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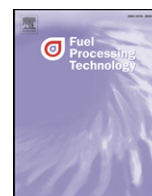
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Research article

Multi-domain spectroscopy for composition measurement of water-containing bio-ethanol fuel



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ABSTRACT

Measuring the ethanol/water ratio in biofuel of high ethanol content, such as E85, is important when used in a flex-fuel engine. A capacitive probe is generally used for measuring the ethanol/gasoline ratio. However, the water content in E85 biofuel cannot be disregarded or considered constant and full composition measurement of biofuel is required. Electric impedance spectroscopy with a customized coaxial probe operating in the 10 kHz to 1 MHz frequency range was investigated. An in-depth investigation of the electrical impedance domain has led to the conclusion that additional information is required to unambiguously determine the composition of the ternary biofuel mixture. Among the different options of measurement domains and techniques, optical absorption spectroscopy in the UV spectral range between 230 and 300 nm was found to be the most appropriate. The typical absorbance in the UV range is highly dominated by gasoline, while ethanol and water are almost transparent. This approach is experimentally validated using actual fuels.

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1. Introduction

Bio-ethanol has been introduced as a renewable source of energy in an attempt to reduce our 'carbon footprint'. Bio-ethanol has been made available as biofuel in the form of ethanol–gasoline mixtures. In Europe the standard low-ethanol content type of biofuel obtainable at the gas station is typically conventional gasoline mixed with 10% bio-ethanol by volume (referred to as E10 fuel). In the USA, bio-ethanol is available as both a low-ethanol content biofuel and a high-ethanol content biofuel, with 85% bio-ethanol by volume (referred to as E85). First-generation bio-ethanol is produced from biomass, such as sugar cane or corn [1]. However, this type of bio-ethanol has become controversial. It does reduce carbon emission, albeit not as much as initially expected, but it has also triggered debates on biodiversity and the ethical issue of using of high-quality farming land for the production of energy, rather than food [2]. For

this reason, new generations of biofuel are presently investigated, which are based on organic waste and algae [3].

Conventional gasoline combustion engines can burn E10 without problems, so the gasoline pump station can simply be modified for dispensing the ethanol blend without the customer even noticing that there is actually a slight decrease in energy content per unit volume, while so-called flexible-fuel vehicles are specially designed to run on E85 by simply turning a switch to notify engine management system of the higher-ethanol blend in the fuel tank. Although the ethanol/gasoline ratio is strongly varying in different countries, the E85 mixture is dominating the international market for high-ethanol content biofuel. Flex-fuel vehicles should be able to run on mixtures of gasoline and ethanol in any ratio and are, therefore, equipped with a sensor for measuring the gasoline/ethanol. However, measuring the ethanol/water ratio in biofuel of high-ethanol content is important in engine management to ensure smooth engine operation and a reliable cold start.

Approaches for fuel composition measurement include optical techniques and impedance measurements. Roy [4] presented an optical fiber sensor to measure the degree of adulteration of petrol and diesel by kerosene. Lima et al. [5] proposed photo-thermal analysis for the detection of adulterants in gasoline. In this case, the

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fuel is analyzed in the vapour phase. The measurement was based on the change of the thermal diffusivity in time, which results from the change in vapour concentration. Continental has been working on a sensor based on infrared absorption [6]. Santos [7] developed an impedance sensor for determining the concentration of alcohol (ethanol) in Brazilian gasoline. Rocha and Moreira [8] developed a coaxial sensor using a pair of stainless steel electrodes and the impedance is used as a measure for the mixtures of ethanol and gasoline. Hoffmann et. al. [9] developed a liquid composition sensor for measuring impedance using inter-digitated electrodes. Furthermore, Jafari [10] used electrochemical impedance spectroscopy to investigate the corrosion behavior of metallic components of the fuel system, caused by fuel mixtures containing gasoline and ethanol, while Wiziak et. al. [11] exploited mass and capacitance transducers simultaneously to quantify the ethanol content in gasolines.

Impedance measurement is generally considered to be the most suitable approach. Especially the capacitive probe has been extensively tested for measuring the ethanol/gasoline ratio. A commercially available capacitive sensor is produced by Continental [12,13]. This sensor measures the capacitance at a low frequency (10 kHz) and the information is used for determining the ethanol/gasoline fractions in a binary mixture.

However, water is an almost unavoidable additional component in a biofuel/gasoline mixture for different reasons. Firstly, ethanol is hygroscopic and therefore attracts water vapour from the air. As can be derived from the ternary phase diagram, all the gasoline in the E85 mixture can in principle be replaced by water without phase separation and water deposition [14].

Secondly, water can be introduced during the production process of the ethanol, which in turn is depending on the source of biomass. Ethanol is produced by fermentation of this bio-mass in distillation plants. Ethanol production from sugar cane results in hydrous ethanol, also called wet-alcohol or AEHC (Hydrous Fuel Ethanol). The wet-ethanol is mainly produced in Brazil, because of the huge production of sugar cane [3]. According to the ANP (National Agency of Petroleum, Natural Gas and Bio-fuels, Brazil) AEHC must have an ethanol content between 92.6 and 93.8 INMP (which refers to mass content) [15]. When we translate these values into volume fractions, AEHC must contain between 94.1 and 95° GL (Degree Gay-Lussac) alcohol by volume at 15° C (59° F), which implies that the maximum water fraction is equal to 5.9%. Apart from this wet-alcohol, also dry alcohol or EACA is used, which is dehydrated and contains maximally 0.7 INMP of water, which corresponds to a volume fraction of 99.7° GL [15]. Dry alcohol typically results when corn is used as the organic source, which is for instance the case for bio-ethanol produced in the USA.

Thirdly, water can be added by less-trustworthy vendors of car fuels. Obviously, 5% of water can be added to turn EACA into 'illicit AEHC'. The art of adulterating fuel with a few percent of water is also referred to as 'fouling'.

To compensate for water content in a capacitive probe, a fixed water concentration is assumed and corrected for, which is actually implemented in the Continental probe. However, such a fixed-value correction relies on a well-defined fixed water concentration in the biofuel and, consequently, on ethanol of a single origin, which is a questionable proposition if biofuel is considered an internationally traded commodity. Since the dielectric constant of water ($\epsilon_r = 80$) is much higher than of ethanol ($\epsilon_r = 25$) or gasoline ($\epsilon_r = 2$), a variable water content in the fuel strongly affects the measurement. The measurement of one single property of the mixture (i.e. de weighted dielectric constant) fundamentally restricts the approach to the use in a binary mixture. Consequently, the simple dielectric measurement is inadequate for measuring the conventional fuel/ethanol/water composition of biofuel and approaches need to be investigated to derive additional information.

The first (and most obvious) approach is to use the same probe over a range of frequencies and to measure both the real and imaginary parts of the impedance (i.e. perform full impedance spectroscopy in an attempt to derive fluid-specific spectral dependencies of the dielectric behavior). However, as is indicated in the next Section, the spectral signature is not very distinctive and the resistive part of the impedance is insufficiently reproducible to ensure a reliable measurement of the full composition of the biofuel.

2. Electric impedance spectroscopy

The frequency dependence of the dielectric behavior of a medium is due to resonance of the dipole molecules in the medium at an imposed oscillating electric field and has been discussed extensively in literature [16]. The components in biofuel have polar molecules with a different relaxation frequency. The dipole molecules can be assumed to be non-interacting and the frequency dependence of the permittivity of each component can be expressed by the Debye relaxation [17]:

$$\epsilon(\omega) = \epsilon_{INF} + \frac{\epsilon_S - \epsilon_{INF}}{1 + j\omega\tau} \quad (1)$$

where ϵ_{INF} is the permittivity at the high frequency limit, ϵ_S the low frequency (static) permittivity, and τ the time constant of the medium. The Debye relaxation also applies to fluidic media as the values for the components of the biofuel are listed in Table 1.

The conductivity of gasoline is very low compared to ethanol and water. It should be noted that the conductivity of a practical gasoline is higher than the value listed, because of the presence of so-called static dissipaters to avoid charge build-up, which are added to gasoline for safety reasons. Moreover, gasoline hydrocarbons have a non-polar molecule structure, which results in a negligible relaxation effect. Consequently, the frequency dependence is not significant and is not considered. This has enabled Arik et al. to measure ethanol content in gasoline [18]. Furthermore, the conductivity of tap water is much higher compared to distilled water as a result of the concentration of dissolved ions.

With the aid of the values for the low-frequency permittivity, the permittivity above the relaxation frequency and the relaxation time, the dielectric relaxation effect according to the Debye Model is simulated using MATLAB. This simulation is performed for water and ethanol. The result is included in Fig. 1. From this result it can be seen that the real part of the total permittivity $\epsilon(\omega)$, thus the dielectric constant, rolls off beyond a certain frequency. This effect is caused by increasing inter-molecular friction, which acts against the rotation of the dipole molecules that are rotating in the E-field. As a result the loss factor is maximum at the frequency where the relaxation effect takes place. Additionally, it can be noted that the relaxation frequencies of water and ethanol are significantly separated, which would imply that a RF implementation even above 10 GHz would be desired for using this effect in a Flex-Fuel sensor. The simulated relaxation behavior of the two components are in good agreement with experiments presented in literature [20] and [21].

Within this work several wideband frequency measurements were carried out. An open-ended coaxial probe, the 85070E Dielectric Probe from Agilent, in combination with an Agilent E5071C ENA Network Analyzer, which ranges from 300 kHz up to 14 GHz, were

Table 1
Conductivity and Debye values for the three main components [18,19].

Component	σ [nS/m]	ϵ_0	ϵ_{INF}	τ_1 [ps]
Gasoline	0.050	2.12	1.94	3.18
Ethanol	1000	24.35	2.12	161
Distilled water	500	78.36	4.57	8.25

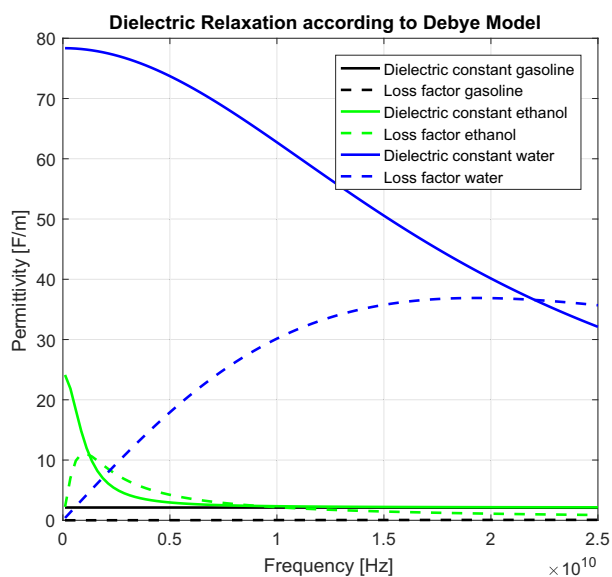


Fig. 1. The simulated values for the dielectric constant and the loss factor of all of the three components.

used. With this setup, the magnitude of the scattering parameter S_{11} was measured. From this parameter, in combination with the measured phase behavior, the permittivity ϵ can be determined. However, the measurement setup was not capable of delivering a reliable phase measurement. As a consequence the S_{11} measurements cannot be used to uniquely determine the real and imaginary parts of the complex permittivity. An algorithm like the SCL algorithm or the NRW method could be used for this purpose [22]. The measurement results of the magnitude of the S_{11} parameter are already useful, as is shown for different binary and ternary mixtures in Fig. 2. The strong influence of water in the measured RF range qualitatively confirms the relaxation behavior that was shown in Fig. 1.

A customized probe, depicted in Fig. 4, was designed to meet the special objective of enabling a reproducible measurement at changing biofuel compositions. It was decided to design a coaxial probe with a characteristic impedance of 50 Ω in air for flexible use in combination with a Agilent 4294A impedance analyzer. The approach is

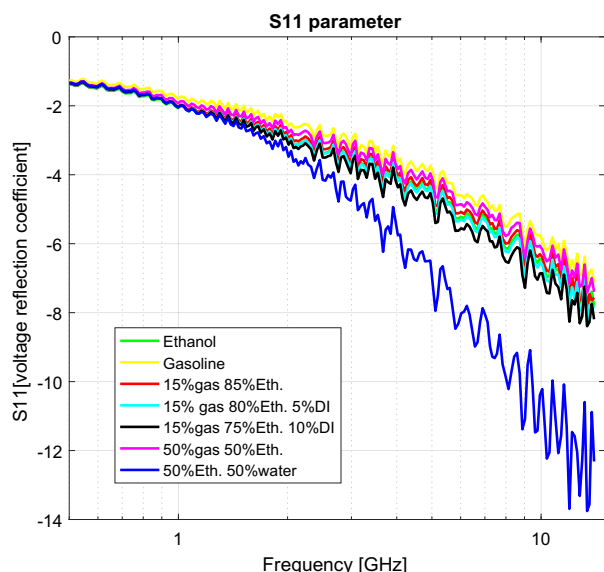


Fig. 2. The S_{11} scatter parameter measured up to 14 GHz.

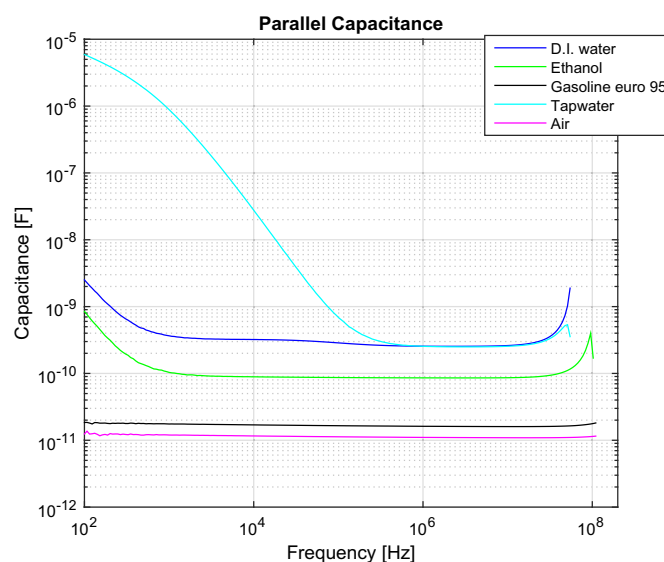


Fig. 3. Parallel capacitance of the three main components and tap water.

based on the measurement of ϵ , which implies that the impedance of the fuel is naturally depending on the composition. Therefore, impedance matching with the probe cannot be maintained over a wide range of fuel compositions. Coaxial probes with outer electrodes of fixed diameter and interchangeable inner electrodes of different diameter were used for impedance matching to a nominal composition of the fuel. Brass was chosen as the construction material, which was silver-plated to decrease series resistance. The measurement system was calibrated to correct for parasitic effects. The reproducibility of the measurement relies heavily on the cleaning of the probe after each measurement and the use of fresh fuel at each measurement. Therefore, an additional advantage for a coaxial geometry are that the probe is easy to clean and that the liquid under test flows in and out of the structure reliably. The impedance is assumed to be comprised of a capacitance in parallel to a conductance. These are measured in air, deionized water, ethanol, gasoline and tap water and the results are plotted in Figs. 3 and 5 in the frequency range from 100 Hz up to 100 MHz.

The results for an empty (air) and gasoline filled dielectric confirm that the medium behaves purely capacitive. Furthermore, deionized water and ethanol have the similar behavior and a scaling of the capacitance proportional to their ϵ_r , while resonance due to probe parasitics is at frequencies beyond about 50 MHz. Tap-water shows an increasing impedance with decreasing frequency below 100 kHz, which is due to the so called 'double' layer capacitance. Tap-water contains many free ions, which diffuse through the liquid as a result of the electric field. At the boundaries (the electrodes) this diffusion causes a charge build-up. When the field is opposite (AC excitation), this process is reversed and the charge builds up on the



Fig. 4. Structure of the impedance probe.

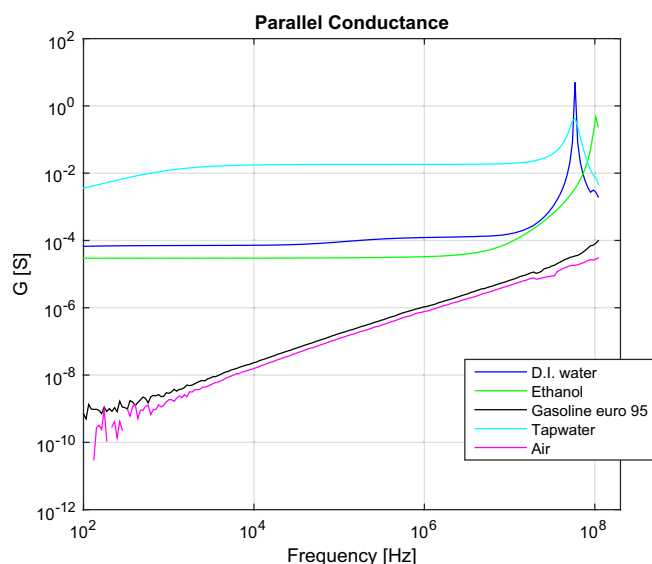


Fig. 5. Parallel conductance of the three main components and tap water.

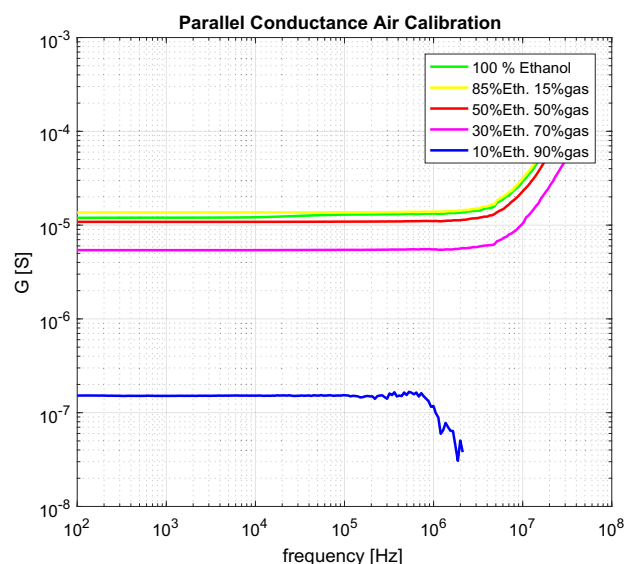


Fig. 7. Measured conductance for different ethanol/gasoline compositions.

opposite side. This effect is called electrode polarization and is represented by a series impedance to the probe parallel RC combination, which is comprised of a resistor and a capacitor; the polarization impedance [23,24].

A series of experiments was performed to evaluate the suitability of the impedance spectroscopy probe for identifying different biofuel mixture compositions and the results are shown in Figs. 6 and 7. The measured capacitance provides reliable information and different fuels can be identified. However, the conductivity measurement is limited by a non-linear sensitivity to the ethanol concentration and saturates at larger ethanol fraction. The data in Fig. 7 is shown in more detail in Table 2. This result is in agreement with literature [25].

Experimental results on repeatability are shown in Figs. 8 and 9. The measurements were carried out on the same sample within 30 min at constant temperature of 293 K. The capacitance measurement were repeatable with in 5% over the spectral range between 30 kHz and 30 MHz, whereas the conductance measurements exceeded any practical criterion. The poor repeatability of the conductance

measurements is consistent with literature and is due to: a complex temperature dependence, an ethanol sample dependency, high sensitivity to free ions/contamination and the influence of static dissipaters [8,25].

These results indicate that only the capacitive part of the impedance can be practically used for measuring biofuel composition. The additional information that is required to unambiguously determine the composition of the ternary mixture cannot be retrieved by impedance spectroscopy for two reasons. The first is

Table 2

The measured parallel conductance as function of ethanol concentration at $f = 9.98$ kHz.

Ethanol concentration	Parallel conductance
10%	1.52×10^{-7} S
30%	5.41×10^{-6} S
50%	1.08×10^{-5} S
85%	1.21×10^{-5} S
100%	1.36×10^{-5} S

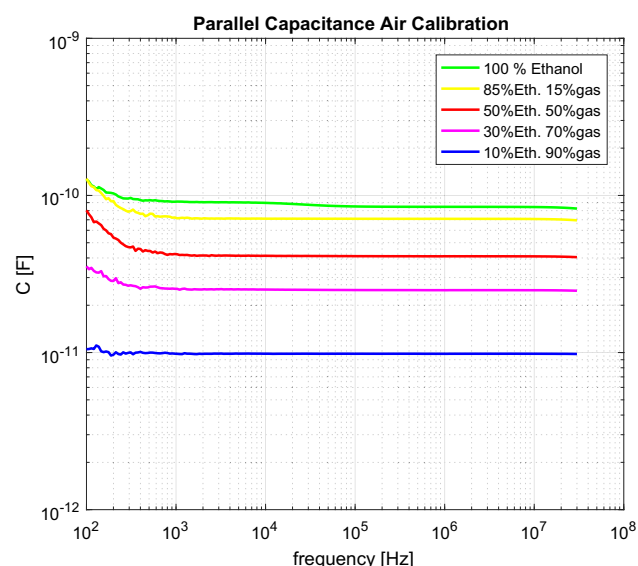


Fig. 6. Measured capacitance for different ethanol/gasoline compositions.

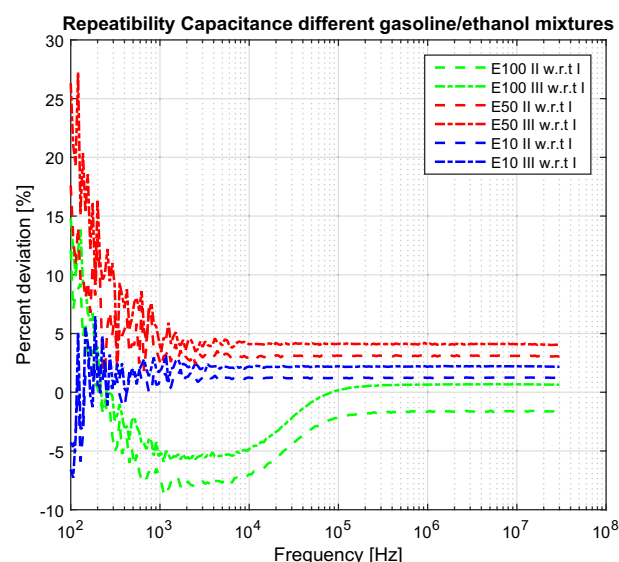


Fig. 8. Repeatability of capacitance measurement.

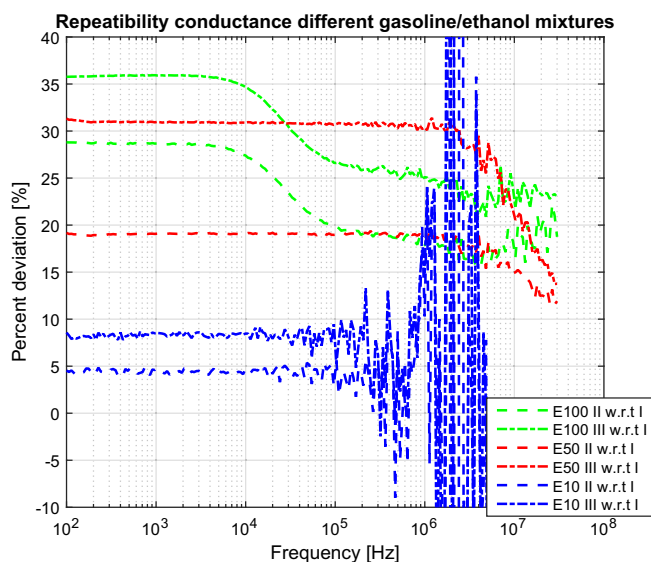


Fig. 9. Repeatability of conductance measurement.

the limitation of the frequency range to values lower than the relaxation frequency of ethanol, because of parasitic impedances in the probe. This problem may in principle be resolved using an improved probe design. However, such a device would not be suitable for use in a consumer product where the acceptable range of the price tag of an additional measurement system is highly constrained. Moreover, the non-reproducibility of the conductance measurement does not allow practical implementation and other techniques have to be investigated.

Among the different options considered, such as surface acoustic waves [26], density measurement [27], thermal conductivity [28] and optical properties, the optical absorption spectroscopy was found to be the most suitable. Absorption spectroscopy in the visible is not suitable because of the addition of colorants to the gasoline, while absorption spectroscopy in the IR is hampered by the water absorption bands. However, absorption spectroscopy in the UV in the range between 230 nm and 300 nm offers interesting opportunities.

3. Optical absorption spectroscopy

Gasoline contains several components with aromatic bonds [29], for example benzene and toluene (methyl-benzene). According to literature [30], benzene for example shows strong light absorption near 180 nm (which is in the vacuum-UV) and more suitable absorption bands at 200 nm and 254 nm [31]. The lack of uniformity on the choice of colorants significantly complicates optical absorption spectroscopy in the visible range. The dyes used in the US make regular gasoline appear green for example, whereas most gasolines in Europe are colored yellow.

For experimental validation 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. Therefore, in addition to the initial dark- and full-exposure calibration, the device is corrected in real-time for possible variations of the spectrum of the light source over time. Since the output power of the light source and the integration time of the detector are not adjustable, the optical path length is critical.

A 1 mm path length was found the most suitable to obtain the spectral information. Since saturation (i.e. reduction of the intensity of a spectral component of the light down to the equivalent noise level of the detector, due to the high absorption coefficient of the

gasoline) still occurs with the 1 mm cuvettes, it was decided to dilute the gasoline (mixtures) with a suitable solvent. This way the absorption behavior of the gasoline (mixtures) would fall into the lower absorption ranges and the measurements would give the best spectral information. 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. According to literature [32], the cut-off wavelength in the UV range of cyclo-hexane is at 195 nm.

Indolene 50E clear was used in combination with the so-called 200 proof ethanol (99.98% pure). Indolene is a gasoline that is used in testing laboratories because it does not contain the additives and colorants that are routinely added to regular fuels. The dilution ratio of 1/10 is used to enable optimum use of the dynamic range of the spectrophotometer. No dilution is applied when measuring pure ethanol to prevent further loss of spectral information. As is shown in Fig. 10, two absorption features are present. One local minimum in the absorption at 240 nm and a peak around 265 nm. Despite the dilution ratio of 1/10 and the path length of only 1 mm, saturation at minimum sensitivity occurs at 70% indolene concentration and at wavelengths beyond about 265 nm. 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 ternary mixture problem, indolene 50E was replaced with a different kind of an 'off the shelf' test fuel, namely Unleaded Low Octane gasoline 87 RON (Research Octane Number) in a new series of identical measurements. The results are shown in Fig. 11. The absorption behavior closely resembles the measurements on indolene gasoline.

Additional absorption measurements were carried out to investigate the dependency on octane number. The result is shown in Fig. 12. The effect of the octane content on the absorption behavior is very small.

Also the effect of E85 summer/winter blends was investigated and the result is shown in Fig. 13. It can also be concluded that the higher volatility of winter fuel does not significantly affect the measurement result. The invariance to these types of uncertainty does confirm the robustness of the UV absorption spectroscopy in the UV for measuring the gasoline concentration in biofuel. Having determined the gasoline fraction, impedance spectroscopy can be used to measure the water and ethanol fractions.

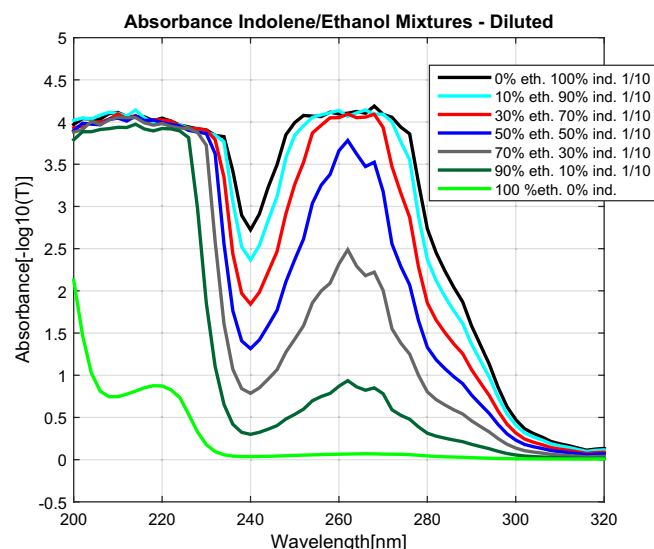


Fig. 10. UV absorption spectroscopy of indolene 50E.

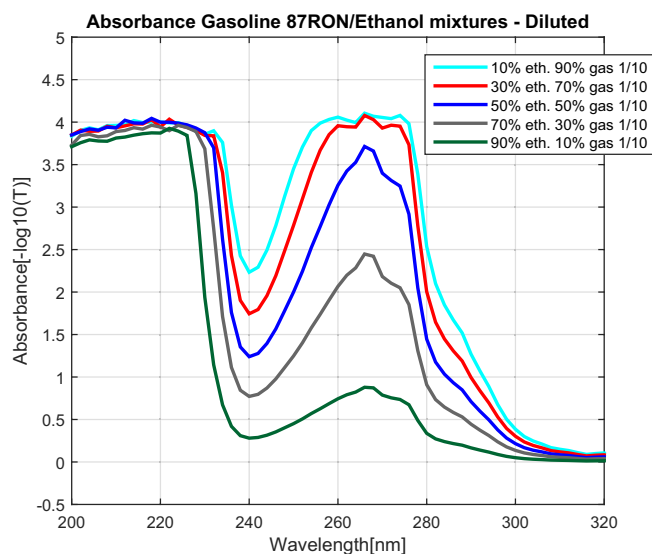


Fig. 11. UV absorption spectroscopy of a low octane gasoline.

The uniformity of the spectra presented suggests the influence of an aromatic bond. This was confirmed by additional optical absorption measurements on aromatic hydrocarbons. Toluene for example showed similar behavior as the test gasolines and it was verified that the aromatic bond is likely to be responsible for the absorption behavior observed in gasoline, possibly among other hydrocarbon structures. However, it should be emphasized that a full chemical composition analysis should be performed, in order to unambiguously identify all absorbing species in the spectrum of interest for the gasolines tested.

Different dilution ratios were used to prevent full absorption and loss of spectral information. The short absorption path length is the main complication of the optical absorption for gasoline detection. The measurement presented are based on a 1 mm long path and up to 1/10 dilution was nevertheless required. However, it should be noted that the probe is intended for use in E85, which nominally consist of only 15% gasoline.

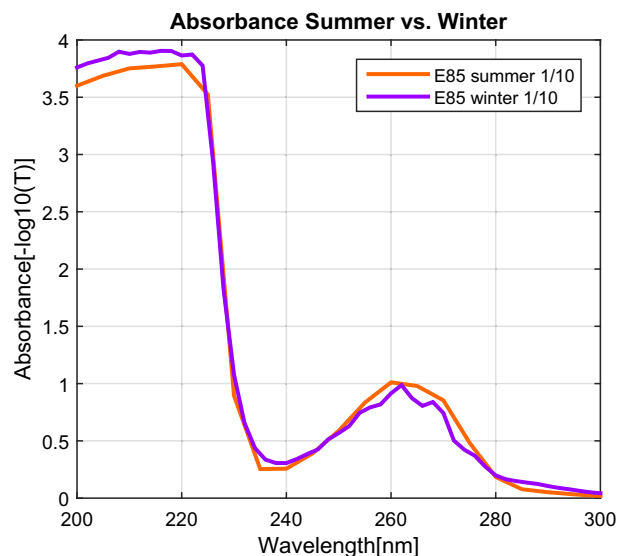


Fig. 13. Sensitivity to summer/winter blend.

The combined electrical/optical probe should contain both electrical probe and optical path in one unit. The advantage of the measurement of a full optical spectrum in the measurement range of interest in the UV is that more detailed information about the absorption features becomes available. Especially, the peaks and local minima in the absorption behavior provide the kind of additional information that may be useful in the case of interference or stray light. Moreover, the redundancy provided by multi-channel information could be used to improve the quality of the measurement. A simple implementation based on a Linear Variable Optical Filter (LVOF) that is designed for operation over the 230–300 nm band is promising for this application [33].

4. Combining impedance spectroscopy with absorption spectroscopy

Merging the information provided by low-frequency impedance spectroscopy with that of the optical absorption spectroscopy in the UV spectral range is highly suitable for measuring the biofuel composition. The absorption behavior in the UV range of the optical spectrum is highly selective for gasoline content. Although the information provided by the two domains is not orthogonal in a strict mathematical sense, it is sufficiently complementary to provide an unambiguous composition measurement at realistic specifications.

A more quantitative analysis is included to highlight the contributions of the two domains. The basic approach is used in earlier work with only data from impedance spectroscopy [34]. For this analysis, a first order linear description is used. For the relative permittivity measurement, different equivalent medium approximations were considered, for example the Maxwell-Garnett equivalent medium approximation [35]. However, empirical results indicated that a linear mixing rule was closest to reality for the concentrations of interest. For the case of optical absorbance, this linear relationship is described by the Beer–Lambert law. According to the Beer–Lambert law, the resulting absorbance of a mixture is the sum of each of its components, assuming no interaction. $A = \sum_{i=1}^N \epsilon_i c_i l$, where ϵ_i is the extinction coefficient, c_i the molar concentration and l the optical path length.

The matrices below show the first order linear description of the equivalent medium approximation, with α_g, α_e and α_w the volume fractions of gasoline, ethanol and water respectively. The first row

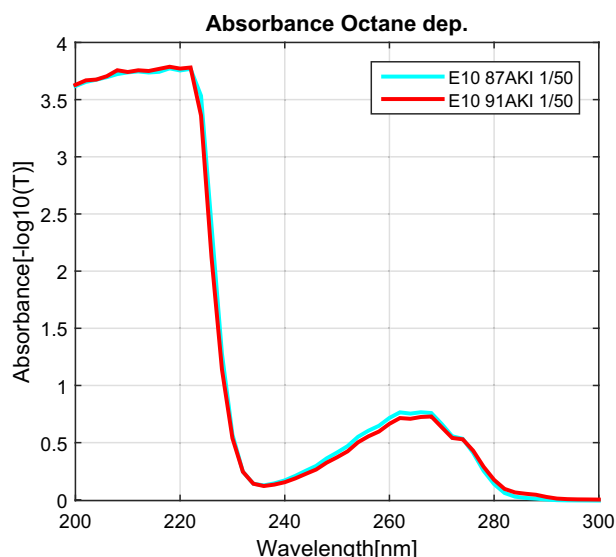


Fig. 12. Sensitivity to octane number.

contains the relative permittivities in the electrical domain of respectively gasoline, ethanol and water and the second row contains the optical absorption in the UV range at 240 nm (a different wavelength can be chosen). The last row states that the sum of the separate fractions is equal to 100% of the volume.

$$\begin{bmatrix} \epsilon_{mix} \\ A_{mix} \\ 1 \end{bmatrix} = \begin{bmatrix} \epsilon_{rg} & \epsilon_{re} & \epsilon_{rw} \\ A_g & A_e & A_w \\ 1 & 1 & 1 \end{bmatrix} \times \begin{bmatrix} \alpha_g \\ \alpha_e \\ \alpha_w \end{bmatrix}.$$

The matrices below result by inserting the measured values in the matrices above. When looking at the values, it seems more convenient to normalize in order to be able to compare between selectivity and contributions in each of the domains. In the case of water, it can be concluded from that last matrix that the contribution of gasoline is 40 times smaller than water in terms of permittivity, and that the water content therefore dominates this figure. The absorption behavior in the UV range of the optical spectrum is solely selective for gasoline content. Note that the sensitivity of the optical absorption for water and ethanol is below the resolution of the dataset. Hence, zero is used. These two domains provide therefore a subset of linear independent equations, which can be solved to find a solution to the ternary mixture problem.

$$\begin{bmatrix} \epsilon_{rg} & \epsilon_{re} & \epsilon_{rw} \\ A_g & A_e & A_w \\ 1 & 1 & 1 \end{bmatrix} = \begin{bmatrix} 2 & 24 & 80 \\ 2.723 & 0 & 0 \\ 1 & 1 & 1 \end{bmatrix} \rightarrow \begin{bmatrix} 0.0250 & 0.300 & 1 \\ 2.723 & 0 & 0 \\ 1 & 1 & 1 \end{bmatrix}.$$

This set of data can be used to solve the ternary mixture problem. When the relative permittivity of the mixture is measured (which is basically the parallel capacitance corrected with the cell constant) in combination with the optical absorption (in this case the value at 240 nm), the separate fractions of the mixture are found by multiplying the inverse matrix consisting of the figures of the pure components.

$$\begin{bmatrix} \alpha_g \\ \alpha_e \\ \alpha_w \end{bmatrix} = \begin{bmatrix} \epsilon_{rg} & \epsilon_{re} & \epsilon_{rw} \\ A_g & A_e & A_w \\ 1 & 1 & 1 \end{bmatrix}^{-1} \times \begin{bmatrix} \epsilon_{mix} \\ A_{mix} \\ 1 \end{bmatrix}.$$

After insertion of the measured values in the matrix and matrix inversion, the following solution is found.

$$\begin{bmatrix} \alpha_g \\ \alpha_e \\ \alpha_w \end{bmatrix} = \begin{bmatrix} 0 & 0.367 & 0 \\ -0.0179 & -0.512 & 1.429 \\ 0.0179 & 0.144 & -0.429 \end{bmatrix} \times \begin{bmatrix} \epsilon_{mix} \\ A_{mix} \\ 1 \end{bmatrix}.$$

The complementary relation between the electrical impedance spectroscopy and the optical absorption spectroscopy demonstrate that the two-parameter measurement is a suitable approach for full biofuel composition measurement. An error analysis has been conducted in which an error is introduced in the measurement of the UV absorbance and that of the relative permittivity. The resulting compounded error in either of the three components of the biofuel mixture is calculated using the linear equivalent model approximations and plotted. This analysis has been done to visualize dependencies on the different components according to the measurement domain. This results in two contour plots which are close to being orthogonal to each other. The error analysis can subsequently be used to adapt the specifications to meet the requirements of a possible implementation for this biofuel composition sensor. The test scenario is applied to a nominal composition that is defined as an E85 mixture with no water present. The result for the water fraction is included in Fig. 15. The z-axis shows the absolute difference between the correct water fraction percentage and the calculated water percentage based on measurement results in which an error is introduced. The error in

Measurement error influence on gasoline fraction E85, no water assumed

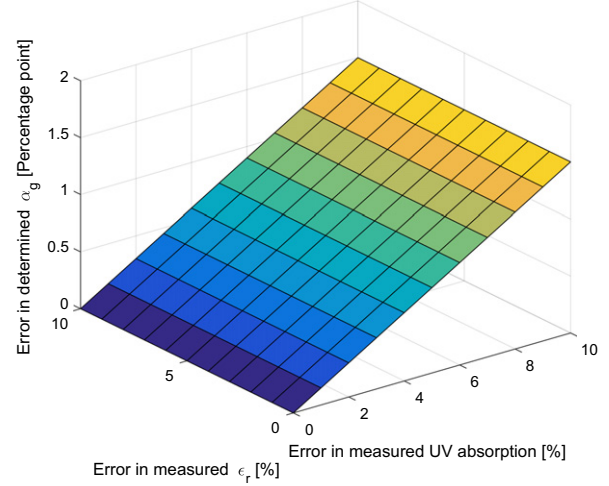


Fig. 14. The resulting error in the gasoline estimation, as function of a measurement error in the UV absorbance and the relative permittivity.

the water estimation is dominated by an error in the measured relative permittivity ϵ_r , which can be expected based on the high value for the relative permittivity of water as compared to that of gasoline or ethanol.

Similarly, the gasoline fraction as a function of measurement error can be estimated, see also Fig. 14. In contrast to the previous surface plot, the error in the calculated gasoline fraction is solely dependent on the optical absorption in the UV range, which is clearly visible from the result. This can be explained by the optical absorbance, which is in the range of interest ($\lambda = 240$ nm) dictated by gasoline content. Comparing Figs. 15 and 14 confirms the complementarity and actually suggests an orthogonal behavior.

Finally, the result for the ethanol fraction is included, see Fig. 16. The error in the calculated ethanol fraction is really determined by an error in both the optical absorbance as the relative permittivity.

Influence on water fraction E85, no water assumed

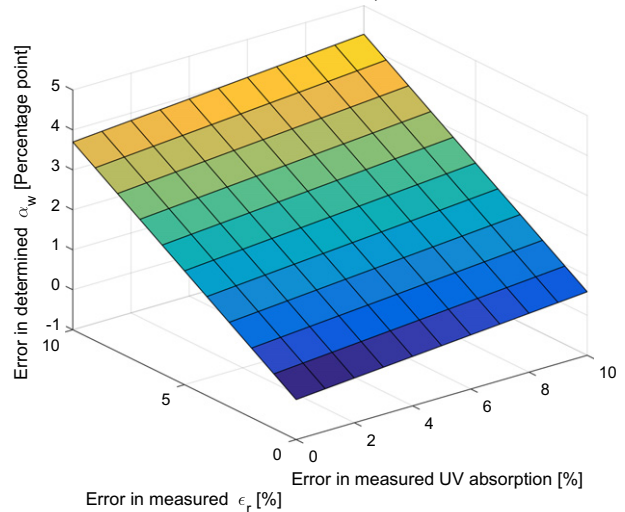


Fig. 15. The resulting error in the water estimation, as function of a measurement error in the UV absorbance and the relative permittivity.

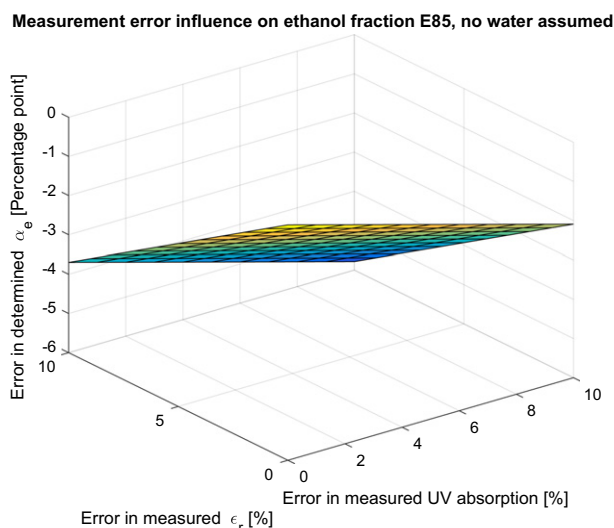


Fig. 16. The resulting error in the ethanol estimation, as function of a measurement error in the UV absorbance and the relative permittivity.

5. Conclusions

The measurement of biofuel (ethanol/gasoline/water mixtures) composition by electrical impedance spectroscopy only is not sufficiently accurate, because of the three components, the limited amount of spectral variability and the poor quality of the conductivity measurement. The capacitance measurement is highly suitable and should be supplemented by another source of information and thus requires the measurement of an additional property. The frequency range which can be best utilized depends on the concentration of dissolved ions in the fuel mixture. Estimations based on measurement within this work on practical fuels would range from several kHz up to 1 MHz, depending on the presence of ion containing contamination.

Absorption spectroscopy in the UV range between 230 nm and 300 nm was found to be highly representative for gasoline, because of the benzene absorption band in this part of the spectrum. Experimental validation has confirmed this conclusion and has demonstrated the viability of the combined electrical impedance/optical absorption spectroscopy for uniquely determining the composition of a biofuel.

An implementation of a Flex-Fuel sensor based on these two measurement techniques is composed of an optical microsystem in the UV that is combined with an integrated system for impedance measurement.

The complication of the short absorption path is aggravated by the fact that gasoline is not diluted in the actual application. However, when the optical microsystem would be designed, the signal power of the (UV) light source and the sensitivity of the detector can be adapted to the high absorbing gasoline medium. Nevertheless, the path length would typically be about 1 mm to avoid full optical absorption by the gasoline in case the spectral absorption is determined by a transmission measurement. An alternative considered is the measurement of the optical absorption spectrum using a device operating on total internal reflection and its interaction with a contacting fluid [36]. Ensuring the unrestricted flow of fuel would require a special probe construction, in which the matching of the impedance of coaxial probe to the nominal fuel impedance is abandoned to enable the functional integration with the optical probe with short absorption path, which is possible because of the relatively low-frequency operation. Multi-line absorption spectroscopy

is considered for alleviating the constraints imposed by the short optical absorption path.

A viable concept for a Flex-Fuel sensor is demonstrated that is based on these two measurement techniques combined and composed of an optical microsystem in the UV in combination with an integrated impedance measurement system.

A linear model was used that demonstrates the complementarity of the two proposed measurement domains and serves as a suitable starting point for the quantification of the requirements to be imposed on a future sensor implementation. An uncertainty of about 4 percentage point is considered acceptable in the intended automotive application (note that this is the absolute error in the relative concentration measurement of a component). Although the requirements for the maximum measurement error in the UV absorption and the permittivity are depending on the measured mixtures, the E85 analysis indicates an acceptable maximum error of 2% in the UV absorption measurement and 8% in the measurement of relative permittivity.

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