OSAC 2022-S-0002 Standard Practice for the Analysis of Organic Gunshot Residue (OGSR) by Gas Chromatography-Mass Spectrometry (GC-MS)

Ignitable Liquids, Explosive, and Gunshot Residue Subcommittee
Chemistry: Trace Evidence Scientific Area Committee (SAC)
Organization of Scientific Area Committees (OSAC) for Forensic Science

Draft OSAC Proposed Standard

OSAC 2022-S-0002

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Prepared by
Subcommittee for Ignitable Liquids, Explosive, and Gunshot Residue
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Standard Practice for the Analysis of Organic Gunshot Residue (OGSR) by Gas Chromatography– Mass Spectrometry (GC-MS)

1. Scope

1.1. This practice covers the analysis of organic gunshot residue (OGSR) by electron ionization-gas chromatography-mass spectrometry (GC-(EI)MS). This practice does not address the analysis of inorganic gunshot residue (IGSR) or primer gunshot residue (pGSR).

1.2. This practice is intended for use by competent forensic science practitioners with the requisite formal education, discipline-specific training (see Practice E2917), and demonstrated proficiency to perform forensic casework.

1.3. Units – The values stated in SI units are to be regarded as the standard, unless otherwise stated.

1.1. This practice does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this practice to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Referenced Documents

2.1. ASTM Standards:

E1588 Practice for Gunshot Residue analysis by Scanning Electron Microscopy/Energy Dispersive X-ray Spectrometry.

E1732 Terminology Relating to Forensic Science.

E2917 Practice for Forensic Science Practitioner Training, Continuing Education, and Professional Development Programs.

E2998 Practice for Characterization and Classification of Smokeless Powders.

E2999 Test Method for Analysis of Organic Compounds in Smokeless Powder by Gas Chromatography-Mass Spectrometry and Fourier Transform Infrared Spectroscopy.

E3255 Practice for Quality Assurance of Forensic Science Service Providers Performing Forensic Chemistry Analyses.

WK56998 Terminology Relating to the Examination of Explosives.

WK72856 Practice for the Collection and Preservation of Organic Gunshot Residue.

3. Terminology

3.1. For definitions of terms that can assist in interpreting this standard, refer to Terminology E1732 and WK 56998.

3.2. Definitions of terms specific to this standard:

3.2.1. *Inorganic GSR (IGSR), n* – Gunshot residues from the primer, cartridge case, projectile (e.g., bullet or shot pellets), or the firearm which are typically identified using scanning electron microscope (E1588).

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3.2.2. *Organic GSR (OGSR), n* – Gunshot residues from the propellant and the priming mixture that are organic (carbon-based).

3.2.3. *Primer GSR (pGSR), n* – Gunshot residues generating from the priming mixture that could be inorganic or organic.

3.2.4. *Reference Sample, n* – A solution containing known target OGSR compounds.

4. Terminology

4.1. Gunshot residue (GSR) examination is typically performed to determine if an individual was exposed to firearm discharge. GSR analysis has historically relied upon the detection of IGSR, as described in Practice E1588, which originates primarily from the ammunition primer (pGSR). OGSR analysis provides information which complements pGSR analysis [1].

4.2. OGSR originates from the combustion of the smokeless powder and the priming mixture following their ignition during the firearm discharge process. After a firearm has been discharged, the combined residue can be found on exposed surfaces in the vicinity of the fired weapon (e.g., hands, other exposed skin surfaces, hair, clothing, and other surfaces). OGSR can also be found in the cartridge case after firing and can be recovered to provide information about the constituents of the propellant or the priming mixture, or both.

4.3. This practice is intended to be used in conjunction with a laboratory's validated standard operating procedures.

4.4. This practice does not cover the interpretation or significance of the OGSR results. Laboratory specific criteria should be established and supported by data obtained during method development and validation (E3255).

4.4.1. Individual laboratory protocol will determine if IGSR/pGSR and GSR will be analyzed from the same sample or separate samples [2,3].

4.5. The analysis of intact smokeless powder grains is beyond the scope of this practice (refer to Practice E2998 and Test Method E2999).

5. Apparatus

5.1. Gas chromatograph (GC) – A gas chromatograph (GC) capable of using capillary columns and being interfaced to a mass spectrometer (MS) (refer to Table X1).

5.2. Mass Spectrometer (MS) – A mass selective detector operating in electron ionization (EI) mode and capable of acquiring mass spectra from mass-to-charge (m/z) 10 - m/z 400 with unit resolution or better.

5.3. Sonicator – For use when extracting OGSR components from sample items collected.

5.4. Centrifuge – Recommended for use after sonication of extract and capable to achieve a minimum of 4000 RPM. Disposable centrifuge tubes that safely fit the centrifuge device are required.

6. Materials

6.1. Purity of Solvents – GC-MS grade or higher.

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6.2. Analytical Solvents – Acetone, acetonitrile, ethanol, isopropanol, methanol, methylene chloride, or other appropriate solvents.

6.3. OGSR Standard(s) or Reference Materials – Certified reference materials are to be used. Individual reference materials or standards, or mixture thereof, may be used in place of a certified reference standard provided that they are verified before use.

6.3.1. The concentrations of standards or reference materials used must be above the limit of detection for the instrument to be used to analyze samples.

6.3.2. Concentrations of OGSR compounds recovered in forensic samples can be as low as 25 ppb [4].

6.4. Internal Standard – Use of an internal standard is not required for qualitative identification of OGSR but can be used to evaluate system sensitivity and reproducibility.

6.5. GC Carrier Gas – Helium or hydrogen of purity 99.995% or higher.

6.6. Drying Gas – Nitrogen, air, or other inert gas.

6.7. Filters – Single use disposable filters of a hydrophobic membrane construction are recommended for use to filter the extract prior to analysis. A filter membrane porosity of 0.4 μm or smaller is recommended.

7. Procedure

7.1. Samples are submitted for OGSR analysis in one or more of the following forms: adhesive tape lifts, swabs, or vacuum filters; refer to WK72856.

7.1.1. Additional analyses can be performed on OGSR components that have been described elsewhere [WK LC-MS] [5, 6].

7.2. Preparation of OGSR samples:

7.2.1. Extract swabs, vacuum filters, or adhesive lifts using a suitable organic solvent, such as methanol, methylene chloride, or acetonitrile [7].

7.2.1.1. The volume of solvent used must be sufficient to extract the entire surface or area of the sample collection item used.

7.2.2. Extract the sample by placing the collection item inside a new disposable vial of a minimum volume required to hold the entire item. Swabs can be folded to fit into the vial. Add a minimum volume of solvent required to submerge the entire item.

7.2.3. Sonicate the vial with the item submerged in the solvent. Remove the extract and either filter or centrifuge the item to remove any solid particulates from the solution.

7.2.4. Analyze the filtered or centrifuged extract directly or the extract can be concentrated, if required for analysis.

7.2.4.1. Concentrate the extract by evaporation down to the required volume using nitrogen gas or another dry gas.

7.2.5. Store extracts at 0°C or colder to maximize preservation, when the sample is not being analyzed.

7.3. GC-MS analysis of OGSR extracts:

7.3.1. Common organic components of OGSR can be identified by GC-MS analysis.

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7.3.1.1. Nitrocellulose needs to be derivatized prior to analysis. Refer to Test Method E2999 and included references for additional information [8,9].

7.3.2. The extract may be diluted, if required, to improve chromatography or mass spectral features.

7.3.3. Suggested GC-MS parameters are listed in Appendix Table X1.

7.3.3.1. Validate this method on the laboratory's instrument before using the method in casework (E3255).

NOTE: Modify GC conditions to ensure that each peak of the reference test mixture has baseline resolution.

7.3.4. Prior to analyzing samples, the GC-MS should be tuned and calibrated per validation protocols or the manufacturer recommendations.

7.3.5. Table 1 lists the common target compounds and their target ions that can be used to identify the presence of OGSR.

7.3.5.1. Data analysis is limited to the qualitative identification of the target compounds listed in Table 1. Parameters used for identification can be observed retention time(s), ions detected, their ion masses, and associated fragmentation pattern of the molecule.

7.3.5.2. Each specific retention time is measured by analyzing a reference material (see Sec. 6.3), using the GC-MS system and method under the same instrumental conditions [8,9,10].

7.3.5.3. At this time, there are no satisfactory studies completed to determine the common background presence of OGSR. Therefore, quantitative analysis of OGSR by GC-MS is not recommended.

7.3.5.3.1. It is the responsibility of each individual laboratory to verify any research study completed in their region concerning the background presence of OGSR [10,11].

7.3.5.4. Interpretation of the presence or absence of target compounds in Table 1 is not covered in this standard practice (see Sec. 4.4).

TABLE 1: Typical OGSR related compounds and m/z of target ions in EI MS found by GC-MS analysis

Target Compound	**Significance/ Application**	**Target Ions (*m/z*)**	**Ref.**
Akardite II (AK II)	Stabilizer	169, 226	[12]
2-amine-4,6-dinitrotoluene (2-ADNT)	Degradation products	197, 180	[13]
Dibutyl phthalate (DBP)	Plasticizer	149, 223	[13,14]
Diisoamyl phthalate (DIP)	Plasticizer	149	[E2999]
2,4- and 2,6-dinitrotoluene (2,4-DNT and 2,6-DNT)	Flash suppressor	165, 182	[13]
Dioctyl phthalate (DOP)	Plasticizer	149, 279	[E2999]
Diphenylamine (DPA)	Stabilizer	169	[4,13,14]

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Ethyl centralite (EC)	Stabilizer	120, 268	[4,13,14]
Ethyleneglycol dinitrate (EGDN)	Explosive	46, 76	[12]
Methyl centralite (MC)	Stabilizer	134, 240	[13]
2 and 4-nitrodiphenylamine (2-NDPA, 4-NDPA)	Degradation products; stabilizer	167, 214	[4,13,14]
Nitroglycerin (NG)	Explosive	46, 76	[13,14]
4-nitrosodiphenylamine (4-NODPA)	Degradation products	167, 198	[14]
N-nitrosodiphenlyamine (N-NODPA)	Degradation product	Detected as DPA	[14]
Nitrotoluenes (NTs)	Sensitizer	65, 91, 120 or 137	[13,15]
2,4,6-trinitrotoluene (TNT)	Flash suppressor/sensitizer	89, 210	[4,13]

8. Identification of OGSR Compounds

8.1. The identification of a compound in an unknown sample should be based upon direct comparison with a known reference standard of the compound.

8.2. The unknown sample should be run on the same instrument using the same method as the known reference standard.

8.3. Identification criteria is provided for the gas chromatography and mass spectrometry.

8.3.1. Gas Chromatography

8.3.1.1. 8.4.1.1.The retention time of the compound in the unknown sample should be within ± 0.1 minute of the reference compound.

8.3.2. Mass Spectrometry

8.3.2.1. The unknown and reference samples should have the same base peak and the same molecular ion, if present, refer to section 9.2.1. The measured m/z value of the molecular ion should be within the instrument manufacturer’s tolerance (mass accuracy) of the theoretical value of the target compound.

8.3.2.2. The fragmentation patterns and relative abundances of ions in the mass spectra of the unknown sample and the reference OGSR sample will generally agree across the majority of the ions.

8.3.2.3. Isotopic ions present in the reference spectrum shall be present in similar proportions in the unknown sample spectrum; low abundance ions (less than 5% of the total spectral abundance) may be absent without precluding an identification.

8.3.2.4. Background subtraction may be necessary to remove any background contribution to the sample.

8.3.2.5. There shall be no unexplained extraneous ions that have a significant abundance.

9. Quality Control

9.1. For minimum quality assurance protocols refer to Practice E3255.

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9.2. Quality assurance protocols specific to this standard practice:

9.2.1. Analyze a quality control sample with questioned extracts.

9.2.1.1. The quality control sample should be analyzed, at minimum, at the beginning and the end of the analytical sequence on the instrument.

9.2.1.2. Quality control sample contains at least five compounds commonly observed, as chosen by the individual laboratory, from the chemicals listed in Table 1. NOTE: An example of a quality control sample is as follows: NG, EC, 2-NDPA, DPA, and 2,4-DNT.

9.2.1.3. Establish protocols to ensure stability of the quality control sample.

9.2.1.4. Store quality control sample under appropriate conditions (see 7.2.5).

9.2.1.5. Replace the quality control sample when degradation is observed from the previous analysis of the sample. Examples of degradation include: the absence of peaks, the presence of new peaks. The laboratory can also determine an expiration date for the quality control sample in accordance with laboratory policy.

9.2.2. Analyze blank samples with questioned extracts.

9.2.2.1. Prepare a method blank using the same procedure(s), reagents, and conditions for analysis as the questioned extracts.

9.2.2.2. A solvent wash blank shall be analyzed between each sample.

10. **Records**

10.1. Document the following, electronically or hard-copied, refer to Practice E3255:

10.1.1. GC-MS instrument settings and method parameters used for analysis.

10.1.2. Calibration and tuning of the instrument used for analysis.

10.1.3. Chromatograms of method blank(s), reference material(s), and questioned samples. Annotate peaks of interest with retention times.

10.1.4. Mass spectra of OGSR compounds identified and the associated material(s) used for comparison.

10.1.5. All analytical notes from the analysis including the details of sample preparation and instrument maintenance.

10.1.6. Maintain reports in accordance with laboratory policy and Practice E3255.

11. **Keywords**

11.1. OGSR; GC-MS

12. **References**

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APPENDIX

(Non-Mandatory Information)

X1. Instrumental Operation Parameters

X1.1 Suggested GC-MS parameters

X1.1.1 An example GC-MS instrumental method, from literature, to analyze OGSR compounds is provided below as a starting point for the method validation by the laboratory.

TABLE X1: Suggested GC-MS conditions derived from ASTM E2999.

Parameter	**Condition**
GC column:	30 meter, DB-5
Injector Temp:	180° C
Initial Temp (T_0):	40-50° C
Hold time (T_0):	3 minutes
Ramp 1:	15° C/minute to 150° C (T_1)
Hold time (T_1):	2 minutes
Ramp 2:	20-40° C/minute to 265° C (T_2)
Hold time (T_2):	8 minutes
Mode:	EI
Scan Mode	Full Scan or Selected Ion Monitoring
Split Ratio:	Splitless (n/a)
MS range:	40 to 400 *m/z*
Source Temp:	230° C
Solvent delay:	1-2 minutes

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