Optical Spectroscopy for Analysis and Monitoring of Metalworking Fluids

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Abstract
For various industrial manufacturing processes, water-based metalworking fluids (MWFs) are of high relevance due to their cooling and lubricating ability. They commonly form oil-in-water emulsions or solutions and hence their composition and stability is crucial for their performance in the metalworking process. To ensure a long service life of the MWF, intense monitoring is obligatory. However, examination techniques which display comprehensive and precise information about the actual state of the cooling lubricant in use are currently not available. The present study aims at testing the suitability of spectroscopic methods in terms of Fourier transform infrared, Raman, and laser-induced fluorescence spectroscopy for analyzing and monitoring MWFs. It is shown that all three techniques are capable of determining the initial composition, i.e., the ratio of water and concentrate. Fourier transform infrared provides the best performance regarding monitoring the state of the fluid over an extended period of time. The spectral signatures show distinct changes during a five-month service life in a technical environment.

Keywords
Emulsion, metalworking fluid, laser-induced fluorescence, LIF, Raman, Fourier transform infrared, FT-IR

Introduction
Metalworking fluid (MWF) emulsions are employed in a wide range of metalworking processes. They play an important role as they act as lubricants and coolants at the same time.1 Chemically, MWF emulsions are highly complex systems. Water-based MWFs contain between 3–10% oil-based concentrate. They usually form oil-in-water (o/w) emulsions, i.e., they exhibit a continuous water phase with oil droplets as dispersed phase. In addition, there are a large number of additives to obtain the desired properties: emulsifiers, pH buffers, coupling agents, corrosion inhibitors, antioxidants, etc.2,3 Moreover, as the MWF is supposed to remain in the machine tool for an extended period of time, biocides are added to prevent or limit microbial growth.1,4 As a consequence, a commercial MWF emulsion can easily contain over a hundred individual chemical compounds. The interaction of all these compounds is yet to be fully understood and the development of new MWFs is therefore often based on trial-and-error experiments.1

The chemical complexity also poses a challenge to the analysis of MWFs. Water-based MWFs are provided as a concentrate, which is mixed with water prior to use. The analytical task can be to determine the ratio of individual components of a prepared fluid. Moreover, it is desirable to be able to evaluate the quality of the concentrate, e.g., to identify adulterated products. Thirdly, monitoring the quality of the MWF frequently during the service life is another important goal. The latter is particularly challenging as the chemical composition and biological contamination will change with time. The current state of the art is basically the monitoring of certain physical, chemical, and biological parameters such as pH value, the MWF concentration, the microbial burden or concentration of nitrate and nitrite,5 or the measurement of the oil concentration.6,7 Most of the methods employed require sampling and sample preparation, are time-consuming, require experienced personnel, and suffer from low accuracy. Examination techniques...
which display comprehensive and precise information about the current state of the cooling lubricant are currently available only to a very limited extent.\(^6\)

Recent developments on the other hand have shown that optical methods are promising in this context. For example, Fritsching and co-workers have established that turbidity spectroscopy in the UV and visible spectral range and laser diffraction are potential tools for monitoring MWF emulsions.\(^9,10\) They also demonstrated their method for monitoring the aging of a MWF emulsion over a period of 13 months.\(^11\) On the other hand, fluorescence and vibrational spectroscopy have not been used for this purpose to date, to the best of our knowledge. For completeness, we note that fluorescence, Raman, and Fourier transform infrared (FT-IR) spectroscopy have generally been applied to other emulsion systems, e.g., in the food and oil and gas sectors.\(^12–18\)

Therefore, the present study aims at testing and evaluating the potential of the following three methods: laser-induced fluorescence, Raman, and FT-IR spectroscopy. They are applied to fresh and aged MWFs. In the first part of the study, the capability of the methods for determining the concentrate content of a sample is evaluated. The second part focuses on the use of FT-IR spectroscopy for monitoring the MWF state during the five-month service life in a technical environment.

**Experiment**

*Applied Metalworking Fluid (MWF)*

The applied MWF was a conventional product based on mineral oil, but free of biocides in order to accelerate the aging process. The dilution series included samples of 2%, 3%, 4%, 7%, 10%, and 15% concentration. The dilutions were prepared mixing the MWF concentrate with tap water under stirring. The freshly prepared mixtures had a yellowish color and appeared rather transparent. For the Raman and fluorescence spectroscopy experiments, about 1 mL of each solution was filled into a vial (Duran culture tube, 5 mL), sealed by a three-layer septum (silicone rubber, type 76006, Hamilton AG, Bonaduz, Switzerland) and fixed with a GL 14 screw cap (Duran Group GmbH, Mainz, Germany).

The aging experiments were conducted with the same MWF in a 10% concentration emulsion. The aging process was conducted on a test facility, which simulated the technical environment of a metalworking machine tool. After 1, 3, 5, 7, 13, 15, 17, and 21 weeks, MWF samples (five times 1 mL) were taken and frozen to prevent microbial activity and stop the aging process prior the subsequent analysis.

**Fluorescence Spectroscopy**

Fluorescence spectroscopy is a widely used technique in engineering and the life sciences.\(^19–22\) The common approach is to illuminate the sample with radiation from a laser, the wavelength of which is matching an electronic transition of the molecules of interest. As a consequence, photons will be absorbed and the molecules reach an electronically excited state. In a second step, photons are emitted spontaneously when the molecules return to the electronic ground state. Between the absorption and the emission, internal energy transfer can lead to a redistribution of energy in the excited state. As a result, the emitted radiation is shifted in wavelength with respect to the incident photons leading to a characteristic fluorescence spectrum. A detailed account of fluorescence spectroscopy can be found in Lakowicz.\(^23\)

Fluorescence spectra were recorded with a custom-made experimental setup. The radiation of a frequency-doubled, diode-pumped solid state Nd:YAG laser (532 nm, 10 mW, continuous wave) was focused into the center of the sample contained in a vial using a 100 mm focal length lens. The emitted radiation was collected at 90° with an achromatic lens (75 mm focal length, 2.54 cm diameter), spectrally filtered (dielectric longpass filter, 550 nm cut-off, angle-tuned to shift cut-off wavelength close to laser line), and focused with a second achromatic lens (200 mm focal length, 2.54 cm diameter) onto the entrance slit of an imaging spectrograph (Acton, 300 mm, 1200 grooves/mm) equipped with an intensified CCD camera (Andor iStar).

**Raman Spectroscopy**

Vibrational spectroscopy is commonly performed in terms of Raman scattering and infrared (IR) absorption spectroscopy.\(^18,24\) Raman spectroscopy is the inelastic scattering of monochromatic laser light. Unlike fluorescence, the molecules are not excited resonantly and therefore the light-matter interaction can be considered instantaneous, as the lifetime of the intermediate state is negligibly short. During the scattering process, energy is transferred from the incident photon to the molecule, which remains in an excited rotational-vibrational state. Hence, the scattered photon has a reduced energy, which gives rise to a frequency shift with respect to the incident light. Since every molecule has a unique vibrational structure, the Raman spectrum represents a molecular fingerprint.

The Raman spectra of the fluids were recorded using an Avantes Raman bundle (Ava-Raman-C) with a 785 nm excitation laser and a resolution of ~6 cm\(^{-1}\). Recording ten spectra (1 s acquisition time each) from an individual sample showed very good reproducibility, i.e., the qualitative appearance of the spectra (relative intensities and peak shapes) remained almost identical between acquisitions and the absolute intensity varied less than 10%. The samples in the vials were used for the Raman measurements. However, here, the fiber optical probe (Avantes laser-probe combination) of the instrument was employed so that the spectra were recorded in backscattering mode.
The measurements were performed directly through the glass wall.

**Fourier Transform Infrared (FT-IR) Spectroscopy**

Infrared spectroscopy is an absorption method, in which the molecules are vibrationally excited directly by taking up a photon. The absorbed photon is removed from the radiation passing the sample, which gives rise to the absorption spectrum. Due to the different selection rules for absorption and scattering, the Raman and IR spectra provide complementary information. Detailed descriptions can be found in the literature.25–28

The IR spectra of the fluids were recorded on an Agilent Cary 630 instrument equipped with a diamond unit for attenuated total reflection (ATR) spectroscopy. The spectra were acquired from 650 to 4000 cm\(^{-1}\) with a nominal resolution of 2 cm\(^{-1}\). Before each measurement, the background was corrected. To perform a measurement, one droplet of a sample was placed on the diamond crystal. The instrument was located in a box made from Perspex and spilt with dry air to avoid the absorption of water from the surroundings. For each spectrum, 16 scans were averaged in order to obtain an appropriate signal-to-noise ratio.

**Data Analysis**

Two different methods have been employed to extract quantitative information from the data sets: a classical univariate technique and a multivariate method. For a systematic assessment of the univariate approach, a method that was originally developed for identifying suitable spectral features of ionic liquid solutions was utilized.29–31 The algorithm plots the intensity or absorbance values at a given wavelength as a function of concentration and then fits a linear function to the data points. The slope of the curve yields an estimate of the sensitivity of the spectral position to changes in the concentration, while the coefficient of determination \(R^2\) allows an assessment of the accuracy. This procedure is performed for all data points in the spectra and, consequently, the slope and \(R^2\) values can be plotted as a function of wavelength. High absolute values of the slope mean high sensitivity and \(R^2\) values close to \(R^2 = 1\) mean good accuracy. On the other hand, partial linear least squares regression (PLSR) was the multivariate method of choice.32,33 For this purpose, the plsregress routine implemented in Matlab was used with the number of components equal to 2, which was found to provide low complexity and high accuracy at the same time from plotting the root mean square error against the number of components.

In all cases, the raw spectra were fed into the data analysis without pre-processing (e.g., normalization, centering, smoothing, baseline removal, etc.).

**Results and Discussion**

**Analysis of Metalworking Fluid (MWF) Concentration**

A key task of the MWF monitoring is the determination of the composition. This does not necessarily mean to measure the detailed chemistry, which can consist of more than a hundred individual compounds. From a practical viewpoint, even the ratio between water and MWF concentrate is a useful quantity as it allows extracting information about the mixing or de-mixing status. In operation, the MWF concentration can fluctuate heavily depending on variables such as temperature (vaporization) and drag-out.

Fluorescence, Raman, and FT-IR spectra of the MWF samples exhibiting systematically varied amounts of the concentrate were recorded. The fluorescence spectra of the MWF samples are displayed in Fig. 1a. The spectrum of water is shown as a reference for comparison. It does not contain any appreciable signals, as the laser does not excite water molecules resonantly to fluoresce and is not powerful enough to generate significant amounts of Raman signals.

**Figure 1.** Fluorescence spectra and their evaluation. (a) Raw spectra of the fluids and reference spectrum of a water sample; (b) normalized slope and \(R^2\) spectra from the univariate evaluation; and (c) fitted vs. observed concentration determined by PLSR. The norm of residuals of the fit was 0.309.
signal. Consequently, the water spectrum represents a baseline. When the concentrate is added to water, the fluorescence spectrum reveals a distinct emission band peaking between 600 and 610 nm. The intensity of the overall band increases monotonically with the amount of concentrate. Figure 1b shows the slope and $R^2$ spectra of the univariate data analysis. The $R^2$ values are rather close to unity across the entire emission band between 550 and 800 nm. The slope spectrum, on the other hand, has a maximum at the position where the emission band peaks. This indicates that the optimal wavelength for determining the concentration of the MWF concentrate is around 610 nm.

Figure 1c shows the results of the PLSR analysis. The fitted versus observed MWF concentration values lie almost perfectly on the $x=y$ line. Hence, it can be concluded that PLSR is capable of extracting reliable concentration information from the fluorescence spectra.

Figure 2a displays the Raman spectra of the MWF samples and water. Despite the excitation in the near-infrared (NIR) at 785 nm, the spectra are dominated by a broad background. This background is most likely due to fluorescence as the previously discussed fluorescence spectra exhibit a certain intensity at 785 nm and beyond. Consequently, there are molecular transitions in this region, which can be excited resonantly to result in NIR fluorescence signals as the ones observed in Fig. 2a. The narrower and comparatively weak spectral signatures on top of the broad background are the Raman signals. They can be mainly observed in the fingerprint region (300–1700 cm$^{-1}$). At higher wavenumber, the sensitivity of the silicon-based detector of the instrument is low so that the CH and OH stretching modes of hydrocarbons and water do not manifest as appreciable signals. Without the use of sophisticated baseline correction methods, it must be concluded that the emission spectrum is governed by fluorescence despite the NIR excitation.

The $R^2$ and slope spectra in Fig. 2b are similar to the fluorescence case discussed above. The $R^2$ is close to unity across a wide spectral range and the slope exhibits a maximum where the signal in the raw spectra peaks. The PLSR results in Fig. 2c show a slightly increased scattering of the data points compared to the corresponding fluorescence plot in Fig. 1c.

For comparison, the same evaluation was performed after a baseline correction with the aim to extract the Raman signals and remove the fluorescence background. For this purpose, the method described by Schulze et al. was applied as it was successfully used in a recent study with data from the same instrument.$^{34, 35}$ The window size was varied systematically and the best results were found for a window size of 13. The results obtained are illustrated in Figs. 2d, 2e, and 2f. A strong band at low wavenumber dominates the background-corrected spectra. This can be attributed to elastically scattered light rather than a Raman

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**Figure 2.** Raman spectra and their evaluation. (a) Raw spectra of the fluids and reference spectrum of a water sample; (b) normalized slope and $R^2$ spectra from the univariate evaluation; (c) fitted vs. observed concentration determined by PLSR; the norm of residuals of the fit was 1.432. (d) Background-corrected Raman spectra; (e) normalized slope and $R^2$ spectra from the univariate evaluation derived from background-corrected Raman spectra; and (f) fitted vs. observed concentration determined by PLSR of the background-corrected Raman spectra; the norm of residuals of the fit was 2.026.
signal. The fingerprint region contains a number of low intensity peaks but they hardly correlate sufficiently well with the MWF concentrate content, as can be seen in Fig. 2e. A univariate evaluation with appropriate accuracy and sensitivity is virtually impossible if the spectral window around the elastic scattering peak is disregarded. In contrast, the multivariate PLSR works to some extent. However, it must be noted that the norm of residuals of the resulting fit is significantly larger than before the background correction: 2.026 versus 1.432, respectively.

Figure 3a displays the FT-IR spectra of the MWF samples and water. The spectra are clearly dominated by the signatures of water, i.e., the strong OH stretching band between 3000 and 3600 cm$^{-1}$, the bending mode around 1650 cm$^{-1}$, and the broad fingerprint bands. With increasing amount of concentrate in the sample, the OH stretching band becomes moderately weaker. At the same time, the signatures of the compounds in the concentrate appear. For example, there are CH stretching bands of hydrocarbons around 3000 cm$^{-1}$ and their corresponding deformation modes are present around 1400 cm$^{-1}$. Moreover, a weak signature appears around 1000 cm$^{-1}$ (see zoomed in region in Fig. 3a). The chemical richness of the commercial MWF concentrate makes it difficult to assign the individual peaks unambiguously. However, this work aims at a quantitative analysis rather than gaining structural information. In order to further emphasize the systematic changes with concentration, Fig. 3d shows the enlarged difference spectra. They were produced by subtracting the water spectrum from each individual mixture spectrum.

Beyond providing structural insights, the shape of the OH stretching band can be utilized as an indicator of the hydrogen bonding network. Previous work in emulsions has shown that the detailed analysis of this band can reveal valuable information about the working mechanism of the emulsifier.$^{12,13}$ In the MWF spectra, a characteristic change of the shape of the band compared to pure water is present. The observed reduction of the low-wavenumber wing indicates a weakening of the hydrogen bonding network in the water phase. Interestingly, the resulting shape is virtually identical for all MWFs suggesting that the effects are not concentration dependent in the considered range. This is in accordance with IR data from water-in-oil emulsions,$^{13}$ which suggests that the water-oil interfaces are rather saturated with emulsifier.

The $R^2$ and slope spectra in Fig. 3b are significantly different from those in the above fluorescence and Raman cases. There are only a few spectral positions where the $R^2$ value is sufficiently high for measurements with reasonable accuracy. Individual wavenumbers at the OH and CH stretching bands can be found, but the highest values are located in the fingerprint region around 1000 cm$^{-1}$. The slope spectrum shows distinct features as well. In terms of absolute value, the OH stretching band is highly sensitive to changes in the concentrate content. The corresponding $R^2$ indicates that the high sensitivity is at the cost of accuracy. In contrast, the CH stretching peak at 2932 cm$^{-1}$ is a better choice combining an $R^2$ of 0.9891 with a high slope. The optimal spectral position, however, is found at 1067 cm$^{-1}$: the normalized slope is 1 and $R^2 = 0.9986.$
Hence, the band highlighted in Fig. 3a is best suited for a univariate data analysis. The PLSR results in Fig. 3c show an excellent correlation as well.

From the above results and discussion, we can conclude that fluorescence and FT-IR spectroscopy are well suited for measuring the content of the concentrate in a MWF sample. Both methods provide good sensitivity and accuracy. Raman spectroscopy suffers from strong fluorescence interference and thus additional effort, experimentally and/or in the data analysis, is necessary to make it a useful approach. Experimentally, the excitation at 1064 nm would be an option shifting the spectrum closer to the IR. Other approaches include the use of shifted excitation Raman difference spectroscopy (SERDS) or the resonance enhancement of certain target species.

For univariate data analysis, suitable spectral signatures must be selected carefully. This selection is less crucial for fluorescence as a broad spectral range provides good sensitivity and accuracy. For the FT-IR spectra, two distinct spectral positions could be identified as best suited for the univariate data analysis. The evaluation with multivariate methods initially requires a thorough knowledge for performing the selection, calibration, and validation of the optimal approach. Once the method is established and calibrated carefully, it can be applied in a rather straightforward manner.

**Metalworking Fluid (MWF) Monitoring**

The second part of this study evaluates the capability of the analytical methods for monitoring the state of a MWF during long-term aging experiments in a technical environment. The spectra from the Raman instrument in the preceding section showed that the main features are due to fluorescence and the Raman signatures are weak. Therefore, Raman spectroscopy with 785 nm excitation was found to be of limited use here. The fluorescence spectra recorded with 532 nm excitation provided excellent results in the above assessment. However, for monitoring the MWF, fluorescence seems to be of limited use as well. Figure 4a shows photographs of the freshly prepared and used MWF samples. It can be seen that color and turbidity change significantly over the course of time, and so does the fluorescence spectrum. Extraction of reliable information was not possible. The only robust method for the MWF monitoring was FT-IR. The proof-of-concept is shown in the following.

The FT-IR difference spectra recorded from samples that were taken in intervals of a few weeks are displayed in Fig. 4b. From each FT-IR spectrum, the spectrum of the initial MWF sample was subtracted in order to highlight the changes. The difference spectra are plotted in chronological order from bottom to top. A number of distinct features can be observed. For example, there are increasingly negative signatures at the spectral positions of the OH stretching and bending bands. On the other hand, positive peaks can be found in the CH stretching and in the fingerprint region. Positive values mean an increase compared to the initial fluid, and negative values mean the opposite.

The development of these signatures is clearly correlated with the duration of use. This is further supported by a PLSR analysis with respect to the sample age in weeks; see Fig. 4c. It emphasizes that there are systematic changes in the spectra that allow the monitoring of the aging process. It is therefore possible to determine, how long the MWF has been in operation. However, it must be stressed that for the field deployment of the method, a significantly larger calibration data set will be required in order to capture the numerous independent processes that contribute to the overall aging state.

Moreover, the spectra indicate that the water content is decreasing with time and, consequently, the amount of non-water components increases. Water represents the continuous phase of the MWF and therefore the interface between the MWF and the ambient air is dominated by water, which can evaporate more easily than the other components.

![Figure 4. Spectroscopic MWF monitoring. (a) Photographs of the fresh and used (after five weeks) MWF; (b) FT-IR difference spectra; and (c) fitted vs. observed age determined using PLSR. The norm of residuals of the fit was 0.604.](image-url)
Conclusion

In this study, fluorescence, Raman, and FT-IR spectroscopy were tested as tools for analyzing and monitoring metalworking fluids (MWFs). The data sets obtained from freshly prepared samples and a fluid extracted from an aging experiment in the course of >20 weeks were evaluated using univariate and multivariate methods.

Fluorescence and FT-IR spectroscopy were found to be most suited for determining the content of MWF concentrate in a freshly prepared sample. The simplest and most straightforward approach to determine the concentration could be to excite the sample with a laser pointer at 532 nm and detect the emitted radiation with a photodiode equipped with a 610 nm bandpass filter. This approach could easily be implemented into a fluorescence-based sensor concept. FT-IR spectroscopy on the other hand usually requires a lab instrument.

Raman spectroscopy with NIR excitation at 785 nm resulted in strong fluorescence interference. It was in principle possible to determine the amount of concentrate, but the results were mainly based on the fluorescence signals rather than Raman scattering. Raman spectroscopy with a 1064 nm excitation laser or sophisticated SERDS and resonance Raman schemes may be a solution here.

For monitoring the state of the MWF over an extended period of time, FT-IR spectroscopy was found to be the optimal method as fluorescence suffered from the changes in color and turbidity of the sample. Extensive calibration may compensate for the effects, but this would no longer be a simple and straightforward analytical tool. The FT-IR spectra show distinct changes with time, which can readily be interpreted in terms of compositional changes. Another benefit of FT-IR is that the metal particles introduced into the fluid during operation will not cause any issues. In contrast, in Raman and fluorescence spectroscopy the additional light scattering by these particles may need to be dealt with. However, it must be kept in mind that the MWF is an emulsion; therefore, the level of scattered light is high anyway and the fluorescence measurements in the present work were not affected at all.

Eventually, it can be concluded that spectroscopic methods are capable of analyzing and monitoring MWFs. The most suitable technique for a given application however must be selected carefully. This regards both the experimental method and the data analysis approach. Future work will also aim at extending the analytical capabilities towards monitoring lubricant oxidation, identifying demulsification, and predicting possible failure.

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Conflict of Interest

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