



<b>ATF-LS-FD2</b> <b>High-Temperature Gas Chromatography-Mass Spectrometry</b> <b>Analysis</b>	Published Online: <b>March 2018</b>
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**I. Scope:**

This policy and procedure guideline establishes a standard method for identification and classification of materials by High Temperature Gas Chromatography-Mass Spectrometry (HTGC-MS). This method is useful for the analysis of oils, waxes, lubricants (such as petroleum jelly), and plasticizers.

High temperature GC uses injector and column temperatures above 330°C to separate high boiling compounds and the mass spectrometer to detect the components with electron ionization.

Oils, waxes, and lubricants may be analyzed at lower, “normal”, temperatures (below 330°C), but higher boiling hydrocarbons above C44 may not be eluted from the column. Examiners who use normal temperature GC-MS for the analysis of these materials should follow the ATF Fire Debris protocol on GC-MS.

**II. References:**

ASTM D5442, Standard Test Method for Analysis of Petroleum Waxes by Gas Chromatography.

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Nogare, SD and Juvet, RS, Gas-Liquid Chromatography: Theory and Practice, Interscience Publishers, 1966.

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U.S. Customs Laboratory Methods (USCL Method 34-07), Quantitation of paraffin in beeswax and other waxes by high temperature capillary gas chromatography, March 2003.

### **Validation**

HTGC-MS is a well-known and scientifically accepted technique for the analysis of oils and waxes. Relevant examples of the broad nature of the method and related literature can be found in Section II (References).

### **III. Apparatus/Reagents**

1. Gas Chromatograph with capillary column and electron ionization (EI) MS detector
2. Programmable Temperature Vaporizer (PTV) injection system that can be operated in either split or splitless mode and ramped up to at least 400°C.
3. A cross-linked or bonded phase capillary column (5% phenyl or equivalent), rated to handle temperature limits of at least 400°C.
4. A GC oven capable of a reproducible temperature program up to at least 450°C.
5. A computerized data station able to store chromatographic data from sample runs. The system must be capable of performing, either through its operating system or by user programming, various data handling functions, including input and storage of sample data files, generation of produced chromatograms and mass spectra, and ability to search mass spectral database libraries.
6. The system must be able to retrieve chromatograms from a data file and compare it against a library of chromatograms available to the data system.
7. Syringes capable of introducing a sample size of 0.1-10.0 µL.
8. A quality control hydrocarbon mixture, such as Restek D2887 mix or equivalent, containing n-alkanes C20, C24, C28, C32, C36, and C44.
9. A reference collection including of a broad variety of materials expected to be analyzed.

### **IV. Safety Precautions:**

1. Personal protective equipment such as lab coat, safety glasses and gloves should be available and used, if necessary, when preparing samples and conducting analyses.
2. All gas cylinders should be properly secured/stored. Pressure regulators should be inspected whenever the cylinders are replaced.
3. Proper precautions and care should be exercised when performing manual injections, performing maintenance on the injector or column (hot surfaces), and performing diagnostics (electrical hazards).

4. Material Safety Data Sheet (MSDS) references for solvents should be available and read by user.

**V. Procedures:**

The identification of materials is performed using retention time and spectral data compared with a known reference liquid and/or pattern recognition techniques, which involves examining the sample chromatograms and comparing them to applicable references.

Refer to ATF Fire Debris protocols on the Analysis of Lubricating Oils and the Analysis of Waxes for sample preparation guidelines. For other samples, such as plasticizers, which are not covered in these protocols, analysts should extract samples in trichloroethylene (TCE), pentane, or other solvent appropriate for the sample and the chosen GC capillary column at a recommended concentration of 0.1% by weight. Sample preparation is critical to avoid overload and carryover.

**VI. Quality Control**

Each day that the instrument is used for analysis it will be autotuned using perfluorotributylamine (PFTBA). The tune report shall be examined to insure that all parameters are within their normal expected range specified by the manufacturer. The tune should monitor ions 69, 219, and 502. If the 502 ion falls below 0.1% of the 69 ion, appropriate instrument maintenance should be performed. Tune reports are maintained near the instrument. In cases where sequences carry over into the next day, the autotune will be considered still valid for the sequence.

Each day the instrument is used for analysis, a quality control sample must be run. In cases where sequences carry over into the next day, the quality control sample will be considered still valid for the sequence. The quality control (QC) should contain at least C20, C24, C28, C32, C36, and C44 in trichloroethylene (TCE) or other solvent appropriate for the chosen GC capillary column. The quality control may also be used as the reference. Restek Calibration Mix D2887 or equivalent is recommended diluted at least 1:200 in TCE. Each day the QC is run, the signal to noise ratio of the C44 peak will be monitored and should be no less than 100:1. If the C44 peak falls below this, instrument maintenance may be required.

Each day cases are run, a materials control (also known as a system blank) will be run prior to any samples. This materials control insures that the instrument, solvent and method of analysis are free of contamination. In cases where sequences carry over into the next day, the materials control will be considered still valid for the sequence. A solvent blank will be run between each case sample. This blank insures that no carryover from the previous sample exists. In some situations, a solvent blank may serve as the materials control. The data for the materials control(s) and solvent blanks will be maintained in the case record.

Logs shall be maintained as to operator use and service/maintenance by vendors or primary operators.

When changes outside the acceptable parameters (as defined by manufacturer) occur in the "autotune" or the quality control sample (i.e. air leaks, decreased resolution, decreased sensitivity) check the following items:

- Septum

- Column nut
- GC/MS interface nut
- Injection Port Liner
- Capillary column
- Mass Spectrometer Source

**Sources of Error**

1. If a large volume of sample is injected and/or the sample is too concentrated, peaks may broaden and become distorted.
2. Extraneous peaks may result from impurities in the solvent, carryover from previous runs or other materials used in the method of analysis.
3. If no peaks are observed, check sample concentration and the mass spectrometer. The sample may need to be concentrated or the MS source may need to be cleaned.