from the side shelf; they carry samples to their workstation as needed.

As a prelude to the discussion of the various Exploration Activities, each procedure is only outlined. A copy of the actual experiment can be obtained from the author. Certain traditional classification tests such as the solubility of the organic compound in concentrated sulfuric acid solution, the reaction of alcohols with acetyl chloride to form esters, the reaction of carboxylic acids with thionyl chloride to form acid chlorides which can be esterified, and the use of a solution of bromine in carbon tetrachloride to indicate unsaturation in the organic molecule, are purposely omitted in order to avoid using potentially dangerous chemicals. Labeled waste containers must be placed at the workstations into which students discard their reaction mixtures rather than dumping them into the sink.

The hazardous nature of certain chemicals that are used in the classification procedures requires cautious experimentation by the student. Safety glasses must be worn. Organic chemicals are combustible, and many are volatile; consequently, heating operations should be carried out on hot plates or in hot water baths. Inhaling solid dust or liquid vapor during manipulative procedures must be avoided. Students should be warned that when any chemical inadvertently comes in contact with the skin, they should immediately flush the area with copious amounts of water. They should notify the teacher when chemicals are spilled on the work surface to receive instructions as to how to clean the area. Even though the procedures are performed on a semimicro scale, accidents can occur. Those chemicals that are especially hazardous will be identified as part of the Exploration Activity.

**Exploration 1. The Solubility in Water, HCl Solution, and NaOH Solution: The Acid-Base Characteristics of the Functional Groups.** The solubility of 20-30 mg of solid compound or 1 drop of liquid compound is determined in 2 mL of distilled water, in 2 mL of 1.2 M hydrochloric acid solution, and in 2 mL of 1.2 M sodium hydroxide solution. For water soluble compounds, the acid-base character of the solution is determined using universal indicator solution. For water-insoluble compounds, their solubility in 1.2 M hydrochloric acid solution and, if insoluble in the acid, in 1.2 M sodium hydroxide solution determines their acid-base character. Test the set of known organic compounds and categorize the functional group types as:

Basic: Amines;

Neutral: Alcohols, aldehydes, amides, esters, ethers, hydrocarbons, and ketones;

Acidic: Acid anhydrides, carboxylic acids, and phenols.

Acid anhydrides are neutral compounds; however, they rapidly hydrolyze to carboxylic acids in water. The instructor should be certain that each student categorizes the functional group types correctly.

**Exploration 2. The Ferrox Test, a Qualitative Test to Indicate the Presence of Oxygen in Organic Molecules.** The ferrox test as described by Davidson (1940) depends upon the solubility of ferric thiocyanate (ferric



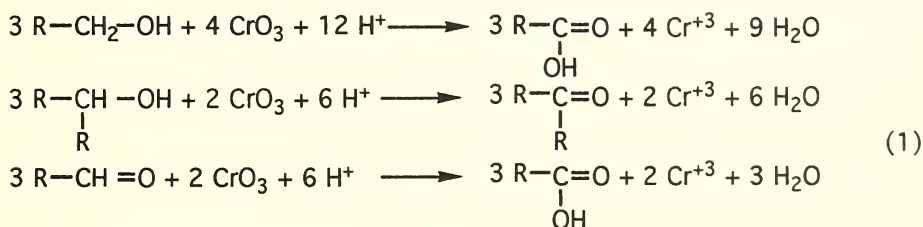
hexacyanoferrate) in liquid organic compounds that contain oxygen. Some amines give a positive ferrox test. However, the test is most effective when used to distinguish hydrocarbons from the remaining types within the neutral category.

Crush and mix solid ferric ammonium sulfate dodecahydrate and solid potassium thiocyanate together until a dark solid is formed. Transfer a few crystals of the solid to a dry test tube. Cover the crystals with 3-4 drops of the liquid organic compound. Oxygen containing organic liquids will dissolve some of the solid; a red solution is produced.

A strong, positive ferrox test was observed with all of the alcohols, aldehydes, ketones, esters, dialkyl ethers, and amides that were tested: allyl alcohol, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-2-propanol, 2-methyl-1-propanol, 2-pentanol, 3-ethyl-3-pentanol, cyclohexanol, cyclooctanol, benzyl alcohol, 1,4-butanediol, acetaldehyde, propanal, butanal, pentanal, benzaldehyde, p-tolualdehyde, acetone, acetophenone, cyclohexanone, 4-methyl-2-pentanone, 3-pentanone, 2,4-pentanedione, methyl acetate, ethyl acetate, phenyl acetate, methyl benzoate, butyl butanoate, benzyl butanoate, diethyl phthalate, ethyl 4-methoxybenzoate, p-tolyl acetate, diethyl ether, 1,2-dimethoxyethane, 1,4-dioxane, tetrahydrofuran, dibutyl ether, isoamyl ether, N,N-dimethylformamide, N,N-dimethylacetamide, and N-methylacetamide. The alkyl-aryl ethers, phenetole, anisole, and p-methylanisole, gave a faint ferrox test, but the diaryl ether, diphenyl ether, gave a negative test. All of the hydrocarbons that were tested gave a negative ferrox test: benzene, toluene, hexane, octane, mesitylene, cyclohexane, cyclohexene, pentane, p-xylene, and pinene.

### Exploration 3. The Chromic Acid Oxidation of Alcohols and Aldehydes.

Bordwell and Wellman (1962) discuss the use of chromic acid reagent to distinguish between tertiary and primary or secondary alcohols; Morrison (1965) extends its use to distinguish between aldehydes and ketones. Chromic acid reagent reacts rapidly with acetone solutions of primary alcohols, secondary alcohols, and aldehydes with the formation of a green to blue-green precipitate (Equation 1).



**Warning!** Chromic acid is a strong oxidizing agent and is a known human carcinogen. Caution your students to handle the chromic acid reagent with care. Clean up any spills immediately, and if any reagent is spilled on the skin, wash the area immediately with water.

Primary and secondary alcohols react within 15 seconds without heating; aldehydes react less rapidly and may require heating in a water bath at 50° C. Those alcohols and aldehydes that react positively with the chromic acid reagent are methanol, ethanol, 1-propanol, 2-propanol, 2-methyl-1-propanol, 1-butanol, 2-butanol, 1-pentanol, 2-pentanol, 2-phenylethanol, benzyl alcohol, 4-methoxybenzyl



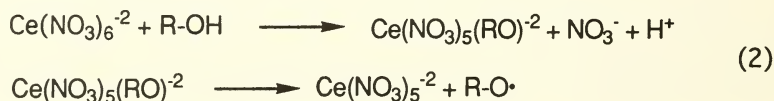
alcohol, 1,10-decanediol, 2-methoxyethanol, cholesterol, cyclohexanol, cyclooctanol, acetaldehyde, propanal, butanal, 2-methylpropanal, pentanal, heptanal, benzaldehyde, o-chlorobenzaldehyde, o-methoxybenzaldehyde, p-nitrobenzaldehyde, naphthaldehyde, piperonal, cinnamaldehyde, and 4'-formylacetanilide.

Phenols give a dark precipitate with chromic acid reagent. Amines form an orange salt that is insoluble in acetone. 2-Aminoethanol and 2-(N,N-dimethylamino) ethanol form an orange salt rather than the oxidation product. Tertiary alcohols, amides, carboxylic acids, acid anhydrides, esters, ethers, ketones, and hydrocarbons do not react.

**Exploration 4. The Ceric Nitrate Reagent Test for Alcohols and Phenols.**

Duke and Smith (1940) describe the use of the hexanitrate cerate ion to detect the presence of alcohols and phenols. Ceric nitrate reagent reacts with water-soluble alcohols in aqueous medium producing an orange to orange-red complex. A similar reaction occurs for water-insoluble alcohols dissolved in tetrahydrofuran (THF). Those alcohols that gave a positive ceric nitrate reagent test are methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-2-propanol, 2-methyl-1-propanol, 3-ethyl-3-pentanol, cyclohexanol, benzyl alcohol, 2-phenylethanol, cholesterol, 2-methoxyethanol, cyclooctanol, 1,10-decanediol, glycerol, 2-phenoxyethanol, isoamyl alcohol, and allyl alcohol.

The color is transient with alcohols because cerium(IV) is an oxidizing agent. The color is due to the formation of a pentanitratealkoxy cerium(IV) anion complex. An electron is then transferred to the cerium(IV) species from the alkoxy ion producing the colorless pentanitrate cerium(III) anion and an alkoxy radical, which is eventually oxidized to an aldehyde or a ketone (Equation 2).



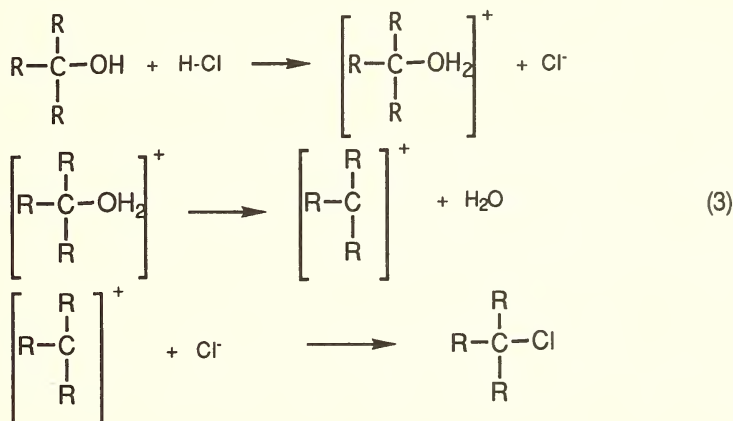
Substituting a phenol or an aromatic amine for the alcohol in the THF procedure produces an intense red, soluble complex. This test is especially useful as a supplementary test for phenols. Some phenols (e.g., 2-naphthol) do not give a positive ferric chloride test (Exploration 9). Those phenols that gave a positive test are phenol, salicylaldehyde, methyl, salicylate, o-hydroxybiphenyl, N-acetyl-p-aminophenol, p-hydroxybenzaldehyde, p-methoxyphenol, p-benzylphenol, p-nitrophenol, p-hydroxybenzoic acid, p-chlorophenol, and propyl p-hydroxybenzoate.

**Exploration 5. The Lucas Test for Primary, Secondary, and Tertiary Alcohols.** The test procedure is from the text by Cheronis and Entrikin (1963). This test is limited to water-soluble alcohols and depends on the relative times required for cloudiness to develop throughout the solution, when the alcohol is mixed with a solution of zinc chloride dissolved in concentrated hydrochloric acid solution. This cloudiness is due to the formation of an insoluble alkyl chloride. As a rule of thumb, tertiary alcohols react within 1 minute, secondary alcohols within 5 minutes, and primary alcohols in 10 minutes or more. Exceptions are the primary alcohols, allyl alcohol, benzyl alcohol, and cinnamyl alcohol, which react as though they are tertiary alcohols.

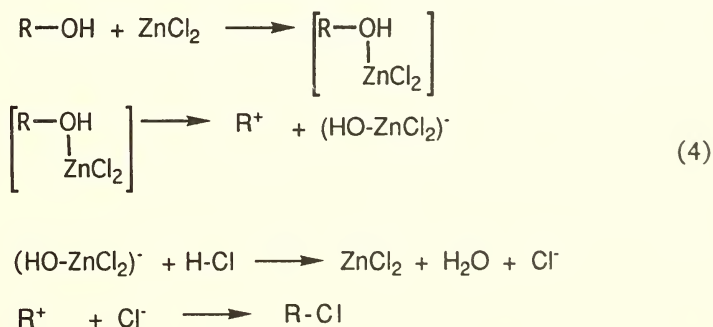


Warning! Concentrated hydrochloric acid solution is a hazardous substance. Avoid inhaling its vapors, and if it comes in contact with the skin, immediately flush the area with water. Then swab the area with a solution of sodium bicarbonate to neutralize any acid that is left. Finally, wash the affected area again.

The chemistry of this reaction offers the opportunity to discuss a reaction mechanism. Tertiary alcohols react with concentrated hydrochloric acid solution in the absence of zinc chloride; primary and secondary alcohols do not. The reaction pathway for tertiary alcohols involves the attack on the alcohol by a proton to form a reactive intermediate, the decomposition of the reactive intermediate to a trialkyl carbocation and water, and the reaction of the carbocation with the chloride ion to form an alkyl chloride (Equation 3).



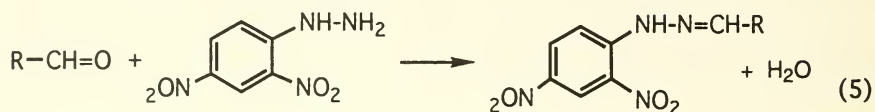
Zinc chloride acts as a Lewis acid with primary and secondary alcohols, initially coordinating with an unshared electron pair on oxygen to form an unstable intermediate. The intermediate loses the dichlorohydroxyzincate anion to form a carbocation. The carbocation then reacts with a chloride ion to generate an alkyl chloride (Equation 4).



**Exploration 6. 2,4-Dinitrophenylhydrazine (DNPH), a Reagent Specific for Aldehydes and Ketones.** The test procedure is from the text by Shriner, Fuson, Curtin, and Morrill (1980). DNPH reacts with the carbonyl group of most

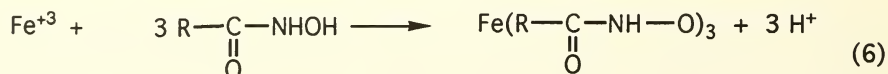


aldehydes and ketones in an ethanol-water medium to form an orange to orange-red precipitate, a 2,4-dinitrophenylhydrazone. The reaction is shown with a representative aldehyde (Equation 5).

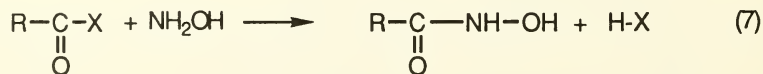


The reaction of aldehydes and ketones occurs almost immediately at room temperature; it was necessary to warm one aldehyde, butanal, and the DNPH reagent at 50° C for 5 minutes to promote their reaction. Esters, amides, acid anhydrides, and carboxylic acids, all of which contain a carbonyl group, do not react with DNPH reagent. Easily oxidized alcohols, such as allyl alcohol, give a positive test as they are first transformed into the aldehyde; however, this reaction is quite slow and only a small amount of product forms. The aldehydes and ketones that gave a positive test with the DNPH reagent are acetaldehyde, pentanal, 2-ethylhexaldehyde, benzaldehyde, 2-chlorobenzaldehyde, butanal, 1-naphthaldehyde, piperonal, p-tolualdehyde, salicylaldehyde, acetone, 3-methyl-2-butanone, 2-pentanone, 3-pentanone, cyclohexanone, 2,4-pentanedione, acetophenone, cyclopentanone, and benzophenone.

**Exploration 7. The Hydroxamic Acid Test for Amides, Acid Anhydrides, and Esters.** Hydroxamic acids may be thought of as N-hydroxy derivatives of amides or as oximes of carboxylic acids. Hydroxamic acids combine with the ferric cation in acid media to form an intensely colored, neutral complex (Equation 6). Hydroxamic acids are synthesized by the reaction of



hydroxylamine with carboxylic acid derivatives such as acid chlorides, acid amides, esters, and acid anhydrides (Equation 7). A comprehensive review of the



utility of organic functional group identification via hydroxamic acid formation and complexation with ferric chloride solution is given by Davidson (1940).

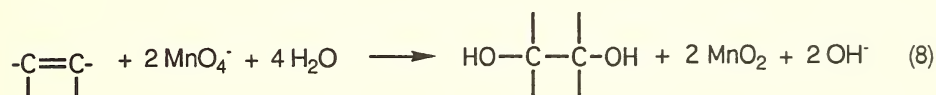
Buckles and Thelan (1950) point out that amides and acid anhydrides form hydroxamic acids when heated in boiling water with 1 M hydroxylamine hydrochloride solution in 95% ethanol in either acidic or basic solution. Esters react only in a basic environment. The procedure of Buckles and Thelan is the basis for the classification test. Suspected amides or acid anhydrides are treated with the hydroxylamine hydrochloride reagent in an acid medium; suspected esters are treated with this reagent in a basic medium. The color of the ferric



hydroxamate complex is most intense and requires the shortest induction period for its formation at a pH between 1 and 2. The excess acid or base is neutralized prior to adding the ferric chloride solution. The development of a red color throughout the solution is a positive test.

The acid anhydrides, amides, and esters which gave a positive ferric hydroxamate test are acetic anhydride, propionic anhydride, butyric anhydride, succinic anhydride, benzoic anhydride, phthalic anhydride, acetamide, N-methylacetamide, propionamide, N,N-dimethylacetamide, N,N-dimethylformamide, benzamide\*, acetanilide\*, p-acetotoluidide\*, methyl acetate, ethyl acetate, methyl propionate, methyl butyrate, methyl phenylacetate, propyl benzoate, isobutyl benzoate, and phenyl benzoate. Those amides that are designated by an asterisk gave a slight, but discernable, positive ferric hydroxamate test. N-Phenylbenzamide did not give a positive hydroxamate test under the reaction conditions in acid media. Because many phenols react with ferric chloride solution to produce a colored complex (Exploration 9), the test is invalid, if a phenolic, hydroxy group is present in the molecule.

**Exploration 8. Tests for Hydrocarbons, Neutral Compounds That Give a Negative Ferrox Test.** *Unsaturation* in hydrocarbons is detectable using the Baeyer Test as described by Cheronis and Entrikin (1963). Unsaturated hydrocarbons react rapidly with neutral potassium permanganate solution, producing a brown precipitate of manganese dioxide (Equation 8); saturated and



aromatic hydrocarbons do not react with this reagent. The initial reaction involves the formation of a glycol. The unsaturated hydrocarbons that gave a positive Baeyer test are 1-pentene, cyclohexene, 1,7-octadiene, 1,3-cyclooctadiene, 1,5,9-cyclododecatriene, 1-hexene, and 1,2-diphenylethylene.

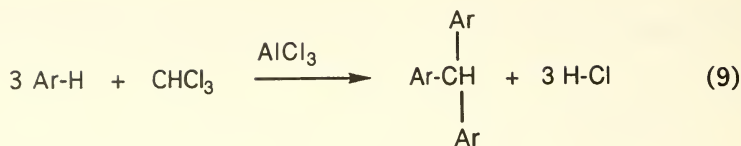
Phenols, aromatic amines, and aldehydes give a positive test; however, phenols and amines are in a different solubility classification than hydrocarbons, and aldehydes react with DPNH reagent whereas hydrocarbons do not. Swinehart (1964) observes that some alcohols do appear to give a positive Baeyer test. He traces the cause to the presence of oxidizable impurities in the alcohol sample.

*Aromatic* hydrocarbons respond using the procedure suggested by Cheronis (1958). The test involves the reaction of the hydrocarbon with chloroform in the presence of anhydrous aluminum chloride. A positive test is indicated by the development of an intense color, which can range from yellow through green to purple, on the surface of the aluminum chloride.

**Warning!** Polynuclear, aromatic hydrocarbons are known human carcinogens. Avoid inhaling any solid dust or liquid vapor. The reaction of anhydrous aluminum chloride with moisture is highly exothermic; hydrogen chloride gas is evolved. Handle this chemical cautiously.

This reaction is a Friedel-Crafts condensation of chloroform with the aromatic nucleus in the presence of an aluminum chloride catalyst (Equation 9). The overall reaction is a stepwise process. The color formation is attributed to

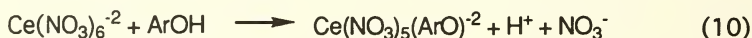




the production of a small amount of the triarylmethyl tetrachloroaluminate ion pair during the reaction. Those aromatic hydrocarbons that gave a positive test are benzene, toluene, naphthalene, phenanthrene, stilbene, and biphenyl.

The test is positive for any neutral compound that contains an aromatic nucleus. The differentiation of hydrocarbons from other neutral molecules depends upon the ferrox test. Those aryl and diaryl ethers which give a negative or faint ferrox test will give a positive test for the aromatic nucleus; hence, they might be identified as aromatic hydrocarbons. Saturated aliphatic hydrocarbons give negative tests for unsaturation as well as for the presence of the aromatic nucleus.

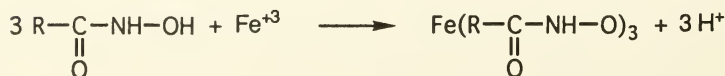
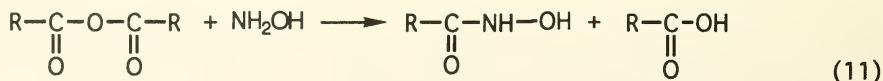
**Exploration 9. Test for Compounds in the Acidic Group: Phenols, Acid Anhydrides, and Carboxylic Acids.** *Phenols* can be identified using ceric nitrate reagent (Equation 10) and THF as described in Exploration 4. The presence of a phenolic



hydroxyl group is indicated by the appearance of an intense red color throughout the solution. Those phenols that are listed in Exploration 4 gave a positive test.

Many phenols in ethanolic solution become intensely colored when a drop of 5% ferric chloride solution is introduced. The color may range from brown to orange, through green to blue or violet. Wesp and Brode (1934) report that 11 of 60 phenols did not give a positive ferric chloride test. In a later study, Soloway and Wilen (1952) observed that 38 of 86 phenols gave a negative ferric chloride test. They suggest that the procedure employ chloroform as the solvent for the phenol and the ferric chloride and that a drop of pyridine be added to the system. Only 11 of the 86 phenols gave a negative test with this modified procedure. The only phenol that is listed in Exploration 4 that does not give a positive ferric chloride test is 2-naphthol.

*Acid anhydrides* react with hydroxylamine when heated in acid medium to form a hydroxamic acid, which reacts with ferric chloride solution to form the colored complex (Equation 11; see Exploration 7). Those acid anhydrides that



are listed in Exploration 7 reacted positively. Carboxylic acids do not interfere, while phenols do, as has been noted previously.



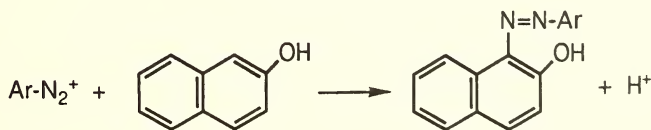
*Carboxylic acids* are recognizable using the procedure of Feigl and Anger (1966). An ethanolic solution of the acid liberates iodine when mixed with a mixture formed from 2% potassium iodide solution and 4% potassium iodate solution (Equation 12). The iodine is characterized by the formation of a blue



complex with a 0.1% starch solution. The acids that gave a positive test are formic acid, acetic acid, propionic acid, n-butyric acid, i-caproic acid, diphenylacetic acid, benzoic acid, 3,5-dinitrobenzoic acid, o-nitrobenzoic acid, phthalic acid, p-hydroxybenzoic acid, succinic acid, o-chlorobenzoic acid, 2-furoic acid, salicylic acid, and oxalic acid. Because acid anhydrides hydrolyze in aqueous solution, they also give a positive test.

**Exploration 10. Test for Compounds in the Basic Group: Primary Alkyl and Aryl Amines, Secondary Amines, and Tertiary Amines.** *Primary alkyl amines* are distinguishable using the Rimini test as described in Cheronis and Entrikin (1963). A very dilute solution of the primary aliphatic amine in acetaldehyde-free acetone reacts within 2 minutes with 1% sodium nitroprusside reagent to form a red-violet solution. The test is specific for primary aliphatic amines; primary aromatic amines, secondary aliphatic and aromatic amines, and tertiary amines do not interfere. The amines that gave a positive Rimini test are 2-phenylethylamine, dl 1-phenylethylamine, ethylenediamine, n-butylamine, isobutylamine, n-propylamine, benzylamine, dl alpha-methylbenzylamine, 1,6-hexanediamine, cyclohexylamine, isopropylamine, 3-amino-1-propanol, and diethylenetriamine.

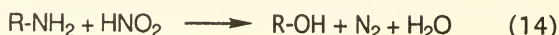
*Primary aromatic amines* can be uniquely detected by initially forming a solution of the diazonium salt of the amine and then coupling the salt with 2-naphthol (Equation 13). The procedure is found in the text by Owen (1969).



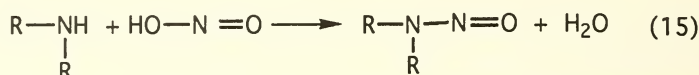
The amine is dissolved in 1.2 M hydrochloric acid solution, cooled in an ice bath, and then 1% sodium nitrite solution is added to the cold amine hydrochloride solution. This cold solution is then added to a solution of 2-naphthol dissolved in 2.4 M sodium hydroxide solution. The formation of an orange to red precipitate of an arylazonaphthol indicates a primary aromatic amine. Those primary aromatic amines that gave an insoluble condensation product with 2-naphthol are aniline, m-toluidine, p-chloroaniline, m-chloroaniline, 2,5-dichloroaniline, m-nitroaniline, 2,5-dimethylaniline, o-aminobiphenyl, 2-ethylaniline, and ethyl p-aminobenzoate.



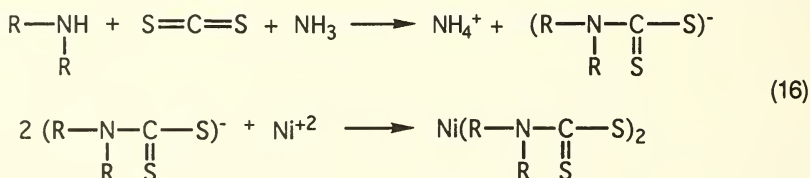
Primary aliphatic amines do react with nitrous acid, liberating nitrogen gas (Equation 14).



Secondary amines also react with nitrous acid to produce an N-nitrosamine which separates from solution as an oil or a solid (Equation 15). Under these reaction conditions, tertiary amines simply protonate forming the tertiary amine cation,  $\text{R}_3\text{NH}^+$ .



*Secondary amines* react with an ammoniacal solution of 0.5% nickel chloride that is saturated with carbon disulfide to form an insoluble, nickel (N,N-disubstituted)dithiocarbamate salt (Equation 16). Duke (1945) discusses the procedure and the reaction parameters.



Secondary alkyl amines form a yellow to green colored precipitate, and secondary aromatic amines form a white to tan precipitate. The secondary amines that gave a test with the nickel chloride-carbon disulfide reagent are dicyclohexylamine, diethylamine, dibutylamine, N-(2-ethylhexyl)cyclohexylamine, N-benzyl-o-toluidine, N-butylaniline, N-propylaniline, N-methylaniline, N-methyl-p-toluidine, and N-methyl-o-toluidine. Primary and tertiary amines do not interfere; however, diethylenetriamine, a mixed primary and secondary amine, only gave a positive Rimini test and failed the nickel chloride-carbon disulfide reagent test.

*Tertiary amines* are identifiable using the procedure in Feigl and Anger (1966). A tertiary amine, when heated at 100° C in a 2% solution of citric acid in acetic anhydride, forms a red to purple colored solution within two minutes. Because the citric acid-acetic anhydride solution decomposes on standing, a fresh solution must be mixed prior to testing for a tertiary amine. Those tertiary amines that gave a positive test with citric acid-acetic anhydride are N,N-diethylaniline, tri-n-butylamine, N,N-diethylaminoethanol, tribenzylamine, 2-aminopyridine, N,N-dimethylbenzylamine, and 5-methyl-2-aminopyridine. Rather than forming a blue complex with the citric acid-acetic anhydride solution, primary and secondary amines form amides under these reaction conditions. An interesting observation was that 2-aminopyridine and 5-methyl-2-aminopyridine gave a positive citric acid-acetic anhydride test, a negative Rimini test, and liberated nitrogen gas in an acidified nitrite solution.



Table 3. A listing of organic functional group-type compounds.

Primary Alcohols	Secondary Alcohols	Tertiary Alcohols
1-butanol	2-butanol	2-methyl-2-propanol
1-hexanol	cyclohexanol	2-methyl-2-butanol
2-methyl-1-propanol	2-propanol	3-methyl-3-pentanol
Aldehydes	Amides	Primary Aliphatic Amines
butanal	acetamide	benzylamine
4-chlorobenzaldehyde	acetanilide	cyclohexylamine
pentanal	N-methylacetamide	butylamine
Primary Aromatic Amines	Secondary Amines	Tertiary Amines
2,5-dichloroaniline	dibutylamine	tributylamine
ethyl 4-aminobenzoate	diphenylamine	tribenzylamine
4-nitroaniline	N-phenylbenzylamine	N,N-dimethylbenzylamine
Anhydrides	Carboxylic Acids	Esters
propionic anhydride	benzoic acid	propyl acetate
acetic anhydride	acetic acid	phenyl benzoate
phthalic anhydride	propionic acid	butyl benzoate
Ethers	Saturated Hydrocarbons	Unsaturated Hydrocarbons
tetrahydrofuran	cyclohexane	cyclohexene
isopropyl ether	pentane	cyclopentene
butyl ether	hexane	1-hexene
Aromatic Hydrocarbons	Ketones	Phenols
benzene	2-butanone	phenol
naphthalene	acetophenone	p-cresol
biphenyl	cyclohexanone	4-nitrophenol

## CONCLUSION

The culmination of this exercise is for the student to classify unknown organic compounds according to their functional group type. Performing the ten Exploration Activities on an unknown will allow a student to determine the identity of the functional group that is present. However, such an approach is quite inefficient. The teacher can profitably require each student to formally outline an experimental procedure before the unknown is issued. As an aid for the preparation of the outline, the instructor should pose a set of questions. These can be specifically designed to stimulate student inspection of the Exploration Activities in order to generate an effective chemical approach to solve a particular problem.



An effective, pedagogical tool to encourage cooperative learning is to have each student formally present his/her experimental observations and to justify his/her conclusion to the class. Class members can then critique the procedure, question the conclusion, and suggest alternate tests that might prove more definitive. After presenting the class report and hearing the ensuing critique, each student can use an additional laboratory period for further experimental study of the unknown compound before turning in the final report to the teacher.

A final observation is that your supply of organic chemicals may preclude doing the experiment in its entirety. However, the organization of the test procedures into separate Exploration Activities permits an easy adaptation to include analysis for a smaller number of functional groups. It is essential to have those chemicals that are required to do the Exploration Activities, the organic functional group test compounds, and a set of unknown compounds. Table 3 provides a listing of organic compounds suitable for this experiment. The amounts of substances that are required are approximately 100 g of a solid and 100 mL of a liquid. The list is only suggestive; any compound that is representative of a particular functional group can be used.

### LITERATURE CITED

- Bordwell, F.G. and K.M. Wellman. 1962. A rapid test to distinguish tertiary from primary or secondary alcohols. *J. Chem. Ed.* 39: 308-310.
- Buckles, R.E. and C.J. Thelen. 1950. Qualitative determination of carboxylic esters. *Anal. Chem.* 22: 676-678.
- Cheronis, N.D. 1958. *Semimicro experimental organic chemistry: A laboratory manual.* John de Graff, Inc., New York, 400 pp.
- and J.B. Entrikin. 1963. *Identification of organic compounds: A student's text using semimicro techniques.* Interscience Publ., New York, 477 pp.
- Davidson, D. 1940. A qualitative test for oxygen in organic compounds. *Ind. Eng. Chem., Anal. Ed.*, 12: 40-41.
- . 1940. Hydroxamic acids in qualitative organic analysis. *J. Chem. Ed.* 17: 81-84.
- Duke, F.R. 1945. Metallo-organic complexes in organic analysis. *Ind. Eng. Chem., Anal. Ed.*, 17: 196.
- and G.F. Smith. 1940. Rapid qualitative test for alcoholic group. *Ind. Eng. Chem., Anal. Ed.*, 12: 201-203.
- Feigl, F. and V. Anger. 1966. *Spot tests for organic analysis*, 7th edition. Elsevier Publ. Co., Amsterdam, 772 pp. (translated by R.E. Oesper).
- Griswold, J.R. and R.A. Rauner. 1991. A brief freshman experience in qualitative organic analysis. *J. Chem. Ed.* 68: 418-420.
- Morrison, J.D. 1965. Qualitative tests for ketones, aromatic aldehydes, and aliphatic aldehydes. *J. Chem. Ed.* 42: 551.
- Owen, T.C., Jr. 1969. *Characterization of organic compounds by chemical methods.* Marcel Decker, Inc., New York, 247 pp.
- Shriner, R.L., R.G. Fuson, D.Y. Curtin, and T.C. Morrill. 1980. *The systematic identification of organic compounds*, 6th edition. John Wiley & Sons, Inc., New York, 604 pp.
- Silvert, D.J. 1987. A problem involving organic qualitative analysis. *J. Chem. Ed.* 64: 971-972.
- Soloway, S. and S.H. Wilen. 1952. Improved ferric chloride test for phenols. *Anal. Chem.* 24: 679-683.
- Swinehart, J. 1964. The decolorization of Baeyer's reagent by primary and secondary alcohols. *J. Chem. Ed.* 41: 392-393.
- Wesp, E.F. and W.R. Brode. 1943. The absorption spectra of ferric compounds, I. The ferric chloride-phenol reaction. *J. Amer. Chem. Soc.* 56: 1037-1042.