

TENNESSEE BUREAU OF INVESTIGATION

Forensic Services Division

Microanalysis Standard Operating Procedures Manual

Oil, Grease and Lubricant Analysis



4.0 Oils, Greases, and Lubricants Analysis

4.1 Scope

This procedure is for the analysis and/or comparison of submitted evidence for the presence of heavy petroleum-based products in the form of oils, greases, and lubricants. The procedure utilizes a high temperature program in a gas chromatograph/mass spectrometer.

4.2 Terms and Definitions

Oil - A viscous liquid derived from petroleum, especially for use as a fuel or lubricant.

Grease - A semi-solid substance composed of oil and a chemical soap or other additive, commonly used as an industrial lubricant.

Wax - Any of various natural, oily or greasy heat-sensitive substances, consisting of hydrocarbons or esters of fatty acids that are insoluble in water but soluble in nonpolar organic solvents.

ASTM 1618 Column Resolution Test Mixture- a thirteen component mixture (including C6 thru C20) used to performance check the gas chromatograph-mass spectrometer.

Blank - An analytical control consisting of the solvent carbon disulfide. It is used to ensure that there is no carryover on the GC/MS and that no components are present that will interfere with analysis. It is run prior to the start of a sequence and between samples.

4.3 References

Lawrence, J. F., et. al., "Characterization of Commercial Waxes by High-Temperature Gas Chromatography", *Journal of Chromatography*, 236 (1982), 403-419.

Reardon, M. R., et. al., "Comparison of Motor Oils Using High-Temperature Gas Chromatography-Mass Spectrometry", *Journal of Forensic Science*, May 2007, Vol, 52, No. 3, 656-663.

4.4 Examination Procedures -

4.4.1 Evidence types - Any item that may contain petroleum-based oil, grease, or lubricant residue. This may include but is not limited to:



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car parts, fire debris, clothing from sexual abuse cases and hit and run accidents. Known oils, greases and lubricants are also submitted for comparison to unknown samples.

4.4.2 Reagents and Chemicals -

Carbon Disulfide

ASTM 1618 Column Resolution Test Mixture

All chemicals and reagents are ACS reagent grade or better unless otherwise specified. If a source is not listed, any source that can provide the equivalent product is acceptable provided it is an approved state vendor.

Reagent Preparation

ASTM 1618 Column Resolution Test Mixture – Combine 1 vial of the ASTM –1618 Column Resolution Test Mixture in 10 ml of Carbon Disulfide.

4.4.3 Procedural and Chemical Precautions

See Section 6.0 of this manual for all safety precautions.

4.4.4 Limitations –

This procedure is limited to petroleum based oils with a carbon number range of 18-60+. For vegetable or animal based oils, see “Analysis of Vegetable Oils and Animal Fats”.

For items supposedly stained with oil, a visible stain has to be present.

Burned material from which a sample has been extracted usually contributes extraneous components. The presence of these extraneous product components is acceptable when sufficient product compounds remain to allow proper classification of the sample. When the product becomes overwhelmed by extraneous components, identification is not possible.

Extracts that meet the criteria for heavy petroleum distillates should be reviewed carefully to determine whether “extraneous components” that are the result of polyolefin or high molecular weight hydrocarbon (asphalt) decomposition are present.



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4.4.5 Quality Control/Quality Assurance Procedures

Each lot of carbon disulfide must be checked for purity by evaporating a sample of the solvent to one half the original volume and analyzing the evaporated solvent in the same manner as submitted cases. This chromatogram will be maintained in the Microanalysis Unit of the laboratory.

Reference oils, greases, and lubricants must be analyzed in the same manner as submitted cases.

Evidence identified as control samples that are received into the laboratory from an officer will be treated the same as all other evidence and reported as such. Sometimes, an officer will submit an empty container to be analyzed to verify the cleanliness of a batch of containers. The results of this analysis will be reported directly to the officer and not included in an Official Report.

An autotune will be run on the GC/MS each day the instrument is used.

4.4.6 Procedure -

Evidence may be photographed as case file documentation.

Document the evidence in the case by filling out a Fire Debris Worksheet (handwritten or electronic, located in the Microanalysis Forms and Log folder in Ensur) for each exhibit or writing the case information on paper.

Based upon the evidence descriptions and case details, determine which recovery method is most appropriate for the submitted evidence. Document recovery method in case notes:

Solvent Wash Recovery

If the item to be solvent washed can be divided, only a portion of the item should be extracted. A description and/or photograph of the extracted item will be included in the case notes.

Place the item over or in a clean beaker or tray free of extractable hydrocarbons and wash with carbon disulfide under a hood. When



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the inside of the container is to be analyzed, the carbon disulfide is placed inside, capped, swirled, and allowed to set. CAUTION: Vapors may cause the lids on the container to pop off, sometimes explosively. Slowly open lids to release pressure.

Collect the liquid and evaporate to an appropriately small volume under a hood.

Place concentrate into an appropriately labeled vial or bottle.

Prepare instrument for analysis using instrumental method "Hi-Temp.m". Instrument parameters are retained as method files on the instrument computer and are electronically attached to each data file. Following are the critical parameters for this analysis.

Oven Temperatures

Initial temp 60°C
Initial time 2.0 min
Ramp rate 20°C/min
Final temp 300°C
Hold time 6.0 min

Gas Type

Helium – constant flow mode

Column Type

30m x 0.25mm x 0.25µm 100% methylsilicone or 5% phenyl methylsilicone with a high temperature limit at or above 300°C

Mass Spectrometer Parameters

Autotune file atune.u
Mode Scan
Solvent Delay 0.00min
Low Mass 20 amu
High Mass 350amu
MS Quad temp 150°C
MS Source temp 230°C

Injection

Volume 1.0 µL

The inlet may be set for splitless injection (0.05 min purge time, 100mL/min purge flow) or split injection (200:1 split ratio) depending on the concentration of the sample.



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Samples will be analyzed as an autosample sequence or hand injected.

Autosample

Create autosample sequence using instrument software. The sequence will contain ASTM check mixture at the beginning and end of sequence, blanks before each sample, and samples in the order they are to be analyzed.

Place vials into autosampler tray and check to ensure they are in the same order as listed in the sequence. Document this check in case notes. Also document in case notes that blank vials, wash bottles and ASTM test mixture vial have been checked. Save sequence and begin the analysis run.

Once the run is completed, re-check the sequence order of the sample vials and document in case file. Each sample will be placed back in the container to which each is related

Hand Injection

If the sample is to be hand-injected, prepare the instrument using the parameters listed above and inject 1 μL of sample. A solvent blank must be analyzed prior to analyzing each sample. The ASTM test mixture must be analyzed with each case.

Known oil, grease, or lubricant standards will be prepared from submitted standards or from a standard in the TBI reference library for comparison purposes.

All data generated during the analysis must be retained in the case file.

Direct Injection

Place a small aliquot of the liquid sample into an autosampler vial and dilute with carbon disulfide. Solid waxy samples will be dissolved in carbon disulfide (or other appropriate solvent) for analysis. Use of other solvents will be documented in case notes.

This sample vial will be analyzed as above.

Interpretation and Comparison



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Total ion chromatograms (TIC) are generated for all known and unknown samples. These TICs are compared based upon retention time and pattern symmetry, width and apex of the unresolved peak envelope. Mass spectra may also be generated and searched against the mass spectral library. If the TICs between the unknown sample and the known standards are consistent, the comparison is complete. If the mass spectra indicate that the composition is inconsistent, the comparison is complete. Chromatograms and mass spectra will be retained in the case file along with the instrument parameters and autosample sequence table.

4.5 Instruments and Equipment

1. Gas Chromatograph/Mass Spectrometer, capable of scanning at least 40-400 m/z, equipped with methylsilicone or phenylmethylsilicone high temperature limit columns. The GC/MS system must be able to retrieve a specified mass spectral scan for a data file and compare it against a library of mass spectra available to the data system.
2. Syringe
3. Scalpel blades/ butcher paper/scissors
4. Beakers/glass trays free of extractable hydrocarbons
5. Photographic equipment with accessories

4.6 Measurement Traceability

Oil, grease, and lubricant examinations and comparisons are qualitative techniques and as such do not utilize measurements that will have a significant effect on the outcome of the analysis.

4.7 Reference Materials

A reference collection of various commercially available oils, greases, and lubricants will be maintained in the Microanalysis section. This collection will be used for classification, training and interpretation purposes. The collection generally will be in the form of small quantities of liquids. The samples will be identified and documented. The collection shall be maintained in a location that protects it from contamination and alteration.

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4.8 Reports—

The following are possible results concluded from the examination:

Analysis of this exhibit did not reveal the presence of any petroleum-based oils, greases or lubricants.

Analysis of this exhibit revealed the presence of a heavy petroleum-based product. Products in this range include but are not limited to: oils, greases, and lubricants.

Analysis of this exhibit revealed the presence of a product which could not be positively identified or classified due to the deteriorated condition of the sample.

Comparison of the recovered heavy petroleum-based product with the submitted standard revealed them to be consistent with respect to (list).

Comparison of the recovered heavy petroleum-based product with the submitted standard revealed them to be inconsistent with respect to (list).