Analysis of Lubricants, Waxes, Oils, and Related Compounds

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1 INTRODUCTION

This procedure allows for the analysis of a wide variety of lubricant materials (e.g., petroleum products, waxes, oils) that may be relevant to many types of investigations (e.g., sexual assault, drug trafficking, vehicular hit-and-run). Identification of a specific substance is not always possible, however a general classification is typically achievable.

2 SCOPE

This procedure applies to Chemistry Unit (CU) personnel that are qualified and authorized to examine evidence for the presence of lubricants, waxes, oils, and related compounds.

3 EQUIPMENT

- General laboratory supplies
- Common laboratory glassware and equipment
- Analytical balance
- Stereo microscope
- Polarized Light Microscope (PLM)
- Digital microscope (includes PLM capability)
- Ultraviolet (UV) light source
- CrimeScope CS-16 light source
- Video Spectral Comparator (VSC)
- Evaporator
- Fourier Transform Infrared (FTIR) spectrophotometer with Attenuated Total Reflectance (ATR), transmission, or microscope attachments
- KBr FTIR transmission cards (International Crystal Laboratories, or equivalent)
- High temperature gas chromatography with flame ionization detection (GC-FID) equipped with a 15 meter Zebron “Inferno” ZB-1HT column (or equivalent)
- Gas chromatograph/mass spectrometer (GC/MS) equipped with an electron impact ionization source and a 30 meter DB-5 column (or equivalent)
- GC/MS equipped with a chemical ionization source and a 30 meter DB-5 column (or equivalent)
- Time-of-flight mass spectrometer with direct analysis in real time ionization source (DART/TOFMS)
- Scanning electron microscope with energy dispersive X-ray spectrometer (SEM/EDS)
- Carbon disulfide
- Chloroform
- Deionized water
- Glycerin
- Hexane
- Iodine
- Methanol
- Nonoxynol-9 (Ipegal®CO-630)
- Polydimethylsiloxane (PDMS, Dimethylpolysiloxane)

- Polyethylene glycol (PEG, 550 average molecular weight)
- Potassium Iodide
- Starch

4 STANDARDS AND CONTROLS

4.1 Negative Control

A Negative Control will be prepared by mirroring the process used to prepare a sample from a questioned item. For example, use the same volume of solvent from the same source and lot and within a similar container used to extract or dissolve a questioned item(s). If swabs are submitted as evidence, a blank swab (preferably from the same source as the evidence swabs) extracted in the same manner as the questioned item(s) will be used as a Negative Control. In some instances, an extract from a portion of the item(s) which does not contain a stain of interest may be selected for use as a Negative Control. It is left to the discretion of the examiner/analyst as to what constitutes an adequate Negative Control.

4.2 Positive Control

A Positive Control will be prepared from an appropriate reference or known material. When appropriate the Positive Control will be prepared within a matrix that best mimics the questioned item(s). Similarly, where relevant, the concentration of the Positive Control will be prepared to mimic the questioned item(s). It is left to the discretion of the examiner/analyst as to what constitutes an adequate Positive Control.

5 PREPARATION OF POTASSIUM IODIDE/IODINE COLOR TEST REAGENT

The Potassium Iodide/Iodine Working Solution will be verified at the time of use through the testing of Negative and Positive Controls. The amounts of materials indicated in this section may be scaled up or down as necessary.

5.1 Potassium Iodide/Iodine Stock Solution

Prepared by adding 6 grams of potassium iodide and 0.8 grams of iodine crystals to 100 mL of deionized water. Store the solution at room temperature in a brown/amber colored glass bottle.

5.2 Potassium Iodide/Iodine Working Solution

Prepared by diluting the potassium iodide/iodine stock solution 1:100 with deionized water. Store the solution at room temperature in a brown/amber colored glass bottle.

6 SAMPLING

Typically, one or more samples (e.g., cuttings) are selected from the stained area(s) of the questioned item. When multiple samples are selected from the same item, the samples are typically combined prior to extraction.

Multiple items that are packaged together (e.g., swabs) or otherwise in contact with each other will typically be sampled as one collective item. For example, if two swabs are packaged

together, one swab (or a portion of the swab) will typically be sampled as representative of the swabs. Multiple swabs may be sampled and extracted together if the staining appears to be minimal.

Statistical sampling is performed according to GENCHEM-301.

When non-statistical sampling is utilized on a heterogeneous item, the results of examinations will be clearly limited to the sample(s) that were selected and analyzed.

7 PROCEDURE

Refer to GENCHEM-302 for specific instrument settings and decision criteria.

7.1 General Lubricants Analysis

A. Perform a visual and/or microscopic examination and note any distinguishing characteristics about the item. Items with no readily visible stain/substance will be analyzed using alternate light sources (e.g., CrimeScope, UV light, VSC). Any stain/substance that is subsequently visualized will be documented by photography or digital imaging, if possible.

B. If possible, directly sample any questioned substance from the substrate with a non-porous utensil (e.g., spatula, tweezers) and transfer to a labeled test tube. Use an empty, labeled test tube as a Negative Control. Analyze the directly sampled substance by FTIR. Analyze Positive Control(s) as deemed necessary.

C. If the stain/substance cannot be directly sampled, take a small cutting and transfer it to a labeled test tube. Use an empty, labeled test tube as a Negative Control.

D. If cutting is not practical, sample the area with a swab (dry or wetted with an appropriate solvent) and transfer the swab to a labeled test tube. Prepare an appropriate Negative Control swab and transfer it to an empty, labeled test tube.

E. Extract any directly sampled substance(s), cuttings, and/or swabs and the associated Negative Control(s) with a solvent such as hexane, carbon disulfide, or MeOH:$CHCl_3$ (1:1).

F. Transfer the extracts to new, labeled test tubes. Save the original test tubes for section 7.2 below.

G. Centrifuge the extracts if any particulate matter needs to be removed. Decant and/or filter the extracts as necessary. Any solids may be analyzed by steps (E), (F), and/or (G) in section 7.2, as deemed necessary [and after adding a minimal volume of deionized water for steps (E) and (F)].

H. FTIR- use either ATR or Transmission Cards as described below. Extracts of directly sampled substance(s) that were previously analyzed by FTIR do not need to be re-analyzed.

1. ATR

Analyze the extracts by FTIR by evaporating 2 or 3 drops of the extract directly onto the ATR accessory. Ensure the ATR accessory is contamination-free prior to analyzing each sample by evaporating 2 or 3 drops of blank solvent (the same solvent and lot used to prepare the extracts) on the ATR accessory and recording the FTIR spectrum. The ATR accessory may need to be cleaned multiple times for the blank solvent to result in a contamination-free spectrum. The extract(s) may need to be concentrated and then re-analyzed if the FTIR spectrum is too weak. If the extract(s) is concentrated, the associated Negative Control(s) will also be concentrated in a similar manner and re-analyzed by FTIR. Analyze Positive Control(s) as deemed necessary.

2. Transmission Cards

Set the Experiment Setup to "Collect background after every sample". An air background is collected for each sample (not a blank transmission card). When inserting transmission cards into the card holder, ensure the cards are fully inserted to be flush with the bottom of the card holder (the beam height is ~3.5" from the base plate). Wait approximately 30 seconds after closing the compartment for purging to occur.

Collect a spectrum of the blank card that will be used to contain an extract residue. Analyze the extracts by evaporating ≥ 5 uL onto the center of the previously analyzed card and then collect a spectrum of the evaporated residue. After collecting a spectrum (blank cards and extracts), perform the following corrections:

- "Process" - "Automatic Baseline Correct", followed by
- "Process" - "Other Corrections" - "Atmospheric suppression"

The corrected spectra will be indicated with an asterisk after each correction.

Additonal sample can be added to a previously analyzed card by evaporating another aliquot of the same extract onto the same area of the card. Alternatively, the extract(s) and associated Negative Control(s) can be concentrated and re-analyzed by evaporating onto the same card or a new card.

Analyze Positive Control(s) as deemed necessary; remember to collect a spectrum of the blank card prior to evaporation of the Positive Control onto the card.

I. Analyze the extracts by high temperature GC-FID. When possible, similar amounts of questioned and known samples will be analyzed for comparison purposes. For most compounds, a solution of ~0.001% to 0.01% provides an adequate signal,

however some compounds (e.g., PDMS, PEG) may require higher concentrations (e.g., ~1% to 2%). Analyze Positive Control(s) as deemed necessary.

J. For comparisons, if a questioned sample was not differentiated from a known sample by high temperature GC-FID, then GC/MS (EI and/or CI) will be used. However, if samples are suspected to contain PDMS or PEG (or other incompatible substances), do not analyze by GC/MS.

K. Elemental analysis (e.g., SEM/EDS) may by employed as necessary on directly sampled substances. For example, some greases may contain metallic soaps (e.g., aluminum, sodium, or calcium stearates). Analyze Positive Control(s) as deemed necessary.

7.2 Analysis for Water Soluble Substances

A. Allow the above extracts test tubes from section 7.1 to air dry.

B. Add a minimal amount of deionized water to extract any water soluble substances that may be present (e.g., nonoxynol-9, glycerin, starch).

C. Centrifuge the aqueous extracts if any particulate matter needs to be removed. Decant and/or filter the extracts as deemed necessary.

D. Analyze the aqueous extracts by DART/TOFMS in the positive ionization mode by sampling the extracts with the closed end of a glass capillary. Analyze the Negative Control(s), Positive Control(s), and PEG within the same data collection file. Negative ionization mode may also be used as deemed necessary.

E. The aqueous extracts and a Positive Control may be analyzed by PLM for indications of starch. Transfer 2 or 3 drops of each onto separate glass slides with cover slips and look for the presence of Maltese crosses. Any positive results will be photographed.

F. If a positive result for starch is obtained by PLM, the glass slides may be processed with Potassium Iodide/Iodine Working Solution. Place 1-2 drops of the Potassium Iodide/Iodine Working Solution onto the aqueous extracts slides and Positive Control and observe under a stereo or digital microscope. The presence of small blue/purple particles indicates the presence of starch. Any positive results will be recorded.

G. The residue from dried aqueous extracts may be analyzed by SEM/EDS and/or FTIR for the presence of talc, silica, or other related components. Analyze Positive Control(s) as deemed necessary.

8 LIMITATIONS

The physical nature of the sample (e.g., sample amount, matrix) may limit or preclude some techniques from being performed. It is not always possible to identify a lubricant, however classification is typically achievable. The following conclusions apply to the analysis of lubricants and/or comparisons involving lubricants:

- Identification (i.e. identified)
- Consistent with
- Not identified
- Cannot be differentiated
- Excluded
- Inconclusive

Refer to GENCHEM-903, GENCHEM-201, and Department of Justice Uniform Language for Testimony and Reports for General Forensic Chemistry and Seized Drug Examinations for examples of reporting examination conclusions and the associated limitations and decision criteria.

Refer to GENCHEM-302 for instrumental limitations and decision criteria.

Refer to GENCHEM-303 for mass spectra comparison decision criteria.

9 REVISION HISTORY

Revision	Issued	Changes
05	05/06/2022	Revised to match new format requirements. No substantive changes to content.
06	11/15/2024	• Added KBr FTIR transmission cards and carbon disulfide to Section 3 equipment list; deleted trichloroethane • Sections 4.1, 4.2- changed “examiner” to “examiner/analyst” • Added procedure for FTIR transmission cards, see Section 7.1 H • Deleted previous Sections 7.1 I and J; merged content into Section 7.1 E • Deleted previous Section 7.1 K (became redundant with reorganization of the section)