I. SCOPE

GC/MS is used for the characterization and identification of many materials, including complex mixtures, which are capable of passing through a gas chromatograph. Typically this includes thermally stable organic compounds with molecular weights less than 500, including explosives. It can be applied to extracts or solutions from intact explosives or from post blast evidence.

This procedure covers the use of forensic applications of GC/MS in electron and chemical ionization modes for the analysis of explosives, components of propellants (like smokeless powders), and other chemical components related to explosive casework (for example unknown chemicals and extracted components of explosive devices) at ATF.

II. REFERENCES


III. Validation
GC/MS is a well-known and scientifically accepted technique for the confirmation of organic components which can be analyzed by GC. Relevant examples of the broad nature of the method and related literature can be found in Section II (References). The use of GC/MS for explosives is no exception and reproducible results on most organic explosives can be found in the references of Section II.

IV. APPARATUS/REAGENTS
Any validated GC/MS instrumentation may be used. See parameter sheets for instrument settings.

Standard Solutions, Reagents and Supplies
- A capillary, bonded phase, methylsiloxane column. Approximately 1-3 meters of precolumn (either deactivated or coated with stationary phase), if needed.
- Syringes capable of introducing sample size in the range from 0.1 to 10.0 μL. Samples are introduced via injection of solutions directly into the injection port of the GC. Most often injections are made via the mass spectrometer autosampler.
- Helium (chromatographic grade) for the GC carrier gas. Methane (UHP) for the chemical ionization reagent gas.
- Any suitable solvent may be used (e.g. High purity (99.9+%) dichloromethane/methylene chloride (DCM))
- A standard solution containing targeted component(s) which is appropriately diluted for the instrumentation and/or analysis. This is considered a system performance check.
- Filters, if needed

V. SAFETY PRECAUTIONS
- Pump exhaust should be vented to a fume hood or other vent whenever facilities permit.
- Used pump oil may contain chemicals that could pose potential health hazards and should be disposed of in an environmentally safe manner. Operators changing oil should wear laboratory coats, protective gloves and goggles or safety glasses.
- All gases should be properly secured/stored. Pressure regulators should be inspected whenever the cylinders are replaced.
- Proper precautions and care should be exercised when performing manual injections or maintenance on the injector or column (hot surfaces).
- Any maintenance or inspection of electrical circuits is to be limited to operators familiar with the specific hazards. Whenever possible the work should be done in the company of a “buddy”.
- The hazards of chemicals and solvents must be understood before working with them. Specifically, the analyst must be aware of the volatile nature of EGDN and NG and their potential hazards on blood pressure.
VI. PROCEDURES

Tuning and Calibration

The mass spectrometer must be tuned (or tune-checked) and calibrated no more than 72 hours prior to sample analysis. This is accomplished with the vapor from the internal mass spectrometer calibration substance (perfluorotributylamine; PFTBA). The instrument must pass the tune requirements as established by the instrument manufacturer. Since acceptable tune response is instrument-dependent, the requirements shall be available for the analysts. The examiner’s initials on the tune indicate that it met specifications. A copy of each tune report applicable to casework shall be maintained (e.g. near the instrument or in the case file).

Acceptable conditions

Each time the instrument is used for the analysis of a sample, a known reference material such as an appropriate standard mixture containing the targeted analyte(s) shall be analyzed. The name and identifying information such as lot number sample and/or date prepared shall be documented.

Sample Analysis

Each time the instrument is used for casework, an entry shall be documented in an instrument logbook. For every sample prepared for mass spectral analysis related to casework an experimental method blank will be analyzed by GC/MS to determine potential contamination sources resulting from solvents, labware, concentration steps, or other sources. All sample analyses including those of reference materials/standards shall be preceded by a solvent blank or a method blank.

The reference material/standard shall be analyzed at the beginning and end of a sequence of injections to assure the proper and continuous performance of the instrument during that sequence. In order to report a positive result, the retention time of a targeted peak(s) shall agree with that of the standard within 2%.

The ionization techniques including EI, PCI, and NCI could be employed in GC/MS analysis of explosives and case related samples. Tables 1-3 list ions of common explosives and other targeted compounds that can be seen via the EI, PCI and NCI techniques.
Table 1: Electron Ionization: **Electron Impact (EI) Ionization Method**

<table>
<thead>
<tr>
<th>Target</th>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>NG</td>
<td>76, 46, 30, 151*, 58*</td>
</tr>
<tr>
<td>2, 6-DNT</td>
<td>165, 148, 135, 121, 89, 63</td>
</tr>
<tr>
<td>2, 4-DNT</td>
<td>165, 119, 89, 63</td>
</tr>
<tr>
<td>Diphenylamine (DPA)</td>
<td>169, 168, 167, 84</td>
</tr>
<tr>
<td>TNT</td>
<td>210, 193, 180, 164, 149, 134, 89, 63</td>
</tr>
<tr>
<td>Methyl centralite (MC)</td>
<td>240, 183, 134, 106, 77</td>
</tr>
<tr>
<td>Ethyl centralite (EC)</td>
<td>268, 164, 148, 120, 104, 92</td>
</tr>
<tr>
<td>Dibutylphthalate (DBP)</td>
<td>149</td>
</tr>
<tr>
<td>2-nitrodiphenylamine (2NPA)</td>
<td>214, 197, 180, 167, 139</td>
</tr>
<tr>
<td>Akardite II (AKII)</td>
<td>226, 169, 168, 167</td>
</tr>
<tr>
<td>Di-n-pentylphthalate (DPP)</td>
<td>149</td>
</tr>
<tr>
<td>4-nitrodiphenylamine (4NPA)</td>
<td>214, 184, 167, 139, 115</td>
</tr>
<tr>
<td>TATP</td>
<td>75, 59, 58, 43</td>
</tr>
<tr>
<td>EGDN</td>
<td>76, 46</td>
</tr>
<tr>
<td>PETN</td>
<td>85, 76, 57, 46</td>
</tr>
<tr>
<td>RDX</td>
<td>205, 148, 128, 120, 81, 75, 56, 46</td>
</tr>
</tbody>
</table>

* Low abundance ions

Table 2: PCI: **Positive Chemical Ionization (PCI) method**

<table>
<thead>
<tr>
<th>Target</th>
<th>m/z (Protonated Molecular Ion [MH+])</th>
</tr>
</thead>
<tbody>
<tr>
<td>EGDN</td>
<td>153</td>
</tr>
<tr>
<td>NG</td>
<td>228</td>
</tr>
<tr>
<td>2,4-DNT</td>
<td>183</td>
</tr>
<tr>
<td>TNT</td>
<td>228</td>
</tr>
<tr>
<td>PETN</td>
<td>317</td>
</tr>
<tr>
<td>RDX</td>
<td>223</td>
</tr>
</tbody>
</table>
Table 3. **Negative Chemical Ionization (NCI) Method**

<table>
<thead>
<tr>
<th>Target</th>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>EGDN</td>
<td>62, 46</td>
</tr>
<tr>
<td>NG</td>
<td>62, 46</td>
</tr>
<tr>
<td>2,4-DNT</td>
<td>182, 152</td>
</tr>
<tr>
<td>TNT</td>
<td>227, 210, 197</td>
</tr>
<tr>
<td>PETN</td>
<td>62, 46</td>
</tr>
<tr>
<td>RDX</td>
<td>176, 160, 129, 102, 46</td>
</tr>
</tbody>
</table>

In addition to full mass scans a selected ion monitoring (SIM) procedure can be used. To maintain adequate specificity at least three ions will be monitored.

The following targeted compounds shall be included when performing the following analysis types:

- **High explosives** – EGDN, NG, TNT, PETN, RDX
- **Smokeless powder** – NG, DPA, 2-NDPA, EC, MC, AKII, DBP, DnPP, 2,4-DNT, TNT
- **ICAO chemical detection agents in plastic explosives** – dimethyldinitrobutane (DMNB), o-mononitrotoluene (2-MNT), p-mononitrotoluene (4-MNT), EGDN

**Identification Criteria**

A GC/MS spectrum will be examined if the retention time compared to a reference material agrees within 2 percent (as determined by relative retention time = reference retention time/sample retention time). The peak for the targeted component in total ion chromatogram (TIC) or extracted ion chromatogram (EIC) shall have a signal-to-noise of at least 3.

Comparison of sample retention times and mass spectra to a reference is required for identification. The presence or absence of significant ions (as determined by their relative abundance) in a sample which is inconsistent with the reference standard will prevent an identification unless it can be explained. For example, ions from filters and solvents may be explained in the case jacket and not prevent an identification. Subtraction of background spectra is permissible and may be required to remove chemical noise. Any response to a targeted component in a solvent blank or control sample shall be documented and addressed.

At least 4 identification points are required to identify an analyte. The retention time is one identification point. One identification point is assigned for each low resolution mass spectrometry ion. Separate techniques (like EI and CI) can be combined to achieve the identification points.

Examples. A peak at the right retention time on a quadrupole GC-MS gives 3 ions, this is a total of 4 identification points. An analyte is run on an EI method which gives 2 ions and then is run on the same instrument/column with a CI method which gives 2 ions; this gives a total of 5 identification points.
When recording the result of a GCMS analysis in case notes, the use of terminology such as “possible”, “indicated” or “insufficient points for identification” shall be used if an analyte cannot be identified.

Note: when examining components of a mixture like smokeless powder or dynamite, it may not be necessary to have a mass spectral identification of each component in order to identify the mixture. See the Standard Approach for specifics.

Identification of a sample using other sample information
In the case where an analyte can’t be identified by GC-MS alone, identification points can be gained from other sources such as from other detectors, or other known sample information. The number of points and/or ions required for identification in order to report an analyte remains 4. Sample information that can be considered an identification point includes physical and chemical properties. For example, in the case of a yellow, viscous liquid which yields a retention time matching that of nitroglycerin and only two diagnostic ions, the examiner may identify nitroglycerin based on 4 identification points; the retention time and two characteristic ions in the MS matching in relative abundance to a reference compound, and the physical characteristic of the material. If the physical properties of the sample are not known, for instance in post blast samples, additional identification point(s) are required for samples having only two structurally significant ions and a retention time matching a reference. Additional identification points may be attained through alternate ionization and/or chromatographic methods or analysis on another instrument.

Instrument and Periodic Maintenance
All instrument maintenance which is necessary for proper instrument performance such as filament exchange, pump oil replacement, ion source or analyzer cleaning will be documented in an instrument maintenance log. The logbook will also document the maintenance and symptoms from any electrical component failures, which might occur. This does not need to include replacement of carrier gas, septa or injection port liners.

VII. QUALITY ASSURANCE AND QUALITY CONTROL

Sources of Error
Possible sources of MS error include:

- Impurities from solvents and instrument background and/or carryover from prior analyses.
- Overloading the injector. Samples should be diluted to proper concentration prior to the GC/MS analysis.
- Calibration errors and gradual de-tuning of the instrument, which normally do not contribute to the generation of false positives.
- A false negative for a component which can occur on some ion trap instruments due to coeluting contaminants obscuring a response. This is avoided using the ion trap in conjunction with another analytical technique and proper cleanup methodology.

VIII. GLOSSARY
Mass Spectrum – a plot of ion concentration versus mass-to-charge ratio for a single mass spectrometer scan or series of scans, reflecting scan summation or background subtraction

Tune – adjustment of mass spectrometer lens voltages and other parameters to maximize and
normalize ion production, transmission and detection.

Calibration – electronic adjustment of a mass spectrometer’s analyzer to measure the correct m/z values.

Experimental Control – a sample prepared for GC/MS or other analytical technique using the same procedures as one prepared from a forensic exhibit. Analysis of this sample and demonstration that an analyte is not detected, precludes the possibility of a false positive.

False positive - a spectral response originating from the instrument, solvent, sample extraction or otherwise originating from sample workup.

Ion Trap - a mass analyzer used in some mass spectrometers functioning by trapping ions in a combination of electric and radio frequency fields and selectively ejecting them

Quadrupole - a common mass analyzer used in mass spectrometry to analyze the mass-to-charge ratio (m/z) of ions produced in the ion source. The quadrupole consists of four metal rods which carry radio frequency and electric fields which are varied in such a way to sequentially and rapidly transmit ions of known mass.

Retention Time - the time which it takes a component to travel through the GC column

Selected Ion Monitoring (SIM) - an alternative to a full scan of masses on a quadrupole or ion trap MS involving jumping over a few selected masses. Often this results in increased sensitivity.