Identification of General Unknowns

1 Scope

These procedures describe 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 analysis procedure. These procedures apply to caseworking personnel conducting work in explosives chemistry analysis.

2 Introduction

Analytical approaches to an unknown substance will vary depending on the physical state and the quantity of the substance. In addition, information furnished by the contributor, as well as specific requests by the contributor, may aid in directing the appropriate examination methods.

3 Equipment/Materials/Reagents

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

3.1 Equipment

- 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)

3.2 Materials

- Autosampler vials and caps
- Hammer
- Kraft paper
- Lighter, torch, or matches

- Test strips (e.g., pH, peroxide, water-finding)
- Various disposable glassware and plasticware

3.3 Reagents/Solvents/Reference Materials

- 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

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 procedure, the Verification of Reference Materials procedure, and the Records of Items Used As Known Materials procedure. Refer to the Instrument Parameters and Reagent Preparation procedure for information regarding the components and preparation of all standards and controls.

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 or other appropriate solvent. Cover the clean work surface with a disposable material such as kraft paper. Refer to the Explosives Contamination Prevention Guidelines for additional details.

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.

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

procedure for instrument usage procedures, parameters, and reagent preparation information. Prior to evidence analysis, follow the Performance Monitoring Protocol (PMP) for the instrument to conduct a QA/QC check to verify the instrument's reliability and reproducibility from analysis to analysis.

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 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 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).

6.5 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 3mL 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.

6.6 Density testing may be performed on aqueous solutions to estimate concentration. Use a balance to record the weight of an empty test tube. Using a pipette, transfer 1 mL of sample into the test tube. Reweigh the test tube and record the weight 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.

6.7 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. Redact

Solvent compatibility and miscibility with other liquids needs to be considered for safety and effectiveness.

6.8 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.

6.9 Unknown solids and residues of evaporated liquids may be analyzed by SEM/EDS for elemental components.

6.10 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.

6.11 Samples that are sufficiently volatile may be analyzed by GC/MS in electron ionization (EI) or chemical ionization (CI) modes. Prepare an approximately 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.

6.12 Samples may be analyzed on the headspace GC/MS using a heated headspace needle for volatile compounds. A 0.5 mL sample of the headspace GC/MS volatiles testmix in an autosampler vial may serve as a positive control. Redact

Redact A sealed, empty autosampler vial 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.

Redact

6.15 Samples may be analyzed by LC/MS (ESI or APCI configurations). Prepare an approximately 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. Redact

6.16 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 Calculations

Not applicable.

8 Measurement Uncertainty

Although infrequent, the mass of a crude material may be requested by the contributor. When requested, refer to the Administrative Structure and Operating Guidelines for information regarding measurement uncertainty of these results.

9 Limitations

Redact

10 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 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

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, latest revision.

Explosives Procedures: Chemistry, Federal Bureau of Investigation, Laboratory Division, latest revision.

Instrument Operations Manuals for the specific models and accessories used.
Budavari, Susan, editor, *Merck Index*, 12th edition, Merck and Co., Inc.: Whitehorse Station, NJ, 1996.

Eckroth, David, editor, *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd edition, Wiley-Interscience: New York, 1984.

Gosselin, Robert E., Smith, Roger P., and Hodge, Harold C., *Clinical Toxicology of Commercial Products*, 5th edition, Williams and Wilkins: Baltimore, 1984.

Lewis, Richard J., editor, *Hawley's Condensed Chemical Dictionary,* 12th edition, Van Nostrand Reinhold: New York, 1993.

Rev. #	Issue Date	History
6	07/15/2020	Updated SOP title in section 6.17.
7	09/01/2021	Minor updates to Scope. Updated Introduction for clarity. Removed SOP throughout. Minor updates to section 3. Expanded macroscopic and microscopic exams in section 6.1. Added sensitivity/reactivity testing. Added density testing, consolidated headspace GC/MS, removed UPLC/MS. Moved statement from Introduction to Limitations. Minor updates throughout section 6 for clarity. Updated numbering throughout.

Approval Redact - Signatures on File

Explosives Unit Chief Date: 08/31/2021

TL Approval

Explosives Chemistry
Technical Leader Date: 08/31/2021