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## Analysis of Explosives and Explosive Residues. Part 1: Chemical Tests

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Since the amount of physical evidence associated with a bombing is usually vast, the examination of these samples necessitates the use of quick, reliable screening tests to isolate the few productive evidence samples that may be present.

Over the past few years, this laboratory has been using spot tests for this screening process. Many of these tests have been developed by the Bureau of Alcohol, Tobacco and Firearms (ATF) laboratories in Washington, D.C. and Cincinnati, Ohio. Many of the color tests were originally presented in the literature as quantitative tests. These have been modified and generally found satisfactory for use as quick, qualitative spot tests. The modifications do not appear to have affected the selectivity of the tests.

In this paper the results of various tests on a select number of ions and organic compounds found in explosives and explosive residues are presented. In a subsequent paper [1], thin-layer chromatographic (TLC) methods used for the confirmation of spot tests will be given. Pristera et al [2] present the infrared (IR) spectra for a number of explosives. IR is a good confirmatory tool if a sufficiently pure sample is obtainable.

The physical and microscopic examination of bomb residues has been explained by Washington and Midkiff [3] and Hoffman and Byall [4]. Washington and Midkiff have also discussed the use of vapor trace analysis in screening for dynamite residue [5]. Any unexploded explosive particles found by physical examination can be tested by the methods given here.

### **Extraction Procedure**

If microscopic and physical examination of the samples discloses no noticeable particles of explosive material, the sample may be extracted and filtered if necessary. Pristera et al [2] present an extraction procedure for explosives. In this laboratory a somewhat different procedure is used and has been found to be relatively easy.

An initial extraction is done with acetone. This has a dual advantage, in that it extracts sufficient inorganic ions and explosive organic compounds to perform the spot tests and to use in TLC and IR. (Of the organic compounds used in this study, nitroglycerin, ethyleneglycol dinitrate cyclotrimethylenetrinitramine (RDX), pentaerythryl tetranitrate (PETN), tetryl, and the nitrotoluenes are all soluble in acetone to sufficient degree to give good tests. The least soluble is RDX, where 1 g dissolves in approximately 25 ml of acetone. While nitrocellulose and nitrostarch are not truly soluble in acetone, they are completely

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dispersed in it to form colloidal "solutions." The acetone solution is then filtered if necessary. This extract is allowed to evaporate to dryness *without heating* in a hood. Some explosives, for example, nitroglycerin, are extremely temperature sensitive and may decompose upon excessive heating. The residue may be scraped from the evaporating dish and spot tests run on the solid or, as is often more convenient, it may be taken up in a small amount of acetone. For spot tests, one to two drops of this solution are placed on a spot plate and allowed to evaporate to dryness. The test reagent is added and the results noted.

If necessary, a water extraction is performed to obtain possibly stronger tests for the inorganic ions. The extractant is filtered, if necessary, and evaporated down to less than one millilitre. One to two drops of this solution are placed on a spot plate and the test reagent added.

Unfortunately, the acetone extraction also carries with it extraneous material, which may interfere with the spot tests. This is particularly true for those reagents in a concentrated sulfuric acid solution. The acid tends to char organic materials present, thereby obscuring the tests. In these instances, a methanol or ether extraction or both may be performed instead of the acetone extraction. Alternatively, the dried acetone extract may be taken up in methanol or ether rather than acetone. This presents fewer interferences or less masking of the spot test. However, it has the disadvantage that many explosives are less soluble in methanol and ether than in acetone.

### Substances Tested

The following is a list of the ions and compounds encountered in this laboratory during explosive residue analysis and used in this study. Not all the substances listed are used in explosives but they may be found in explosive residues as contaminants from various sources. These substances are included to show the effects, if any, they may have on the reagent spot tests.

#### *Ions and Compounds*

*Aluminum*—Present in powdered elemental form as a constituent of flash powder and present in small amounts in a few dynamites.

*Ammonium Ion*—In most dynamites as ammonium nitrate. May also appear as a contaminant arising from ammonia-based fertilizers.

*Bromide Ion*—Not usually present in explosives but included here as a possible contaminant of explosive residue.

*Carbonate Ion*—A minor constituent of some explosives but quite often a contaminant of explosive residues, for example, in rocks, soils, and plasters.

*Chlorate Ion*—A constituent of some flash powders.

*Chloride Ion*—A constituent of permissible dynamites as sodium chloride. May also be a contaminant in the form of NaCl or CaCl<sub>2</sub>, especially during winter months when the salts are used for ice melting.

*Cyclotrimethylenetrinitramine (cyclonite, RDX)*—A constituent of military explosive C-4. Of the military explosives, this one is most commonly encountered by our laboratory.

*2,4-Dinitrotoluene (2,4-DNT)*—Used as a coating on many smokeless powders.

*2,6-Dinitrotoluene (2,6-DNT)*—Not normally present in explosives but included here to compare with 2,4-DNT.

*Ethyleneglycol Dinitrate (EGDN)*—Generally a constituent of dynamites which contain nitroglycerin.

*Iodine Ion*—Not normally present in explosives but included here as a possible contaminant of explosive residue.

*Nitrate Ion*—A constituent of most dynamites as ammonium nitrate or sodium/potassium nitrate or both, of black powder as potassium nitrate, and of a few flash powders. May also appear as a contaminant arising from nitrate-based fertilizers.

*Nitrite Ion*—Not normally present in explosives but sometimes a contaminant of explosive residue.

*Nitrocellulose (NC)*—A constituent of smokeless powder and some dynamites.

*Nitroglycerin (NG)*—A constituent of most dynamites along with EGDN and of double-base smokeless powder.

*Nitrostarch (NS)*—A constituent of water-resistant dynamites, confirmed microscopically.

*Perchlorate Ion*—A constituent of most flash powders.

*Pentaerythryl Tetranitrate (PETN)*—A constituent of detonating cord and explosive primers.

*Potassium Ion*—Present in most flash powders as potassium perchlorate, in most black powders as potassium nitrates, and in small amounts in various formulations in some dynamites.

*Sodium Ion*—Present in many dynamites as the nitrate, chloride, or carbonate. Respective sodium salts may sometimes be used in place of the potassium salts in flash powder and black powder. May also be present as a contaminant from many possible sources.

*Sulfate Ion*—Not normally present in explosives but may be present in explosive residues as a product of sulfur combustion.

*Sulfur*—A constituent of flash powder, black powder, and some dynamites.

*2,4,6-Trinitrophenylmethylnitramine (Tetryl)*—A military explosive not normally encountered in civilian cases.

*2,4,6-Trinitrotoluene (TNT)*—A military explosive not normally encountered in civilian cases.

## Tests and Reagents

Listed below are various test reagents and procedures used in this laboratory for analysis of explosives and explosive residues. Unless otherwise specified, all chemicals used are of reagent-grade quality. Specimen size is dependent upon the condition of the sample. For pure compounds, the amount may be less than one half the size of a pinhead.

The tests listed below were compiled from nine primary references [6-14]. These references offer suggestions for overcoming most interferences which may exist in explosive residue samples. Not all the interferences cited in the literature are listed here, since many of them are from exotic substances or uncommon ions not normally present in significant amounts in explosives or explosive residues. We have found no interferences other than the ones given here and in the references. Results of the tests given in Table 1 may be used as a reference for interferences occurring from the more common substances found in explosives and explosive residue.

In general, differences exist between the reagents and procedures given here and among those in the references. However, in most cases the exact composition of test reagents and precise performance of tests as written are not critical to a conclusive outcome of these tests for qualitative analysis.

Unless otherwise specified, the procedure for each test consists of adding one drop of reagent to the sample in a white spot plate. If two reagents are needed for the test, one drop of each is used. Color development is observed and compared with knowns and the results given in Table 1. If a black spot plate is specified, then the type and color of precipitate is noted.

TABLE 1—Spot test results.

Substance Tested	Reagent											
	Aniline Sulfate	Barium Chloride	Brucine	Cupric Tetrapyrindine	Diphenylamine	Griess	J-Acid	Nessler	Nitron	Methylene Blue	Silver Nitrate	Sulfuric Acid
Bromide	yellow to yellow-orange	NR	yellow to orange	NR	yellow <sup>a</sup> NR <sup>b</sup>	NR	dirty orange <sup>a</sup> NR <sup>b</sup>	NCD	NR	light purple <sup>a</sup> NR <sup>b</sup>	creamy white precipitate	yellow to orange-NCD
Carbonate	NCD	white precipitate	NCD	NCD	NCD	NCD	NCD	NCD	NR	NCD	creamy white precipitate	NCD
Chlorate	yellow to orange	NR	orange to red	NR	blue to blue-black	NCD	orange-brown	NR	dirty white precipitate	NR	NR	yellow
Chloride	NCD	NR	NR	NR	NR	NR	NCD	NR	NR	NR	white	NCD
Iodide	brown to purple to black	NR	brown to purple to black	brown precipitate	purple	NR	brown to purple	NR	dirty white precipitate	purple	precipitate yellow	brown to purple to black
Nitrate	light yellow to yellow	NR	orange to yellow	NR	blue to blue-black	pink to red	orange-brown	NR	white	NR	NR	NR
Nitrite	NR <sup>a</sup> yellow <sup>b</sup>	NR	orange to red	green	blue-black	red to yellow	NR <sup>a</sup> brown- orange <sup>b</sup>	NR	dirty white precipitate	NR	white precipitate	NR
Nitrocellulose	NR	NR	orange to red	NR	blue-black	pink	orange-brown	NR	NR	NR	NR	NR
Nitroglycerin	NR	NR	orange to red	NR	blue to blue-black	pink to red	orange-brown	NR	light, dirty white	NR	NR	NR
Nitrostarch	NR	NR	orange to red	NR	blue-black	pink	orange-brown	NR	precipitate	NR	NR	NR
Perchlorate	NR	NR	NR	purple crystalline precipitate	NR	NR	NR	NR	white precipitate turns gray-white	purple precipitate	NR	NR
PETN	NR	NR	orange to red	NR	blue	pink to red	orange-brown to red	NR	NR	NR	NR	NR
RDX	NR	NR	orange to red	NR	NR	pink to red	orange-brown	NR	NR	NR	NR	NR
Sulfate	NR	white precipitate	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
Tetryl	NR	NR	orange-red	NR	blue	pink to red	yellow to orange-brown	NR	NR	orange to red	NR	NR
TNT; 2,4-DNT; 2,6-DNT;	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR

NR = no reaction  
NCD = no color development

<sup>a</sup> Solid.

<sup>b</sup> Aqueous.

*Aniline Sulfate Reagent*

Dissolve 0.1 g aniline sulfate (Eastman Organic Chemicals) in 100 ml concentrated sulfuric acid.

*Barium Chloride Reagent*

Dissolve 5 g barium chloride in 100 ml distilled water.

*Brucine Reagent*

Dissolve 5 g brucine sulfate (NF grade, Union Carbide) in 100 ml concentrated sulfuric acid.

*Cupric Tetrapyrindine Reagent*

Dissolve about 5 g cupric nitrate trihydrate in 40 ml distilled water. Add 80 ml pyridine. After adding one drop of reagent to sample in a white spot plate, let stand for a minute or two. Note any crystalline precipitate formed.

*Diphenylamine Reagent*

Dissolve 1 g diphenylamine in 100 ml concentrated sulfuric acid.

*Griess Reagent*

*Solution 1*—Dissolve 1 g sulfanilic acid in 100 ml 30% acetic acid.

*Solution 2*—Dissolve 1 g  $\alpha$ -naphthylamine (Eastman Kodak Co.) in 230 ml boiling distilled water. Cool. Decant the colorless supernatant liquid and mix with 100 ml glacial acetic acid. Store excess reagent in refrigerator. Do not keep over two months.

The appearance of a pink to red color indicates the presence of weak inorganic nitrites. The appearance of a red color fading immediately into a yellow color indicates the presence of strong inorganic nitrites. If no color develops immediately, add a few milligrams of zinc dust. The rapid development of a pink to red color indicates the presence of inorganic nitrates or some organic nitro compounds (see Table 1). The mixed reagents will turn pink upon setting and drying out, especially as Solution 2 ages.

*J-Acid Reagent*

Dissolve 1 g 6-amino-1-naphthol-3-sulfonic acid (technical grade, Eastman Kodak Co.) in 100 ml concentrated sulfuric acid.

*Nessler Reagent*

Stir 10 g mercuric iodide into a thin paste with a little distilled water. Add 5 g potassium iodide. Solution ensues. Dissolve 20 g sodium hydroxide in 80 ml distilled water. Add to above solution and bring to 100 ml. Let the solution stand for several days. Decant and store the supernatant liquid in a brown bottle. An orange to orange-brown to brown color indicates the presence of ammonium ion or an amine group.

Many organic solvents, including acetone, methanol, and ethanol, interfere with and may completely obliterate the Nessler test for the ammonium ion. Therefore, all organic solvents should be completely evaporated before this test is performed.

*Nitron Reagent*

Dissolve 1 g nitron reagent (Eastman Kodak Co.) in 20 ml of 88% formic acid. Use a black spot plate.

"Nitron is used to precipitate nitrate, perchlorate, perrhenate, fluoborate, and tungstate ions. Other ions which may yield precipitates are bromide, chlorate, chromate iodide,

nitrite, and thiocyanate [15].” However, if no other interfering ions are present, one can learn to distinguish the nitrate precipitate from that of other anions.

#### *Methylene Blue Reagent*

*Solution 1*—Mix 0.1 ml of 1.6% aqueous solution methylene blue (USP) with 25 ml 50% aqueous solution zinc sulfate.

*Solution 2*—Dissolve 40 g potassium nitrate in 100 ml distilled water.

Aluminum metal may obscure the test but can be removed by extracting the sample with water and filtering off the aluminum. For best results the resultant filtrate should be evaporated to dryness and the test run on the solid.

#### *Potassium Test Paper*

Potassium test paper is manufactured by Macherey, Nagel & Co., Duren, West Germany and distributed by Gallard-Schlesinger Chemical Manufacturing Corp., Carle Place, N.Y.

*Procedure*—Apply one drop of the neutral solution to be tested to the paper. Apply one or two drops of dilute nitric acid (1:10) to the same spot. The paper turns yellow, whereas the spot with the solution containing potassium remains orange. Check the manufacturer's instructions for possible interferences.

#### *Silver Nitrate Reagent*

Dissolve 5 g silver nitrate in 100 ml distilled water. Use a black spot plate.

#### *Sodium Test Reagent*

*Solution A*—Dissolve 10 g uranyl acetate in 50 ml distilled water.

*Solution B*—Stir 30 g zinc acetate with 3 g 30% acetic acid. Dilute to 50 ml with distilled water.

Warm Solutions A and B. Mix them while warm. This must result in a clear solution. Add a trace of sodium chloride, stopper, and let stand for 24 h. Filter off the precipitated sodium zinc uranyl acetate and discard. Store the filtrate in a glass stoppered bottle. This reagent keeps indefinitely.

*Procedure*—Add one or two drops of reagent to sample in a white spot plate. Place spot plate under an ultraviolet (UV) light. Long wavelength UV gives better sensitivity than the short wavelength. We generally use both simultaneously. A bright fluorescence indicates the presence of sodium. A very concentrated potassium solution may also fluoresce, but more weakly. If potassium is present, sodium may be confirmed by atomic absorption (AA) or flame emission.

#### *Sulfur Test*

Use a very small fragment (approximately one quarter to one half the size of a pinhead) of the suspected sulfur in a small test tube. Add approximately 1 ml pyridine. Gently warm the tube. Remove heat and add a couple drops of 2*N* NaOH. Depending upon the concentration of sulfur, a blue to red-brown color is developed in the pyridine layer.

If the sample must be extracted, carbon disulfide may be used. *Completely* evaporate the carbon disulfide over gentle heat (for example, a steam bath) and take up the remaining residue in pyridine. If there are any traces of carbon disulfide remaining a false positive may result. Traces of aluminum metal interfere and inhibit color formation. Thus, explosives like flash powder must be extracted first before the test for sulfur is made.

#### *Sulfuric Acid Reagent*

Add one drop concentrated sulfuric acid to sample in a white spot plate (use caution!).

## Results and Discussion

Table 1 lists, in alphabetical order, the anions and compounds on which various tests were performed. In the table, NR indicates that no reaction occurred, whereas NCD indicates that no color developed but that a nonspecific reaction occurred, generally the evolution of some gas.

A good confirmatory test for nitroglycerin, PETN, RDX, tetryl, and TNT is by TLC [1]. However, they are included here because of the quick screening process which may be done with the spot tests. For example, if no positive Griess test is obtained, then no nitrites, nitrates, or nitro-containing organic compounds are present, with the possible exception of the nitrotoluenes (TNT; 2,4-DNT; 2,6-DNT).

EGDN is present in dynamites containing nitroglycerin. However, since we did not possess a sufficiently pure compound, it is not included in the table. Because of its similarity to nitroglycerin, we would expect comparable spot tests. As with nitroglycerin, EGDN may be confirmed by TLC [1].

In our laboratory we prefer to use the Griess test almost exclusively for screening explosives and explosive residues since it is highly sensitive to nitrates and to most nitro-containing organic explosives encountered. Also, it does not admit to the interferences found with the other tests, such as nitron, diphenylamine, brucine, and J-acid.

If sufficient quantity is available and confirmatory tests are needed for the inorganic ions, then IR spectra are run, usually KBr disks. As the tests for chlorates and perchlorates are rather insensitive and indecisive, IR is the general method of choice for these anions.

The one spot test we have used for aluminum [16] has not proved very satisfactory. Aluminum is best confirmed by dissolving the sample in concentrated HCl and using atomic absorption.

## Conclusion

The tests presented here are good for screening explosives and explosive residues. For some anions they are considered confirmatory and no further analyses are made. For other anions IR is used for confirmation. For the organic compounds either TLC or IR is used to confirm their presence.

Caution should be used in the interpretation of the significance of positive tests for ammonium nitrate. Since this is the primary constituent of fertilizer, it quite often will be found in soil samples and other evidence which has come in contact with dirt (for example, car floor mats and doormats). In this laboratory the presence of ammonium nitrate in a sample, unless accompanied by evidence of other explosive compounds or if it would not normally be present in that particular type of sample, is treated as inconclusive evidence of an explosive being present.

The tests found to be most useful are the Griess test for nitrates, the Nessler test for ammonium, silver nitrate for chloride, barium chloride for sulfate, the sulfur test, the potassium test papers, and zinc uranyl acetate for sodium.

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