Explosive Residue Analysis

1 Scope

These procedures describe the general process for the analysis of explosive residues. It is suitable for residue samples and samples with an insufficient amount of material to conduct a bulk examination. These procedures apply to caseworking personnel conducting work in explosives chemistry analysis.

2 Introduction

Explosives residue analyses involve several techniques used to identify inorganic and organic compounds. Every explosive has unique properties, and accordingly, different detection methods are employed to identify the various materials encountered in the forensic examination of explosives and their residues.

The procedures for organic explosives will detect many common high explosives. Techniques such as GC/ECD, GC/MS, solids probe MS, and LC/MS analyses allow for the detection of materials Redacted

Alternatively, XRD, SEM/EDS, HPLC, and IC are techniques used to detect the components that make up many Redacted

3 Equipment/Materials/Reagents

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

3.1 Equipment

- Centrifuge
- 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)
- Solids probe mass spectrometer (MS)
- Ultra performance liquid chromatograph with mass spectrometer (UPLC/MS)
- X-ray diffractometer (XRD)

3.2 Materials

- Autosampler vials and caps
- Disposable plastic syringes
- Forceps
- Gloves (cleanroom gloves preferable)
- Kraft paper
- Mortar and pestle
- Probe
- Scalpel
- SEM stubs or carbon planchets with liquid adhesive (e.g., Duro-tak), carbon adhesive tabs, or aluminum or copper tape
- Spatula
- Solid phase microextraction (SPME) fibers
- Swabs (cotton balls or cotton-tipped applicators)
- Syringe filters (0.2 µm nylon)
- Vacuum filters (fiberglass or Teflon)
- Vacuum with filter attachments
- Various disposable glassware and plasticware
- XRD sample holders (zero background holder with or without depression)

3.3 Reagents/Solvents/Reference Materials

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

4 Standards and Controls

All reference materials and reagents will be verified prior to, or in concurrence with, use in casework. Refer to the Verification of Reagents and Solvents Standard Operating Procedure (SOP), the Verification of Reference Materials SOP, and the Records of Items Used As Known Materials SOP. Refer to the Instrument Parameters and Reagent Preparation SOP for

information regarding the components and preparation of all standards and controls referred to in this document.

Redacted

5 Sampling

Refer to the Sampling Procedures in the Explosives Quality Assurance Manual.

6 Procedure

Explosives chemistry personnel will:

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 Contamination Guidelines SOP for additional details.

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.

Review and understand all safety information contained in Section 10 prior to beginning the following procedures.

For each instrumental technique, refer to the Instrument Parameters and Reagent Preparation SOP for Performance Monitoring Protocol (PMP) information, instrument usage procedures, parameters, and reagent preparation information. Prior to evidence analysis, follow the PMP for the instrument to conduct a QA/QC check to verify the instrument's reliability and reproducibility from analysis to analysis.

6.1 Visual and Microscopic Analysis

6.1.1 Perform a visual and/or microscopic examination of the item to detect uninitiated explosives, pyrotechnic or propellant materials, or residues. Post-blast items and/or fragments of IEDs should be examined under the microscope when of appropriate size. Redacted

6.1.2 Look for signs of blast damage and characteristic "smudging" or deposit of products of some initiated energetic materials. Blast damage is a function of energetic material reaction kinetics and can influence the direction of the examination for materials which could possibly cause such damage.

6.2 Mechanical Removal of Residue

6.2.1 If suspected uninitiated material or residues are visible on the item, the material may be removed using clean forceps, scalpel, probe, or similar implement.

The removed material may be analyzed by FTIR, Raman, SEM/EDS, or XRD or the chemist may proceed directly to a particular analytical standard operating procedure.

6.2.2 If uninitiated material or residues 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.

6.2.3 Swabbing is performed by rubbing a dry swab (e.g., cotton ball, cotton-tipped applicator) across surfaces of non-porous materials.

6.2.4 Vacuum samples may be collected using fiberglass or Teflon filters.

6.2.5 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

6.3.1 (Optional) Samples may be analyzed on the Headspace GC/MS using a heated headspace needle for volatile compounds. A 0.5 mL sample of the volatiles testmix in an autosampler vial may serve as a positive control. A sealed blank autosampler vial serves as a negative control. The sample may be heated prior to headspace analysis, based on the individual’s judgment on how much heating is necessary and for how long.

6.3.2 (Optional) Samples may be analyzed on the Headspace GC/MS using a SPME fiber for volatile compounds. Redacted A sealed autosampler vial with deionized water serves as the blank. The evidence may be heated prior to headspace sampling, based on the individual's judgment on how much heating is necessary and for how long. 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 deionized water (for water soluble compounds).

6.4.1 Acetone Extraction

6.4.1.1 Rinse the item (e.g., physical evidence, vacuum filters, dry 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.

6.4.1.2 (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.

6.4.1.3 Prepare a separate 0.2 µm nylon 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.

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

6.4.1.5 When a peak is detected within the decision criteria window when compared 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 material. UPLC/MS may also be used when GC/ECD results are negative if lower levels of detection are required.

6.4.1.6 For UPLC/MS analysis, prepare a new acetone extract or use the filtered extract from step 6.4.1.3.

6.4.1.6.1 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 discretion of the individual conducting the exam. Be careful not to inject an over concentrated sample into the UPLC/MS.

6.4.1.6.2 An example procedure for conducting soil extracts are as follows.

- Add approximately 10 g of soil to a plastic beaker and extract with 10 mL of acetone. Agitate to facilitate extraction.
- 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. A negative control cotton ball should also be prepared using an equal portion of acetone.
- Centrifuge the extract at 3500 rpm for 10 minutes.
- Prepare a 0.2 µm nylon filter (mounted on a plastic syringe) by flushing with acetone.
- Transfer the centrifuged supernatant into the syringe and filter portions of the negative controls and the sample through the filter into new glass test tubes.
- Dilute the filtered extract 1:10 in 50:50 methanol:water and transfer into autosampler vials for analysis by UPLC/MS.

6.4.2 Water Extraction

6.4.2.1 Rinse the item (e.g., physical evidence, vacuum filters, dry swabs, soil samples) with an appropriate amount of deionized 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 will be used as a negative control.

Plasticware should be used throughout these procedures to avoid leaching of ions from glassware when sodium analysis is relevant.

6.4.2.2 Prepare a 0.2 µm nylon filter (mounted on a plastic syringe) by flushing with deionized water. 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.

6.4.2.3 The extract and negative control will be analyzed using IC.

6.4.2.4 When a peak is detected within the decision criteria window when compared to a component in the testmix, the extract will be further analyzed by a secondary IC system, SEM/EDS, or XRD to confirm the presence or absence of the material.

6.4.2.5 (Optional) Water extracts may be evaporated to dryness using heat and/or nitrogen/filtered air as appropriate and analyzed by SEM/EDS or XRD.

6.4.2.5.1 For SEM/EDS analysis, if sample size permits, analyze a portion of the sample (bulk or ground) mounted onto an SEM sample holder to determine its elemental composition.

6.4.2.5.2 For XRD analysis, if sample size permits, grind a portion of the sample to a fine powder, as necessary, with a mortar and pestle and analyze by XRD.

6.4.2.6 (Optional) Analyze the residue by solids probe/MS to determine the presence of benzoate and dicyanodiamide. Submit part of the dried water extract from step 6.4.2.1 for solids probe/MS analysis. Refer to the Black Powder, Black Powder Substitutes, and Pyrotechnics Analysis SOP for further guidance.

6.4.2.7 (Optional) Analyze the water extracts prepared in step 6.4.2.2 by LC/MS (APCI configuration) to determine the presence of Redacted

7 Decision Criteria

7.1 Instrumental Results

The following criteria will be met in order for a qualitative identification to be made. The identity of a material will be confirmed by comparison to a reference or known material, if available. Reference or known materials may be run concurrently with an unknown sample or may be previously analyzed on the instrument under the same parameters. All results should be verified using orthogonal techniques or alternate methods.

When a reference or known material is not available or when only reference data (e.g., from scientific literature, publications, or an instrument library) is used, a material may be reported as "consistent with" a substance.

7.1.1 Chromatography

Peaks should show good chromatographic characteristics, with reasonable peak shape, width, and resolution.

The retention time of the peak of interest should be within ±2% of that for a contemporaneously analyzed reference or known material for gas chromatography and ±5% for liquid chromatography.
The baseline signal-to-noise ratio (SNR) for an analyte should be greater than three to be considered a peak. The signal intensity for an analyte peak should be at least ten times greater than the intensity of any carryover or system peaks which may have been present in analyses just prior to the sample (e.g., blanks or negative controls).

7.1.2 Mass Spectrometry

The mass spectrum of the analyte of interest should compare favorably with that of a contemporaneously analyzed reference or known material.

Characteristic ion plots are reviewed to determine potential presence of a target analyte. The absence of a primary ion indicates a non-detect.

When utilizing high resolution mass spectroscopy, three isotopic masses are required for an identification. If only one or two are present for a specific analyte, it may be reported as "consistent with" a substance.

7.1.3 XRD

The diffraction patterns from the questioned compound should compare favorably to the corresponding reference or known material.

If the unknown material is matched through a library search, a reference or known material may be analyzed for comparison, if available. Tentative identifications may also be confirmed through orthogonal techniques such as FTIR, Raman, SEM/EDS, or GC/MS.

7.1.4 SEM/EDS

Peaks in the EDS spectrum should exhibit a Gaussian peak shape and a minimum SNR of 3:1. The elemental composition of the questioned compound should compare favorably to the corresponding elemental composition of the reference or known material. Elemental assignments made by the software should be verified by the individual conducting the exam.

7.1.5 Other Tests

The results of all tests (e.g., visual inspections, FTIR, Raman, pH) should compare favorably to the corresponding reference or known material.

8 Calculations

Not applicable.

9 Measurement Uncertainty

Not applicable.

10 Limitations

10.1 Redacted

10.2 Redacted

11 Safety

Safety protocols, contained within the FBI Laboratory Safety Manual, will be observed at all times.

Standard precautions will be taken for the handling of all chemicals, reagents, and standards including standard universal precautions for the handling of biological and potentially hazardous materials. Refer to the FBI Laboratory Safety Manual for proper handling and disposal of all chemicals. Personal protective equipment will be used when handling any chemical and when performing any type of analysis.

The handling of some explosive materials is hazardous due to potential ignition by heat, shock, friction, impact, or electrostatic discharge. Personnel should work with small quantities (such as a few grams) and properly store larger quantities in approved containers.

As a safety precaution, it should be noted that dark materials pose a hazard when being analyzed by Raman spectroscopy as they may be initiated by the laser. If this technique will be utilized, then the smallest possible sample amount and reduced laser intensities should be used to minimize the risk and avoid initiation.

12 References

FBI Laboratory Quality Assurance Manual, Federal Bureau of Investigation, Laboratory Division, latest revision.

FBI Laboratory Operations Manual, Federal Bureau of Investigation, Laboratory Division, latest revision.

FBI Laboratory Safety Manual, Federal Bureau of Investigation, Laboratory Division, latest revision.

Explosives Quality Assurance Manual, Federal Bureau of Investigation, Laboratory Division, Explosives, latest revision.

Explosives Standard Operating Procedures: Chemistry, Federal Bureau of Investigation, Laboratory Division, latest revisions.

Instrument Operations Manuals for the specific models and accessories used.

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6	06/15/2020	Updated section 2. Removed section 4.1 and section 4.2. Updated sections 6.1.4.2, 6.3.2, 7.1, 7.1.2, and 11.
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Redacted - Signatures on File

Approval

Explosives Unit Chief Date: 07/14/2020

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