Microscopical Examination and Elemental Analysis of Automotive Lubricating Greases

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INTRODUCTION

Automotive greases may be recovered as stains on the ground at an automotive accident scene or on the garments of a suspect or victim allegedly involved and under investigation. Few studies have been performed differentiating automotive motor oil for forensic applications [1-3], however little research has been conducted to characterize or differentiate automotive greases.

This study aims to determine the physical and chemical properties that allow a reliable identification and differentiation of pure automotive lubricating greases. It also aims to expand the consideration of potential trace materials that could help investigators or forensic laboratory personnel in the commission of crimes involving vehicles.

35 brand new commercially available grease samples were examined using light microscopy for potentially discriminating features. This initial microscopical examination showed the presence of microscopic particles that were part of the original formulation of the grease samples. (Figure 1).

Initially, the use of Fourier Transform infrared (FTIR) spectroscopy yielded less than ideal data for these grease particles [4]. Attempts were then made to characterize the observed particles using scanning electron microscopy coupled with energy dispersive x-ray spectroscopy (SEM/EDS), and this also did not yield informative results due to sample charging and oversaturation of the detector. An oil solid separation method to extract these particles from the grease medium was then developed based on the investigation of three solvents (hexane, pentane and D-limonene).

These particles differed considerably in terms of shapes, sizes, and concentration between the different grease samples and are thought to be characteristic of greases and their additives. The characterization of these particles may enable the differentiation of automotive greases.

MATERIALS AND METHODS

Extraction of particles

- Investigation of 2 petroleum solvents (*n*-hexane and pentane) and 1 green solvent (D-limonene) was conducted
- 0.5 g of each grease was placed into a 20 mL glass vial with 15 mL of each solvent. The sample was capped and left to dissolve for 15 minutes with occasional swirling (Figure 2).
- After dissolving, the solution was decanted into a 125 mm Whatman No.1 filter paper and gravity filtrated for 1 hour (Figure 3).
- The filter paper was then air dried for 1 hour in the fume hood (Figure 4).

Microscopy of extracted samples

- The dried extracts were mounted with xylene and characterized using the Leica DM750p microscope.
- Microscopy revealed that all solvents dissolved with similar efficiency and D-limonene selected for further extractions due to green chemistry concerns

SEM/EDS of extracted samples

- The dried extracts were crushed between two glass slides and stamped with a GSR stub.
- The GSR stub was coated with gold using a Cressington 108 Sputter Coater.
- SEM-EDS data was collected on a Hitachi SEM SU3500 scanning electron microscope with Bruker Quantax XFlash ® 6 energy dispersive spectrometer and backscatter detector with an accelerating voltage of 20 kV and working distance of 10 mm.
- The EDS was calibrated to a copper tape standard.

Figure 2. Five grease samples being dissolved in solvent

Figure 3. Gravity filtration of sample 005 using Whatman filter paper

Figure 4. Sample 005 extract air dried on the filter paper

RESULTS AND DISCUSSION

- Microscopical observations of the dried extracts showed that the three solvents tested dissolved the five grease samples with similar efficiency, while also leaving the microscopic particles of interest intact.
- Considering each solvent was successful for each grease, it is likely a universal extraction using this method could be performed on all grease samples for further analysis.
- Based on the extraction efficiency of the three solvents, D-limonene was chosen over other petroleum derived solvents due to green chemistry concerns.
- The particles were more densely packed following their extraction from the grease, which can be attributed to the removal of the base oil and subsequent conglomeration of the remaining thickener fibers (Figure 5)
- The extraction procedure allowed for the elemental characterization of the particles with SEM/EDS (Figure 6 and 7).
- Particles were found using the backscatter detector and selected based upon size (>5 µm).
- All grease samples tested were observed to contain niobium, molybdenum, and tungsten in levels above 1% /wt (Table 1).
- These elements are characteristic of solid lubricant additives within greases
  - Zirconium (Zr)→ α-zirconium phosphate (Zr(HPO4)·H2O)
  - Niobium (Nb)→ NbS_2 or $NbSe_2$
  - Molybdenum (Mo)→ MoS_2 or $MoSe_2$
  - Tungsten (W)→ WS_2
- Solid lubricants extend the useful range of conditions for the grease.
- Selenide (Se) found most likely comes from solid lubricant compounds ($MoSe_2$ or $NbSe_2$)
- Indium was only found in one sample

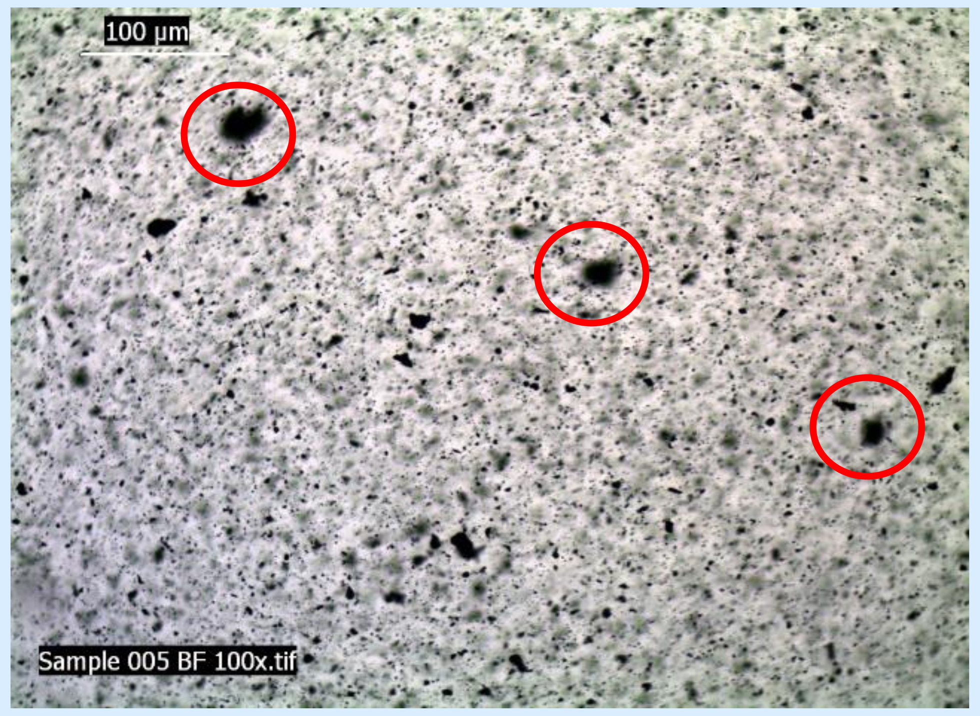

Figure 1. Photomicrograph of grease sample. Red circles indicate the observed particles.

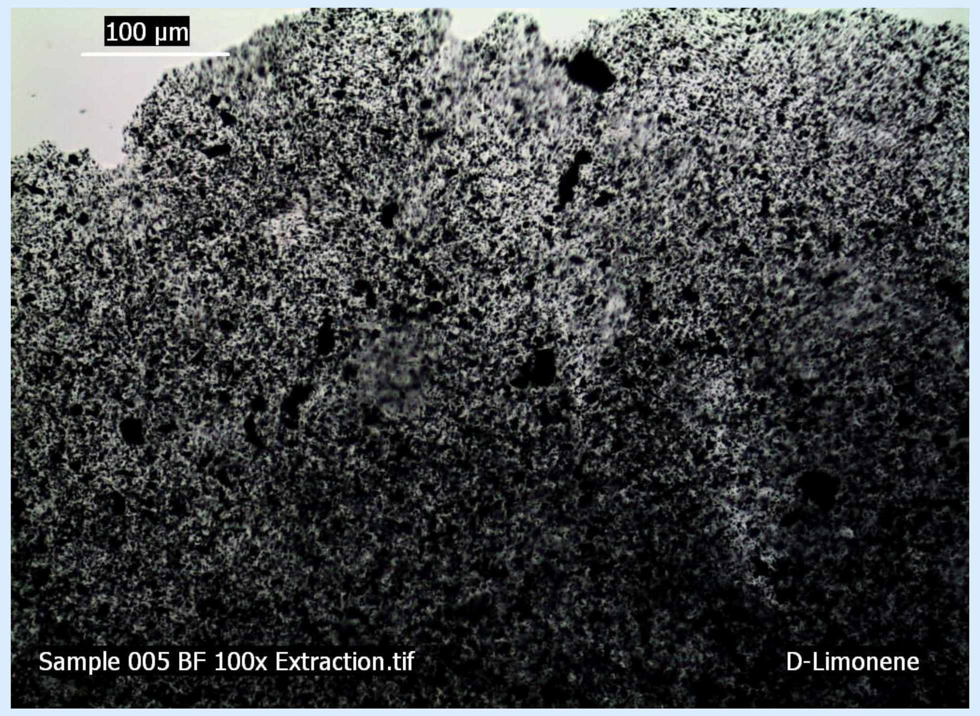

Figure 5. SEM image of grease sample 005 Red arrows indicate particles where measurements were taken

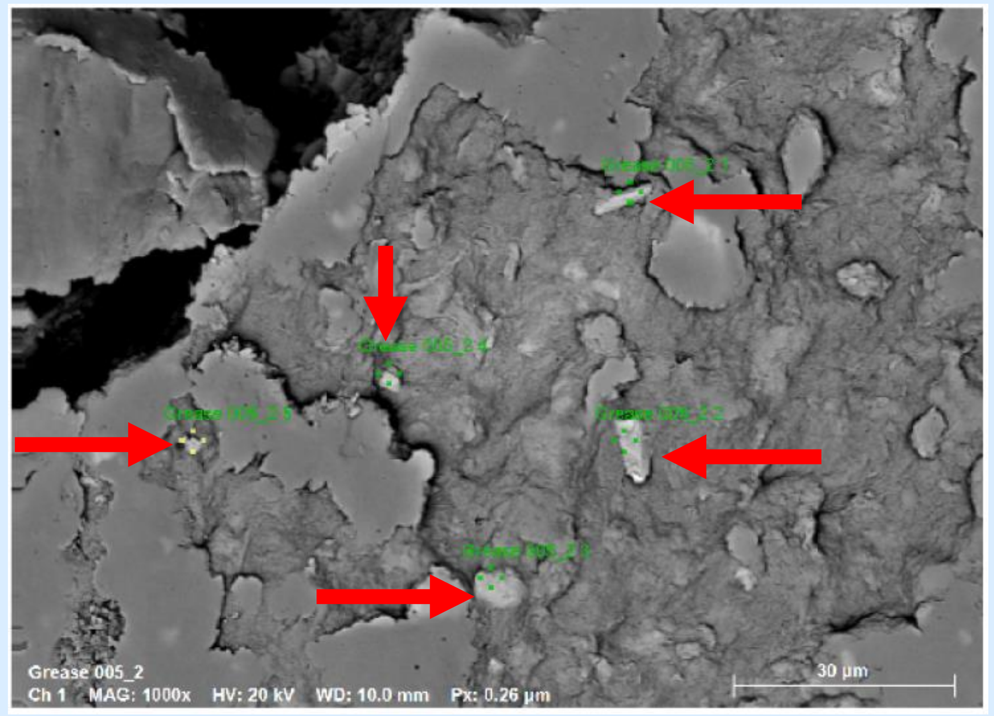

Figure 6. SEM image of grease sample 005 Red arrows indicate particles where measurements were taken

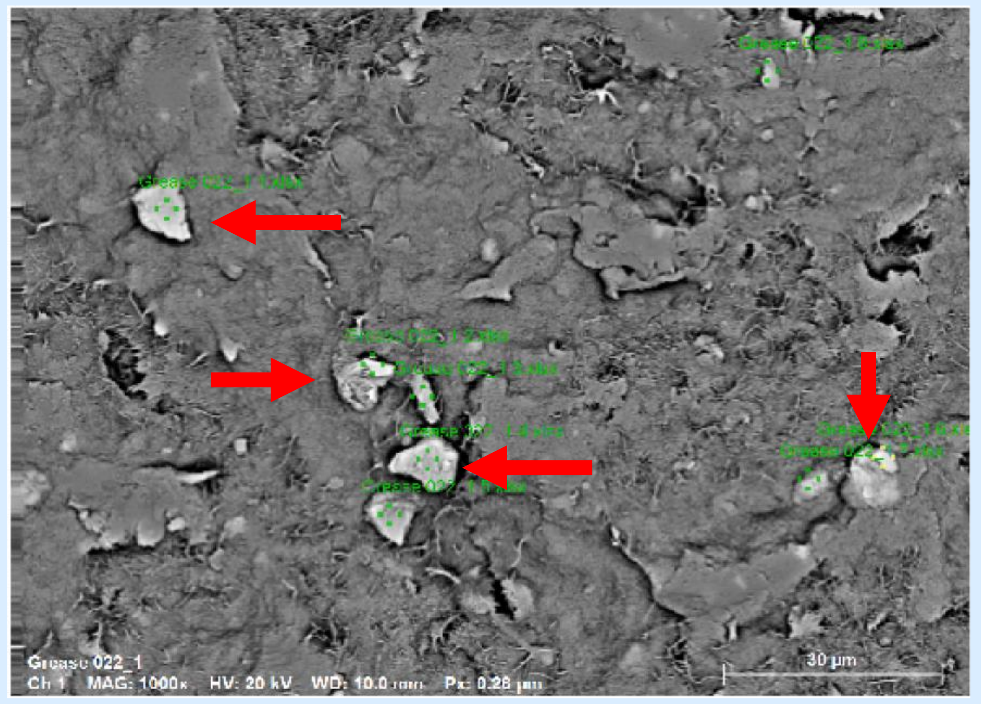

Figure 7. SEM image of grease sample 005. Red arrows indicate particles where EDS measurements were taken.

Normalized mass concentration [%]

Sample	Elements									
	Si	Cr	Se	Zr	Nb	Mo	Ag	In	Ba	W
005	0.00	0.11*	2.67	7.30	43.51	31.87	0.00	0.00	0.00	13.32
007	0.00	0.05*	0.00	16.00	53.86	0.00	0.00	0.00	0.00	28.27
015	0.00	0.05*	1.67	12.68	55.86	12.20	0.00	0.00	0.00	17.10
022	0.00	0.05*	2.39	10.16	48.33	21.82	0.00	0.00	0.00	16.97
023	0.00	0.04*	10.54	5.73	40.63	0.00	0.00	20.39	0.00	22.70
026	0.00	0.05*	11.90	0.09*	8.93	73.62	0.00	0.00	0.00	5.42
027	0.00	0.08*	8.79	1.63	23.44	58.01	0.00	0.00	0.00	8.06
030	0.00	0.06*	7.14	2.20	28.79	53.08	0.00	0.00	0.00	8.73
031	0.00	0.06*	6.26	0.89*	18.86	65.13	0.00	0.00	0.00	8.80

(*) indicates normal mass concentration less than 1%

Table 1. Normalized mass abundances for 9 opaque particle containing greases

CONCLUSIONS

- No relationships were observed between elements detected and grease type (Multi-purpose, marine, etc.)
- Different greases have different elemental composition ratios
  - Must be evaluated with standards
- Microscopical characterization determined 3 particle types
- For the extraction of the particles, D-limonene was chosen as the solvent
- Extraction result comparable to traditional solvents
- Environmentally friendly
- Abundance of the select elements indicates the opaque particles are solid lubricant additives

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