Instrument Parameters and Reagent Preparation

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1 INTRODUCTION

Explosives chemistry utilizes analytical instruments to analyze evidence containing explosives, residues, precursors, and general unknown materials. This procedure describes basic operation of the instruments as well as specific parameters and method information for the analysis of different types of samples.

A performance verification standard or testmix is used during the Quality Assurance and Control (QA/QC) performance monitoring process. It will be analyzed and evaluated prior to the analysis of evidence. Testmixes may contain a substance that is only used to verify instrument performance and is not expected to be found in an evidentiary sample (e.g., lidocaine, tributyoxyethyl phosphate [TBEP]), or it may contain substances that can also act as a positive control or reference material (e.g., sodium, ammonium, and potassium ions).

A positive control, also referred to as a reference material, known material, or standard, is a single substance or a mixture of substances which are of known origin and/or composition and are expected to be found in an evidentiary sample and can be used for comparison between the two samples (e.g., nitroglycerin [NG], trinitrotoluene [TNT], black powder). Positive controls may include laboratory grade chemicals, commercial products, and synthesized materials.

2 SCOPE

This procedure describes instrument parameters, method information, and operations and is to be used in conjunction with the instrument performance documents for individual instruments and the procedures for the analysis of evidence. This procedure applies to caseworking personnel conducting work in explosives chemistry.

3 EQUIPMENT

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

3.1 Equipment

- Chromatography columns (gas, liquid, ion)
- 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
- 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 flame ionization detector (GC/FID)
- 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)
- Ultra performance liquid chromatograph with mass spectrometer (UPLC/MS)
- X-ray diffractometer (XRD)

3.3 Chemicals/Reagents

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- Other purchased reference and known materials for testmixes, standards, and positive controls

4 STANDARDS AND CONTROLS

Refer to the Explosives Quality Assurance and Operations Manual for details regarding verification of reference materials. Testmix components, preparation instructions, storage requirements (if applicable), and re-verification requirements are recorded in the applicable instrument performance document(s). Refer to the Explosives Level 4 Documents for guidance on preparing positive control solutions.

The positive control solutions described below do not expire but should be re-evaluated for continued use after two years unless otherwise noted.

4.1 Positive Controls

Refer to the explosives chemistry technical procedures for specific positive controls and standards that are relevant to the analysis being conducted. The following testmixes that are used for checking instrument performance are also used as positive controls for casework: GC/ECD, GC/FID, headspace GC/MS (volatiles testmix), IC, LC/MS (ESI and APCI), and UPLC/MS. Refer to the Fire Debris and Ignitable Liquid Analysis procedure for ignitable liquid reference material information.

Record stock solution preparations in the reagent log. Other preparations may be recorded in the examination records. PTFE-lined lids must be used with all standards made with hexane. The concentration of testmix or standard components may be modified to coincide with instrument response.

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5 INSTRUMENT PARAMETERS

The following instrument parameters are not intended to be prescriptive nor exhaustive. Minor modifications to the conditions may be used as needed, provided the same parameters (or similar parameters for some techniques, e.g. SEM/EDS) are used for all applicable solvent blanks, control samples, and questioned items; and the Positive Control(s) provide acceptable data. The modified parameters will be recorded and retained with the case notes and/or data.

Mobile phase preparations (i.e., IC, LC, UPLC) may be scaled appropriately.

5.1 FTIR

Most FTIRs include an ATR accessory and may include focusing lenses such as ZnSe or KRS-5 to allow for different scan limits. Analyses should be performed in ATR mode whenever possible. Refer to IOSS-751 for the specific instrument conditions. The scan range may be expanded as allowed by the instrument.

Clean the ATR sampling surface with methanol or another appropriate solvent before and after analyzing samples. Collect a background spectrum with the ATR accessory in the open position prior to or immediately after analyzing a sample.

5.2 GC/ECD

Refer to IOSS-733 for the specific instrument conditions.

5.3 GC/FID

Refer to IOSS-732 for the specific instrument conditions.

5.4 GC/MS in Chemical Ionization (CI) Mode

Method Name: EXPLNICI (or equivalent)

- Inlet/Injector
  - Injection volume: 1.0 µL
  - Inlet: split
  - Split ratio: 10:1
  - Inlet temp: 200°C
- Oven
  - Initial temp: 60°C
  - Initial time: 2 min
  - Ramp: 35°C/min
  - Final temp: 260°C
  - Final time: 2.3 min
  - Total run time: 10 min
- Column
  - Type: J&W DB-5MS, 0.25 mm diameter, 0.25 µm film thickness, ~30 m length
  - Mode: Constant makeup flow
  - Nominal initial flow: 5.0 mL/min
  - Carrier gas: Helium
- Reagent Gas
  - Methane (2.0 mL/min)
- Detector
  - Ionization: Negative ion mode
  - Scan range: 43-400 m/z
  - Solvent delay: 2.5 min

5.5 GC/MS in Electron Ionization (EI) Mode

- Column (used for all methods)
  - Type: J&W DB-5MS or Agilent HP-5MS, 0.25 mm diameter, 0.25 µm film thickness, ~30 m length
  - Mode: Constant makeup flow
  - Nominal initial flow: 3.0 mL/min
  - Carrier gas: Helium

Method name: EXPL (or equivalent)

- Inlet/Injector
  - Injection volume: 1.0 µL
  - Inlet: split
  - Split ratio: 10:1
  - Inlet temp: 250°C
- Oven
  - Initial temp: 60°C
  - Initial time: 3 min
  - Ramp: 30°C/min
  - Final temp: 260°C
  - Final time: 10 min

Method name: SP (or equivalent)

- Inlet/Injector
  - Injection volume: 1.0 µL
  - Inlet: split
  - Split ratio: 10:1
  - Inlet temp: 170°C
- Oven
  - Initial temp: 45°C
  - Initial time: 3 min
  - Ramp: 15°C/min
  - Final temp: 150°C
  - Ramp 2: 40°C/min

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Detector

Scan range: 43-400 m/z
Solvent delay: 3 min

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Final temp 2: 265°C
Final time: 7 min

Detector

Scan range: 41-400 m/z
Solvent delay: 3 min

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<u>Method name: PLASTIC (or equivalent)</u>

Inlet/Injector

Injection volume: 1.0 µL
Inlet: Splitless
Inlet temp: 250°C

Oven

Initial temp: 60°C
Initial time: 2 min
Ramp: 50°C/min
Final temp: 280°C
Final time: 8 min

Detector

Scan range: 40-400 m/z
Solvent delay: 3 min

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<td>
<u>Method name: SUGAR (or equivalent)</u>

Inlet/Injector

Injection volume: 1.0 µL
Inlet: splitless
Inlet temp: 250°C

Oven

Initial temp: 75°C
Initial time: 0 min
Ramp: 35°C/min
Final temp: 180°C
Hold: 2 min
Ramp 2: 10°C/min
Temp 2: 215°C
Ramp 3: 15°C/min
Final temp: 285°C
Final time: 2 min

Detector

Scan range: 50-275 m/z
Solvent delay: 5 min

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5.6 Headspace GC/MS (EI)

The Headspace GC/MS can be used with a heated, gas-tight syringe or with a SPME fiber, ensuring that the compatible liner is used for each technique. SPME fibers should be conditioned as needed using the automated bakeout option and needle heater, by manually inserting into the needle heater, or by manually inserting into the GC inlet at 250°C for 30 minutes.

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Column (used for all methods)

Type: J&W DB-624, 0.25 mm diameter, 1.4 µm film thickness, ~30 m length
Mode: Constant makeup flow
Initial pressure: 5.3 psi
Nominal initial flow: 3.7 mL/min
Carrier gas: Helium

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<u>Method name: Volatiles_Split_HS_10mL and Volatiles_Split_HS_20mL (or equivalent)</u>

Refer to IOSS-712 for the specific instrument conditions.

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<u>Method name: LightGases_HS_20mL (or equivalent)</u>

Inlet/Injector

Injection volume: 300 µL from HS syringe at 40°C
Inlet: Split
Split ratio: 50:1
Inlet temp: 50°C

Oven

Initial temp: 30°C
Initial time: 1 min
Ramp: 10°C/min
Final temp: 50°C
Final time: 4 min
Total run time: 7 min

Detector

Scan range: 20-150 m/z
Solvent delay: 0 min

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• SPME Fiber
  ○ Type: Supelco StableFlex, 65 µm PDMS-DVB coating
• Incubation
  ○ Incubator: 60°C for 1 min
  ○ Extraction time: 5 min
  ○ Desorption time: 30 sec
• Fiber Bakeout
  ○ Pre bakeout time: 5 min at 250°C
• Inlet/Injector
  ○ Inlet: Splitless
  ○ Inlet temp: 150°C
• Oven
  ○ Initial temp: 60°C
  ○ Initial time: 0 min
  ○ Ramp: 20°C/min
  ○ Final temp: 240°C
  ○ Final time: 1 min
  ○ Total run time: 10 min
• Detector
  ○ Scan range: 29-400 m/z
  ○ Solvent delay: 3.5 min
	• SPME Fiber
	  ○ Type: Supelco StableFlex, 65 µm PDMS-DVB coating
	• Incubation
	  ○ Incubator: Not used
	  ○ Extraction time: 0 sec
	  ○ Desorption time: 30 sec
	• Fiber Bakeout
	  ○ Post bakeout time: 5 min at 250°C
	• Inlet/Injector
	  ○ Inlet: Splitless
	  ○ Inlet temp: 150°C
	• Oven
	  ○ Initial temp: 60°C
	  ○ Initial time: 0 min
	  ○ Ramp: 20°C/min
	  ○ Final temp: 240°C
	  ○ Final time: 1 min
	  ○ Total run time: 10 min
	• Detector
	  ○ Scan range: 29-400 m/z
	  ○ Solvent delay: 3.5 min

5.7 IC

Refer to IOSS-741 for the specific instrument conditions.

5.7.1 Mobile Phase Preparation for the Nitric Acid Cations Systems

The mobile phase for the nitric acid cations systems contains 3.0 mM HNO_3 with 0.1 mM EDTA in deionized water. To prepare, add 0.0292 g EDTA and 189 µL HNO_3 to a 1-L volumetric flask and dilute to volume with deionized water.

If preparing a larger stock solution that will be used over an extended period of time, the stock solution will be stored in a plastic container.

5.8 LC/MS

Refer to IOSS-722 for the specific instrument conditions.

Run/acquire time and mass scan range may be adjusted as necessary to identify additional analytes.

5.8.1 Mobile Phase Preparation for EXP Method

The mobile phase consists of the following two components contained within separate reservoirs in the LC system:

A. 3.125 mM ammonium nitrate in deionized water. To prepare, add 0.250 g of ammonium nitrate to a 1-L volumetric flask and dilute to volume with deionized water.

B. 100% Methanol.

5.8.2 *Mobile Phase Preparation* Redacted

The mobile phase consists of the following two components contained within separate reservoirs in the LC system:

A. 1.25 mM ammonium nitrate in methanol. To prepare, add 0.100 g of ammonium nitrate to a 1-L volumetric flask and dilute to volume with methanol.

B. 1.25 mM ammonium nitrate in deionized water. To prepare, add 0.100 g of ammonium nitrate to a 1-L volumetric flask and dilute to volume with deionized water.

5.9 Microscopes (Digital and Optical) with Digital Camera

Microscopes with digital cameras and measuring capabilities will be verified (every magnification level) using a ruler or stage micrometer after each annual maintenance service.

5.10 Raman Spectroscopy

Samples for Raman analysis may be analyzed either in a sample compartment or through a microscope attachment using one or more of the following laser wavelengths: 785 nm, 780 nm, 532 nm.

See IOSS-753 for the specific instrument conditions.

5.11 SEM/EDS

See IOSS-771 for the specific instrument conditions.

The backscatter detector may be used to visualize elemental contrast for imaging or for locating an area to analyze by EDS.

For image collection, values for accelerating (high) voltage, working distance, spot size, beam intensity, stigmation, focus, brightness, and contrast are established at the individual's discretion based on image quality desired.

Trace quantities of elements may require an acquisition time of 500 live seconds or longer to achieve the desired signal to noise ratio (SNR). Decreasing the Amp Time and increasing the beam intensity can be used to increase the count rate and improve the SNR so long as it does not cause sample damage.

Appropriate sample holders include stubs made of aluminum, copper, or brass, a carbon planchet, or sample clamp. Adhesive carbon tabs or liquid adhesives (e.g., Duro-tak) can be used to adhere the sample to the holder. Metallic tapes, such as aluminum and copper tape, may also be used depending upon the analytes of interest.

5.12 UPLC/MS

Method name: EXP (or equivalent)

- Liquid Chromatograph
  - Mobile phase: 60% A1, 40% B1, Isocratic
  - Total flow: 0.5 mL/min
  - Column: C-18, 50 mm length, 2.1 mm internal diameter, 1.6 µm particle size
  - Column temp: 30° C
- Mass Spectrometer
  - Ionization: ESI
  - Scan type: Full scan
  - Runtime: 0 to 2 min
  - Polarity: Negative
  - Resolution: 17,500

- Guard column: 5 mm length, 2.1 mm internal diameter, 1.6 µm particle size
- Injection volume: 8 µL
- Total time: 2.0 min

- Autosampler Parameters
  - Autosampler temp: 14°C
  - Weak wash volume: 600 µL
  - Strong wash volume: 200 µL
  - Cycle Inject Valve: At 1 min
  - Tune file: ESI_EXP_Neg
  - Scan range: 200-400 m/z
  - Data type: Profile
- Source Parameters
  - See validation file

A fresh blank consisting of 50:50 methanol:deionized water should be used between samples.

Run/acquire time and mass scan range may be adjusted as necessary to identify additional analytes.

5.12.1 Mobile Phase Preparation for EXP Method

UPLC systems are vulnerable to clogs due to microbial growth. Mobile phase components should be changed regularly (follow chart below), and associated glassware should be cleaned regularly to minimize this risk.

Mobile Phase Composition		
Component	**Composition**	**Replacement Schedule**
A1	100% Methanol	Replace when low.
B1	3.125 mM Ammonium Nitrate in Deionized Water	Prepare in small quantities. Replace after 4 weeks.
Weak Wash	50:50 Methanol:Deionized Water	Prepare in small quantities. Replace after 4 weeks.
Strong Wash	90:10 Methanol:Deionized Water	Prepare in small quantities. Replace after 4 weeks.
Seal Wash	50:50 Methanol:Deionized Water	Prepare in small quantities. Replace after 4 weeks.

The B1 mobile phase is prepared by adding 0.250 g of ammonium nitrate to a 1-L volumetric flask (or 0.125 g to a 500-mL volumetric flask) and diluting to volume with deionized water.

5.13 XRD

See IOSS-773 for specific instrument conditions. Appropriate sample holders include zero background holders with or without a depression.

6 LIMITATIONS

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.

7 REVISION HISTORY

Revision	Issued	Changes
10	04/06/2023	Updated sections 4.1.4 and 4.1.5.
11	08/01/2024	Removed instrument parameters and added references to IOSS procedures in sections 5.1, 5.2, 5.3, 5.6, 5.7, 5.8, 5.10, 5.11, and 5.13.