Identification of General Unknowns

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1 INTRODUCTION

Analytical approaches to an unknown sample will vary depending on its physical state, quantity, and chemical properties. In addition, information furnished by the contributor, including specific requests, may aid in directing the appropriate examination methods.

2 SCOPE

This procedure describes the general process for the analysis of unknown materials and are suitable for bulk samples which are not able to be analyzed by another explosives chemistry procedure. These samples may include uninitiated explosives, precursors, and/or solid reaction products that can be physically manipulated. This procedure applies to caseworking personnel conducting work in explosives chemistry analysis.

3 EQUIPMENT

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

3.1 Equipment

- General laboratory supplies

3.2 Instruments

- Gas chromatograph with flame ionization detector (GC/FID)
- Fourier transform infrared (FTIR) spectrometer with attenuated total reflectance (ATR) or microscope attachment
- Gas chromatograph with mass spectrometer (GC/MS)
- Headspace gas chromatograph with mass spectrometer (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)
- X-ray diffractometer (XRD)

3.3 Chemicals/Reagents

- Acetone (reagent grade)
- Deionized water (18.2 MΩ)
- Hexane (reagent grade)
- Isopropyl alcohol (70% commercial product)
- Methanol (HPLC grade)
- Various reference materials, as needed
- Various solvents, as needed

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.

5 SAMPLING

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

6 PROCEDURE

Explosives chemistry personnel will:

- Clean work surfaces thoroughly with an isopropyl alcohol solution 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.
- Use appropriate personal protective equipment (e.g., safety glasses, laboratory coat, disposable gloves) when examining evidence. This is intended to protect personnel conducting the examination 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 Macroscopic/Microscopic Examination

Perform a macroscopic and microscopic examination and note the physical state, homogeneity, color, and consistency of the unknown material. Microscopic photographs of the material and relevant positive controls may be recorded.

When possible, physically separate the material if it contains components of different sizes, colors, shapes, or phases (e.g., solids and liquids).

Note the odor of the unknown if it is readily apparent. Do not intentionally smell any sample submitted for analysis.

6.2 Sensitivity/Reactivity Testing

If sample size permits, an impact sensitivity test may be conducted using a hammer and solid surface such as an anvil. Record results such as sound.

If sample size permits, a thermal sensitivity (flame) test may be conducted. Place a small amount (~50 mg) of material on the tip of a spatula and heat with a lighter, torch, or other heat source. Note results such as ease of initiation, flame sustainability, flame color, smoke, sound, and residue.

When appropriate, reactivity between two chemicals may be determined. Place a small amount of the first chemical into an empty test tube in a fume hood. Add a small amount of

the second chemical into the same test tube. Use minimal material for each, as would be needed to observe anticipated reaction (to include synthesis). Note results such as estimated reaction time, flame sustainability, flame color, smoke, and product formation. Reactivity may be determined between two unknown items or between an unknown and an appropriate positive control.

Energetic synthesis is inherently dangerous and should only be conducted if required. If formed, isolate the synthesis product for analysis and determine its chemical composition.

6.3 Miscibility/Solubility Testing

If there is a sufficient amount of sample, miscibility/solubility tests may be performed on the unknown using both aqueous and nonaqueous solvents. Place a small amount of sample in an appropriate solvent (e.g., deionized water, hexane) and record observations.

6.4 Aqueous Solutions

Determine the pH of aqueous solutions by placing 2-3 drops of the unknown liquid onto pH paper. Other colorimetric tests (e.g., peroxide test strips, water-finding paper) may be used for presumptive testing. Verify the test works as designed using an appropriate positive control (e.g., acid/base, hydrogen peroxide, water).

Samples in an aqueous solution may be analyzed by IC for anions and cations. Obtain a portion of deionized water as a negative control. Flush a 0.2 µm filter mounted on a plastic syringe with at least 3 mL of deionized water. Flush portions of the negative control and the sample extracts through the prepared syringe filters into autosampler vials. An autosampler vial of unfiltered deionized water will be used as a blank. Samples may need to be diluted prior to analysis.

Density testing may be performed on aqueous solutions to estimate concentration. Use a balance to record the mass of an empty test tube. Using a pipette, transfer 1 mL of sample into the test tube. Reweigh the test tube and record the mass of the 1 mL sample. Repeat this process for 1 mL of an appropriate positive control (e.g., acid, hydrogen peroxide) at a known concentration. Record the estimated density of the sample and the positive control(s) in g/mL.

6.5 Instrumental Analysis

A. Physical or chemical separation of components may be indicated based on the visual exam and/or instrumental analysis results. Appropriate solvents may be used to extract and isolate components for analysis. For example, organic explosives may be extracted using acetone. Solvent compatibility and miscibility with other liquids needs to be considered for safety and effectiveness.
B. FTIR or Raman analysis may be used to determine or confirm components of unknown mixtures or general classes of components in mixtures. Components should be compared to entries in reference libraries. Commercial products may also serve as comparisons.
C. Unknown solids and visible material remaining from evaporated liquids may be analyzed by SEM/EDS for elemental components.

D. Crystalline solids of sufficient sample size may be suitable for XRD analysis. If necessary, grind a portion of the sample to a fine powder with a mortar and pestle. Do not grind suspected primary explosives.
E. Samples that are sufficiently volatile may be analyzed by GC/MS in electron ionization (EI) or chemical ionization (CI) modes. Prepare a ~100 ppm solution of the sample in a suitable solvent. Results may be compared to spectra in the National Institute for Standards and Technology (NIST) Library, Wiley Library, and/or to a reference or known material.
F. Samples may be analyzed on the headspace GC/MS using a heated headspace needle for volatile compounds. Approximately 0.5 mL of the headspace GC/MS volatiles testmix in an autosampler vial may serve as a positive control. A few solid grains or liquid dilution of other volatile reference material (e.g. TATP, DADP) in an autosampler vial may also serve as a positive control. A sealed, empty autosampler vial serves as the blank. The evidence may be heated prior to headspace sampling (temperature and duration at chemist discretion). Ambient temperature or gentle heating may be sufficient.
G. For samples suspected of containing hydrocarbon fuels, prepare a hexane extract of the material, a hexane blank, and appropriate controls. Analyze the extracts by GC/FID.
    1. If the results of the FID analysis reveal that the carbon-range distribution falls below ~C25, the extracts may be analyzed via GC/MS in EI mode (FIRE method) for classification of the hydrocarbon present. Refer to the Fire Debris and Ignitable Liquid Analysis procedure for the FIRE method parameters.
H. Samples may be analyzed by LC/MS (ESI or APCI configurations). Prepare a ~100 ppm solution in a suitable solvent. The extract may be diluted to coincide with instrument response. Results may be compared to the spectrum of a reference or known material. This method is especially suitable for samples containing thermally labile organic explosives.
I. If in the course of analysis it is determined that an unknown can be classified among materials analyzed by another explosives procedure, conduct further analysis according to the appropriate document.

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 of uninitiated, unknown materials.

7.1 Instrumental Results

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

7.2 Material Identification

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 will be verified using orthogonal techniques or alternate methods, if available.

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.

8 Measurement Uncertainty

Although infrequent, the mass of a crude material may be requested by the contributor. When requested, refer to the Explosives Quality Assurance and Operations Manual for information regarding measurement uncertainty of these results.

9 Limitations

This procedure does not address the analysis and limitations of explosive residue examinations.

When an item is tested, 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.

The identification of an unknown may be limited because of its complexity and sample size; however, general classification of a substance is usually achievable. Where comparison samples are available, comment should be made regarding the consistency of the unknown with the comparison sample.

Only examiners qualified and authorized in fire debris and ignitable liquid analysis may identify a class of ignitable liquid (e.g., heavy petroleum distillate, gasoline). Examiners not qualified and authorized for this analysis may only report general profile characteristics (e.g., oil, wax, petroleum jelly).

10 Safety

The handling of 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 hundred milligrams) and properly store larger quantities in approved containers.

Dark materials may 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 should be used to minimize the risk. The laser power may also be decreased to avoid initiation.

11 References

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

ASTM E3253-21, Standard Practice for Establishing an Examination Scheme for Intact Explosives, ASTM International, West Conshohocken, PA, 2021 (latest version).

12 REVISION HISTORY

Revision	Issued	Changes
08	09/30/2022	Updated to new document template. Added decision criteria section. Updated limitations. Added ASTM references.