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# Optical Spectroscopy for Biofuel Composition Sensing

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**Abstract**

The optical absorption of water-containing bio-fuel is investigated as a parameter to determine the gasoline content of this fuel. Optical measurements reveal that gasoline shows an interesting and useful spectrum with typical absorption behavior in the UV range between 230 and 300 nm. This result indicates that significant information can be obtained to determine the gasoline concentration in bio-fuel by UV absorption spectroscopy. A concept for a low-cost measurement system in the fuel line is presented, by implementing a LVOF in combination with a wide-band light source and detector arrays.

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## 1. Motivation

Bio-fuel typically consists of a gasoline/ethanol blend. The ethanol originates from different sources. Production of ethanol from sugar cane typically results in hydrous ethanol, hence causes some water in the resulting bio-fuel blend. Another cause for the presence of water in bio-fuel is the practice of fouling, water is added to increase profit. As a consequence the ternary mixture of ethanol, gasoline and water should be continuously monitored in the fuel line in order for Flex Fuel Vehicles to start smoothly and to run cleanly and efficiently on different compositions of bio-fuel. Currently available sensor systems only measure the permittivity of the fuel [1]. Their performance is not adequate, as operation is based on an assumed constant water concentration, therefore more information is required for a full fuel composition measurement [2].

## 2. Theory

Based on preliminary measurements the absorption in the UV range between 220 nm and 350 nm is strongly dominated by the gasoline content in the bio-fuel. According to the Beer-Lambert law, the total resulting absorbance is determined by the extinction coefficient $\epsilon_i$, the molar concentration $c_i$ and the optical path length $l$. If there is no

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interaction between the ethanol and gasoline fraction of the bio-fuel, the resulting absorbance should therefore be the summation of the absorbance of the separate components of the bio-fuel. The separate absorbance of gasoline, water and ethanol should therefore add up. If one of the three components is the dominating factor in the total absorbance, a linear behavior over the different mixing ratios is expected.

## 3. Measurements UV

### *3.1. Measurement Setup*

Multiple absorption measurements were carried out, in order to identify which parts of the spectra of the three components would be suitable. For these measurements, a Varian Cary 500 Spectrophotometer was used in combination with quartz cuvettes. This device uses a double beam, one for a reference sample and one for the actual measurement. Initial measurements revealed that the best results were obtained when an optical path length of 1 mm is used and when the gasoline/ethanol mixtures were diluted with a suitable solvent. Cyclo-hexane was chosen as the solvent, because of the low absorption over the entire UV-spectrum and the fact that it dissolves the relevant components well. During initial measurements it was already found that D.I. water does not absorb significant light in the UV range, hence does not interfere using this measurement technique.

Table 1: Measurement parameters

| Parameter | Value |
|---|---|
| Average time | 0.3 s |
| Spectral BW | 2.000 nm |
| Measurement range | 200-400 nm |
| Optical Pathlength | 1 mm |
| Cuvettes | Quartz |
| Solvent | Cyclo-hexane |

### *3.2. Gasoline/Ethanol Mixtures*

The absorption of gasoline/ethanol in different ratios was measured. Indolene 50E clear was used, which is a standardized test gasoline free of additives and coloring, in combination with the so-called 200 proof ethanol (>99.98% pure). The dilution ratio of 1/10 is used to optimally use the dynamic range of the spectrophotometer. No dilution is applied when measuring pure ethanol to prevent further loss of spectral information. As can be seen in figure 1 a suitable absorption peak is visible around 265 nm. Despite the dilution and the pathlength of 1 mm, saturation at minimum sensitivity setting results at 70% Indolene concentration and beyond. On the other hand, no saturation is present and the absorption is dominated by gasoline content at 240 nm. To investigate if this gasoline-dependent absorption behavior could be utilized in determining the composition of the initial ternary mixture problem, Indolene 50E was replaced with Unleaded Low Octane gasoline 87RON (Research Octane Number) in a new series of identical measurements and the results are shown in figure 2. The absorption behavior seems to resemble the measurements of Indolene gasoline, the spectral behavior is very similar. This result can be considered as promising in the final application of a future optical extension of the fuel composition sensor system in flex fuel vehicles.

To compare the absorption behavior of the different gasolines in combination with pure ethanol, the absorbance at two different wavelengths in the UV is plotted against gasoline content. The 240 nm wavelength was chosen, because of the local minimum, which has turned out to be typical for different gasolines. Because of the saturation effect at 265 nm, a higher dilution ratio or smaller optical path-length should be used at and around this wavelength. Because of the saturation effect in this setup at 265 nm, the wavelength 290 nm was chosen instead. The result is included in figure 3. It can be concluded from this plot that the relationship between gasoline content and optical absorbance is linear, and the slope between both is dependent on the used wavelength. Since both gasolines have different compositions, this explains the discrepancy at higher gasoline content.

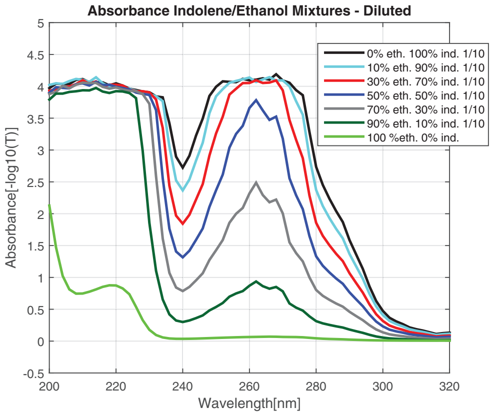


Fig. 1: The measured absorbance of different ethanol/indolene ratio's. The dilution ratio is included in the legend.

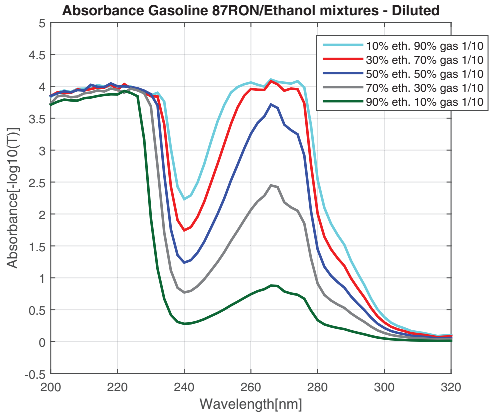


Fig. 2: The measured absorbance of different ethanol/gasoline ratio's. The dilution ratio is included in the legend.

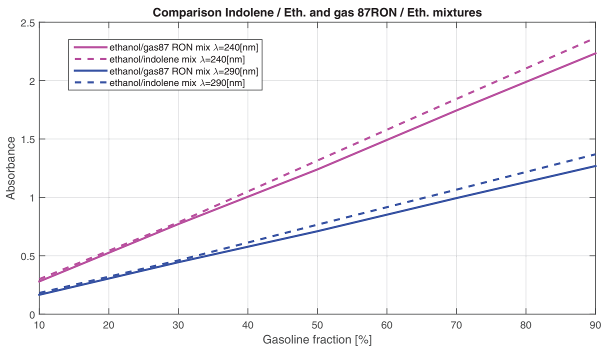


Fig. 3: The absorbance as function of the gasoline fraction. Compared are the 87RON and Indolene mixtures at two different wavelengths.

### *3.3. Octane content and Summer/Winter grade*

During the research, some practical 'off the shelf' fuel blends were available. Again, absorption measurements were carried out to investigate the dependency on octane number and summer/winter blends. The results are included in figures 4 and 5. The effect of the octane content on the absorption behavior is very small, it can also be concluded that the higher volatility winter fuel behaves similarly to the E85 summer version. This result can be considered as promising, since insensitivity for these type of uncertainties is preferred. Note the different dilution ratios that were used to prevent loss of spectral information.

## 4. Implementation technique

As discussed before, a spectral measurement on three optical channels centered at 240 nm, 265 nm, and 290 nm is sufficient for a complete composition analysis. However, according to the spectral measurements presented in Fig 1 and 2, a spectral resolution of about $\delta_\lambda = 1$ nm is required for such an analysis. Mass fabrication of high resolution fixed filters, considering the process tolerances, is challenging. The use of UV LEDs and UV photodetectors would require high performance optical filters, therefore a Linearly Variable Optical Filter (LVOF) type microspectrometer system is proposed [3]. The LVOF is composed of two reflectors separated by a cavity. The depth of the cavity determines the transmission wavelength. The resolution is determined by both the reflectivity and the cavity depth.

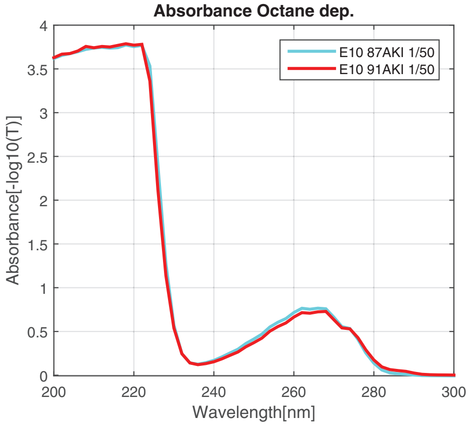


Fig. 4: Two representative American gasolines, low and mid grade octane rating compared. Note the higher dilution ratio.

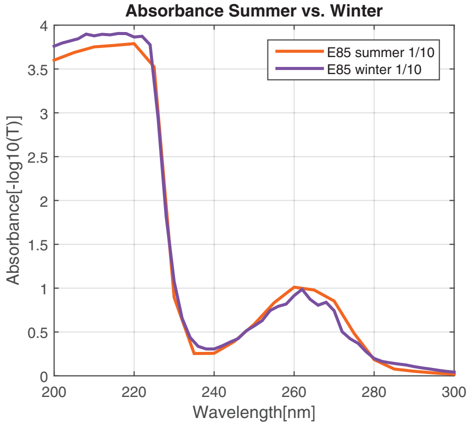


Fig. 5: The summer and winter grade E85 compared. The same dilution as previous gasoline/ethanol mixtures is used.

Figure 6 shows the schematics of the optical sensor design. The structure consists of four main components: 1) a light source, 2) a sample cell, 3) LVOF, and 4) the photo detectors. Advantages of LVOF-microspectrometer designs are the CMOS compatibility and high spectral resolution when operated over a relatively narrow band. Therefore, a sensor system based on multiple-LVOFs centered around the intended spectral channels is promising for this application.

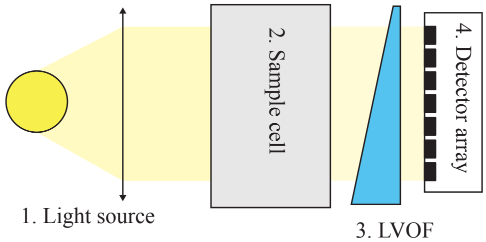


Fig. 6: A schematic overview of the measurement system based on an LVOF.

## 5. Conclusion

Two different gasolines were used to investigate the effect of gasoline content in bio-fuel on the optical absorption. It was found that there is a reproducible linear absorption behavior between both, but at high gasoline concentrations there is a small discrepancy between both. It was found that the octane content and the summer/winter grade had a negligible influence on the spectral behavior. Some more research in this findings, also considering the chemical composition of gasoline, is required to fully understand the underlying mechanisms. An advanced implementation technique based on a LVOF based spectrometer was proposed.

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