Development of an extraction method for the elemental analysis of microscopic particles in automotive greases using SEM/EDS

Forensic Technology CENTER OF EXCELLENCE

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1. Introduction

Automotive greases may be recovered from the ground at vehicle accident scenes or on the clothing of a suspect or victim. These lubricating compounds have the potential to link suspects or vehicles to crime scenes.

It was previously observed that many automotive greases have microscopic particles embedded in their matrix that were part of the original manufacturing process [1] (Figure 1). It is postulated that these particles are a discriminating characteristics of the greases and signatures of their original manufacturer.

Previous work using Fourier Transform Infrared (FTIR) spectroscopy and scanning electron microscopy coupled with energy dispersive spectroscopy (SEM/EDS) on these grease particles yielded inadequate results for characterization. Therefore, it was imperative that an extraction procedure for the removal of these particles from the grease matrix be developed so that they may be elementally characterized.

2. Purpose

The purpose of this work was to develop an extraction scheme for the removal of these microscopic particles from greases and enable their elemental characterization using Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy (SEM-EDS).

Three solvents were chosen based upon polarity and literature, including two petroleum solvents (n-hexane and pentane) and one green solvent (D-limonene) [2-5]. Five greases, identified by previous microscopy to contain the particles, were selected for extraction.

3. Methods

Extraction of particles

- 0.5 g of each grease was placed into a 20 mL glass vial with 15 mL of solvent and 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 removed and air dried for 1 hour in the fume hood (Figure 4).

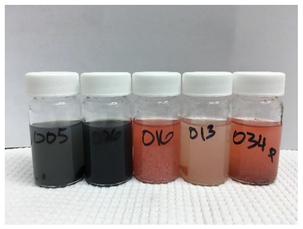

Figure 2. Five grease samples being dissolved in solvent

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

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

Microscopy of extracted samples

- The dried extracts were crushed and then transferred to a glass slide
- They were then mounted with xylene and characterized using the Leica DM750p microscope.

SEM/EDS of extracted particles

- 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.

4. Results and Discussion

- The microscopy 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 three solvents' extraction efficiency, **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).
- Some samples within the sample set also showed an abundance of tungsten and zirconium
- All grease samples tested were observed to contain niobium, molybdenum, and tungsten in levels above 1% /wt. Those were identified as transition metal dichalcogenides (TMDs) commonly used in industry to allow the use of a mixture of solid lubricants called composites which extend the useful range of conditions for the grease.

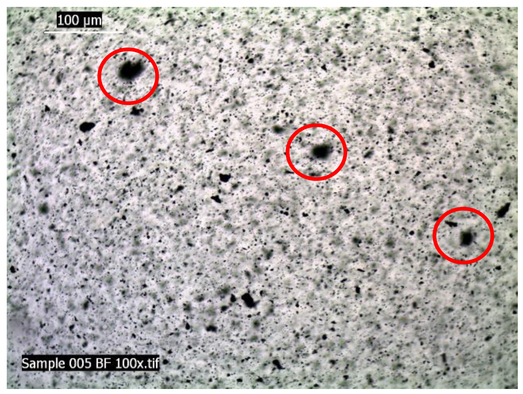

Figure 1. Microphotograph of grease sample. Red circles indicate the observed particles that were part of the original manufacturing formulation

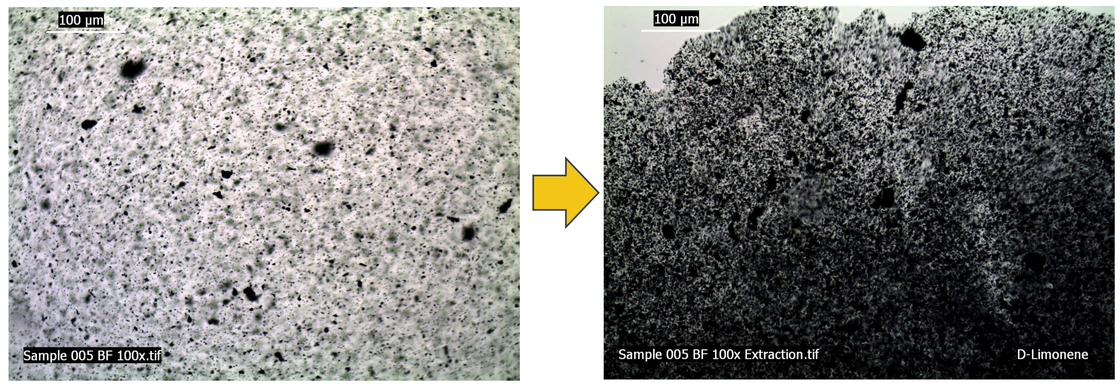

Figure 5. Microphotographs showing before and after extraction with solvent. The density of the components increased, suggesting the removal of the base oil

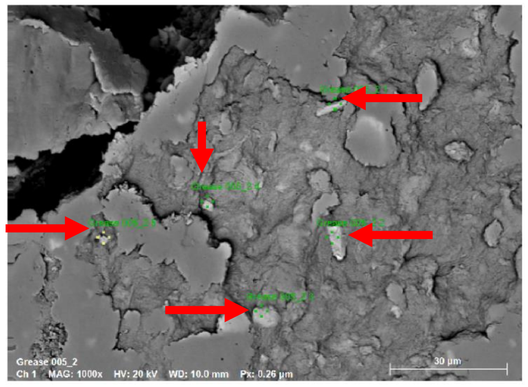

Figure 6. SEM image of grease samples. Red arrows indicate particles where measurements were taken

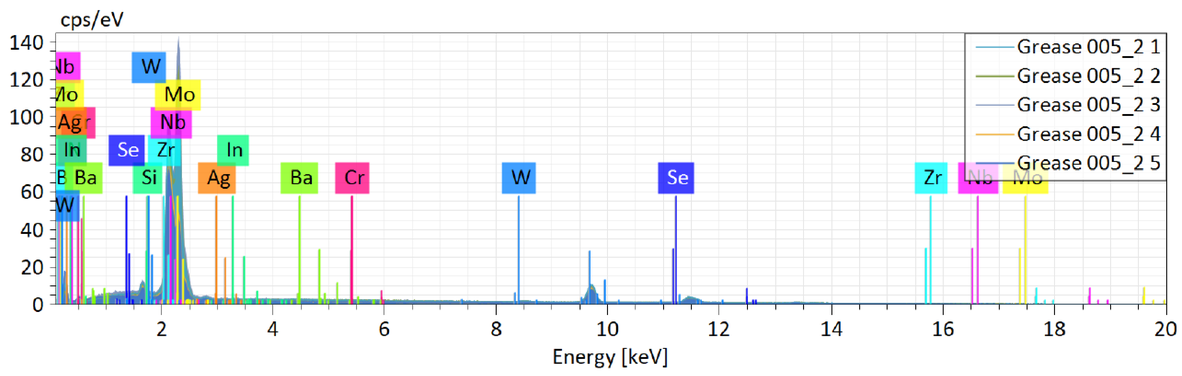

Figure 7. EDS spectrum of particles showing elemental composition of several particles within the greases. The main components found were molybdenum and niobium

5. Potential for Impact

- This work has the potential to expand the consideration of new types of trace materials to automotive greases
- May help add to body of evidence in casework involving a motor vehicle
- Expands the use of the SEM/EDS to other sample types and may help drive innovation in the future

6. Limitations

- Total extraction time on average takes 2 hours and 15 minutes, but this time is dependent on the grease. Some greases take longer in either extraction or drying time
- SEM/EDS is a semi-quantitative technique and outputs elemental data into abundance ratios
- A fully quantitative technique may be used such as inductively couple plasma- optical emission spectroscopy (ICP/OES), but this misses the value of visually selecting targets using SEM

7. Conclusions

- D-limonene is a well-suited solvent because of its efficiency and environmentally friendly nature when compared to other solvents such as n-hexane.
- The extraction procedure presented was able to remove the base oil quickly, and still leave the particles intact for further analysis.
- The developed extraction scheme allowed the grease samples to be characterized using SEM/EDS.
- SEM/EDS allows for the visual selection of particles for elemental composition, shape, size, and general morphology of the extracted particles.
- This study determined these particles to be solid lubricant additives within the greases with potential for discrimination.
- Further work will include the extraction of more greases and their full characterization using SEM/EDS.
- Further work will also investigate the potential of discrimination for these greases using the SEM/EDS data.

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More Information

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