Explosive Residue Analysis

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1 INTRODUCTION

The analysis of residues of explosives involves multiple techniques to identify inorganic and organic materials. Every explosive has unique properties; therefore, different detection methods are employed to identify the various materials encountered in the forensic examination of explosives and their residues.

The procedures for testing for residues of organic explosives will detect many common high explosives. Techniques such as GC/ECD, GC/MS, and LC/MS allow for the detection of materials such as organic peroxides, nitrate esters, nitroaliphatics, nitramines, nitroaromatics, and smokeless powder components. Alternatively, XRD, SEM/EDS, and IC are techniques used to detect the components and reaction products of many inorganic explosives, such as black powder, Pyrodex, pyrotechnic mixtures, dynamites, and ammonium nitrate-based explosives.

2 SCOPE

This procedure describes the general process for the analysis of residues related to explosives and applies to caseworking personnel conducting work in explosives chemistry analysis. It is suitable for residue samples (items with nonvisible amounts of explosives, precursors, and/or reaction products) and samples with an insufficient amount of intact material to conduct a bulk examination. This procedure may also be used to test for residues of propellants used in ammunition.

Evidence suspected of containing residues from both ignitable liquids and explosives may be analyzed by the Fire Debris and Ignitable Liquid Analysis procedure prior to explosives analysis by personnel qualified and authorized in that subdiscipline.

3 EQUIPMENT

Equivalent equipment, materials, and reagents may be substituted as needed.

3.1 Equipment

- SEM stubs or carbon planchets with liquid adhesive (e.g., Duro-tak), carbon adhesive tabs, or aluminum or copper tape
- Solid phase microextraction (SPME) fibers
- XRD sample holders (zero background holder with or without depression)
- General laboratory supplies

3.2 Instruments

- Fourier transform infrared (FTIR) spectrometer with attenuated total reflectance (ATR) or microscope attachment
- Gas chromatograph with electron capture detector (GC/ECD)
- Gas chromatograph with mass spectrometer (GC/MS) and Headspace (HS) GC/MS
- Ion chromatograph (IC)
- Liquid chromatograph with mass spectrometer (LC/MS)
- Microscope (optical or digital) with optional digital camera

- Raman spectrometer with macro compartment or microscope attachment
- Scanning electron microscope with energy dispersive X-ray spectrometer (SEM/EDS)
- Ultra performance liquid chromatograph with mass spectrometer (UPLC/MS)
- X-ray diffractometer (XRD)

3.3 Chemicals/Reagents

- Acetone (HPLC grade)
- Deionized (DI) water (18.2 MΩ)
- Isopropyl alcohol (70% commercial product)
- Methanol (HPLC grade)
- Nitrogen (high purity)

4 Standards and Controls

Refer to the Explosives Quality Assurance and Operations Manual for details regarding verification of reference materials. Testmix components and preparation instructions are recorded in the applicable instrument performance document(s). Refer to the Instrument Parameters and Reagent Preparation procedure for information regarding other positive controls relevant to this procedure (e.g., Redacted

5 Sampling

Refer to the sampling procedures in the Explosives Quality Assurance and Operations Manual.

6 Procedure

Explosives chemistry personnel will:

- Consult the Examination Plan to determine if exams by other disciplines/subdisciplines will be performed on the items to be tested for residues of explosives. If certain aspects of residue testing (e.g., swabbing, rinsing) may affect subsequent exams, then the steps performed may need to be modified and/or consultation may be necessary with other discipline/subdiscipline personnel.
- Clean work surfaces thoroughly with an isopropyl alcohol solution and/or other appropriate solvent. Cover the clean work surface with a disposable material such as kraft paper. Refer to the Explosives Quality Assurance and Operations Manual for additional details regarding explosives contamination prevention.
- Collect a work surface negative control prior to opening evidence items if it is anticipated that evidence will touch the work surface. Prepare other negative controls as appropriate to be representative of the processes used to analyze evidence (e.g., prepare a solvent negative control by adding solvent to a plastic beaker and then filtering it into an autosampler vial, concentrating using heat and/or nitrogen/filtered air as appropriate).
- Use appropriate personal protective equipment (e.g., safety glasses, laboratory coat, and disposable gloves [cleanroom gloves preferable]) when examining evidence. This is intended to protect the individual conducting the exam and to prevent contamination of evidence.

- For each instrumental technique, refer to the Instrument Parameters and Reagent Preparation procedure for instrument usage procedures, parameters, and reagent preparation information. Prior to evidence analysis, follow the applicable instrument performance document(s) to conduct a performance check.

6.1 Visual and Microscopic Analysis

Perform a visual and/or microscopic examination of the item to look for uninitiated materials or deposits of solid reaction products. Post-blast items and/or fragments of IEDs should be examined under the microscope when of appropriate size. Uninitiated material (such as smokeless powder grains) is often found in pipe threads, on adhesive material, and in crevices.

6.2 Mechanical Removal of Residue

A. If suspected uninitiated material or reaction products are visible and removable on the item, the material may be removed using clean forceps, scalpel, probe, or similar tool. Refer to the Identification of General Unknowns procedure for details on recommended techniques (e.g., FTIR, XRD) and extraction procedures to be used on the removed material. Other technical procedures may also be necessary for identifying uninitiated explosive materials (e.g., smokeless powder, black powder).
B. If uninitiated material or solid reaction products are not found from visual and/or microscopic examination, then removal of residue from surfaces must be conducted by swabbing, vacuuming, or by solvent extraction.
C. Swabbing is performed by rubbing a dry swab (e.g., cotton ball, cotton-tipped applicator) across surfaces of non-porous materials.
D. Vacuum samples may be collected using fiberglass or Teflon filters.
E. The swabs or vacuum filters will be subsequently extracted with solvents (see Section 6.4) for instrumental analysis (e.g., IC, GC/ECD, GC/MS in electron ionization (EI) or chemical ionization (CI) modes, LC/MS, UPLC/MS).

6.3 Headspace Analysis

A. (Optional) Samples may be analyzed on the Headspace GC/MS using a heated headspace needle for volatile compounds. Approximately 0.5 mL sample of the volatiles testmix in an autosampler vial serves as the positive control. A sealed blank autosampler vial serves as a negative control. If necessary, the sample may be heated prior to headspace analysis (temperature and duration at chemist discretion).
B. (Optional) Samples may be analyzed on the Headspace GC/MS using a SPME fiber for residues of volatile peroxide explosives. The Redacted serves as the positive control. A sealed autosampler vial with DI water serves as the blank. If necessary, the evidence may be heated prior to headspace sampling (temperature and duration at chemist discretion). Ambient temperature or gentle heating may be sufficient.

6.4 Solvent Extraction/Removal of Residues

Determine whether the item should be extracted with acetone (for organic explosives/components) and/or with DI water (for water soluble components).

6.4.1 Acetone Extraction

A. Rinse the item (e.g., physical evidence, vacuum filters, swabs, soil samples) with an appropriate amount of acetone to extract organic explosive materials/components. The volume of acetone required depends on the size of the item. For large objects that will not fit in available containers, acetone may be rinsed across surfaces and directed into a container or removed directly from the surface. An equal portion of acetone will be used as a negative control.

B. (Optional) Extracts may be pre-filtered through a cotton ball and/or centrifuged at 3500 rpm for 10 minutes to separate the particulates. A negative control cotton ball should also be prepared using an equal portion of acetone if pre-filtering is utilized.
    1. An example procedure for extracting soil is as follows:
        i. Add approximately 10 g of soil to a plastic beaker and extract with 10 mL of acetone. Agitate to facilitate extraction.
        ii. Place a cotton ball into the acetone-soaked soil to serve as a pre-filter. Use a glass pipette to extract the acetone through the cotton ball and add to a glass test tube. Prepare a negative control cotton ball using an equal portion of acetone. Filter the supernatant and the negative control cotton ball extract according to step 6.4.1.C.
        iii. Alternatively, centrifuge the extract at 3500 rpm for 10 minutes then filter the supernatant according to step 6.4.1.C.

C. Prepare a separate 0.2 µm membrane filter (mounted on a plastic syringe) for each item by flushing with acetone. Filter portions of the negative control or the sample through the filter and into their respective autosampler vials or test tubes. Concentrate negative controls and sample extracts similarly using heat and/or nitrogen/filtered air as appropriate.

D. The negative control and extract will be analyzed using the GC/ECD.

E. When a peak is detected that may correspond to a component in the testmix, the extract will be further analyzed by LC/MS (ESI configuration), GC/MS (EI or CI), or UPLC/MS to confirm the presence or absence of the analyte. UPLC/MS may also be used when GC/ECD results are negative and lower levels of detection are required.
    1. If the GC/ECD results include a large number of small peaks that may interfere with the detection of targeted analytes, the extract may be further analyzed by LC/MS (ESI configuration), or GC/MS (EI or CI). Exercise caution in analyzing complex organic extracts by UPLC/MS due to susceptibility to contamination.
    2. For UPLC/MS analysis, prepare a dilution of the negative control and filtered extract in 50:50 methanol:water and transfer into autosampler vials for analysis by UPLC/MS. A 1:10 dilution is recommended but may be adjusted based on sample concentration and chemist discretion. Be careful not to inject an over concentrated sample into the UPLC/MS.

6.4.2 Water Extraction

A. Rinse and/or soak the item (e.g., physical evidence, vacuum filters, dry swabs, soil samples) with an appropriate (but minimal) amount of DI water to extract water soluble compounds. The volume of water required depends on the size of the item. For large objects that will not fit in available containers, water may be rinsed across surfaces and directed into a container or removed directly from the surface. An equal portion of water (and extraction time) will be used as a negative control.
    1. Plasticware should be used throughout these procedures to avoid leaching of ions from glassware when sodium analysis is relevant.

B. (Optional) Extracts may be pre-filtered through a cotton ball and/or centrifuged at 3500 rpm for 10 minutes to separate the particulates. A negative control cotton ball should also be prepared using an equal portion of DI water if pre-filtering is utilized.
    1. An example procedure for extracting soil is as follows:
        i. Add approximately 10 g of soil to a plastic beaker and extract with 10 mL of DI water. Agitate to facilitate extraction.
        ii. Place a cotton ball into the DI water-soaked soil to serve as a pre-filter. Use a glass pipette to extract the DI water through the cotton ball and add to a glass test tube. Prepare a negative control cotton ball using an equal portion of DI water. Filter the supernatant and the negative control cotton ball extract according to step 6.4.2.C.
        iii. Alternatively, centrifuge the extract at 3500 rpm for 10 minutes then filter the supernatant according to step 6.4.2.C.

C. Prepare a 0.2 µm membrane filter (mounted on a plastic syringe) by flushing with DI water. Filter portions of the negative control or the sample through the filter and into their respective autosampler vials or test tubes.

D. Analyze the extract and negative control using IC (anions).

E. When a peak is detected that may correspond to a component in the testmix, and is deemed of interest compared to requisite comparison samples (e.g., control swab or NC), analyze the extract by a secondary anions IC system to confirm the presence or absence of the anion.
    1. If anions of interest are confirmed, analyze the water extract by a cations IC system. Confirm any cations of interest (compared to the control/comparison samples) by a secondary cations IC system.
    2. Time sensitive cases may necessitate analyzing the extract on multiple IC systems simultaneously.

F. (Optional) Water extracts may be evaporated to dryness using heat and/or nitrogen/filtered air as appropriate, and remove any visible material that remains for additional analysis. Refer to the Identification of General Unknowns procedure for details on recommended techniques (e.g., FTIR, XRD) to be used on the removed material.

G. (Optional) Analyze the water extracts prepared in step 6.4.2.C by LC/MS (APCI configuration) to test for the presence of Redac

7 DECISION CRITERIA

Refer to the Explosives Chemistry Report Writing Guidelines and the Report Wording Examples for Explosives Chemistry Analysis document (level 4) for additional details regarding reporting residues of explosives.

7.1 Instrumental Results

Refer to the Instrument Decision Criteria for Explosives Chemistry Analysis procedure for details regarding the acceptance of data generated using the instruments and methods described above.

8 LIMITATIONS

This procedure can identify most explosive-related residues. However, it may not be possible to identify some obscure, explosive-related compounds.

All chemical instrumentation has a limit of detection. If residues of explosives are present below this level, analysis may be limited.

When an item is tested for residues of explosives, a representative sample is tested (if not the whole item). However, the results of the analysis only pertain to the portion of the item tested.

Certain packaging may limit the ability to analyze for specific explosive-related components.

Certain residues may be undiagnostic without appropriate comparison/control samples. Without these, analysis and identification may be limited.

9 REFERENCES

ASTM E3196-21, Standard Terminology Relating to the Examination of Explosives, ASTM International, West Conshohocken, PA, 2021 (latest revision).

ASTM E3329-21, Standard Practice for Establishing an Examination Scheme for Explosive Residues, ASTM International, West Conshohocken, PA, 2021 (latest revision).

10 REVISION HISTORY

Revision	Issued	Changes
08	09/30/2022	Updated to new document template. Removed specific instrument decision criteria and added reference to new Instrument Decision Criteria procedure. Updated scope. Clarified definitions of residues vs. solid, visible reaction products and added links to bulk procedures. Added ASTM references.