



Estimation of dielectric properties of crude oils based on IR spectroscopy



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ABSTRACT

Dielectric properties of crude oils play an important role in characterization and quality control. Measuring permittivity accurately over a wide range of frequencies is, however, a time-consuming task and existing measurement methods are not easily adapted for real-time diagnostics. IR spectroscopy, on the other hand, provides rapid measurements of fundamental molecular properties.

In this paper we show that by using multivariate calibration tools such as PLS regression, it is possible to extract dielectric properties of crude oils directly from IR spectra, in addition to conventional interpretation of the spectra, hence reducing the need for direct electrical measurements. Results on 16 different oil samples show that the dielectric parameters obtained with the proposed method agree well with those obtained using direct permittivity measurements. The PLS regression method has also been extended with Monte Carlo simulation capabilities to account for uncertainties in the data.

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1. Introduction

A dielectric property such as relative permittivity is a measure of the ratio of the amount of electrical energy stored in a material by an applied voltage, relative to that stored in vacuum. The relative permittivity is a dimensionless, frequency dependent quantity which can be described by parameters of the Cole–Cole model [1]. These parameters are used in several Multiphase Flow Metering (MFM) systems in the petroleum industry [2]. MFMs provide online monitoring of the flow rates of oil, water and gas in the pipelines.

MFMs can help in optimizing petroleum production, increasing the oil recovery and lowering the investments and operational costs [3,2]. Fluid properties (e.g. permittivity) of oil, water and gas must be known accurately in order to estimate the flow rates as accurately as possible, and ongoing research seeks to improve the understanding of how polar components in crude oil affect the permittivity of the oil [4–6].

As a complement to direct permittivity measurements, we have also used IR spectroscopy. IR reflectance data contain information about molecular properties; the types and amounts of functional groups in the mixture being analyzed can be detected. Detection of oxygen containing compounds like acids and alcohols, and compounds containing other heteroatoms like nitrogen and sulfur, is possible using IR spectroscopy.

Also, the relative abundance of CH₃ and/or CH₂ in a mixture or pure compounds can be determined. By using multivariate calibration techniques, e.g. Partial Least-Squares Regression (PLSR) [7], one can easily build quantitative models for several physical and chemical properties [8], as well as other responses that might be desirable to quantify [9,10] in a wide variety of mixtures and pure compounds.

In this paper we investigate the feasibility of using multivariate calibration techniques for estimating permittivity spectra from measured IR spectra. A physical model of permittivity is also fitted both to the original permittivity measurements and to those estimated from IR spectra. The resulting model parameters are compared in order to assess the usefulness of the proposed method. To further investigate the quality of the model, a method for evaluating uncertainties based on Monte Carlo simulations has been developed.

If successful, the IR spectroscopy will provide additional information to the traditional permittivity measurements. The time it takes to perform the actual measurements is comparable for both methods, but for dielectric spectroscopy, however, the calibration procedure and the cleaning requirements of the measurement cell is more time consuming. IR spectrophotometers are simple and widely used instruments that are easily portable and can be used on-site at oil production facilities. A considerable number of models based on IR or NIR (Near Infrared) spectra of oils are already in use for predicting crude oil properties [11], thus one set of measurements can be sufficient for a range of property predictions. Dielectric measurements are not available in typical oil analysis laboratories, and it is therefore difficult to get accurate reference data for the permittivity of a specific oil. IR

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spectrophotometers are more widely available in such laboratories, and may be used as a tool for estimating the dielectric parameters.

Section 2 starts with a description of the sample preparation, the measurement configurations used for permittivity measurement and IR spectroscopy. A brief overview of the physical modeling of permittivity is given, along with a description of the model fitting and multivariate calibration used for the analysis. In Section 3 we present experimental results for 16 crude oil samples. In the experiments, a single calibration model was used for both biodegraded and non-biodegraded oils, allowing for estimation of dielectric properties, solely based on IR measurement.

2. Materials and methods

2.1. Sample preparation

The sample set consists of 16 crude oils mainly originating from the North Sea, but also includes one sample from Brazil and one from Nigeria/Angola. 7 of these oils are biodegraded while the remaining 9 oils are classified as non-biodegraded oils, or sweet oils. Biodegradation of crude oils is an alteration of the crude oil composition due to microorganisms degrading certain chemical components in the crude oil. This microbial alteration can occur in oil reservoirs in which surface-derived, meteoric formation water is present. Although no conclusive evidence says that biodegraded crude oils have higher densities (this also goes for other physical properties like viscosity) than non-biodegraded oils, biodegraded oils tend to have densities in the higher range of observed values. This is because the microbes first remove the lighter, straight chain alkanes, inevitably producing a denser liquid than the oil prior to biodegradation [12].

Biodegraded oils are labeled “B” in the sample code, while the non-biodegraded oils are labeled “S”.

All oils have prior to measurements been placed in an oven at 60 °C for 4 h, in order to dissolve waxes that may have precipitated during storage. They have also been shaken and turned upside down multiple times, in order to homogenize the oils thoroughly.

This work suffers in the same way as in many other cases dealing with petroleum samples, i.e. that it is difficult to obtain a data set that is both representative and has large enough spread in properties. Also, the number of samples that can be obtained is usually quite limited. Because of this, we have no separate calibration and validation data sets for the modeling described in the next few sections. Instead, the prediction models are cross-validated using a leave-one-out approach. In addition to this, a Monte Carlo simulation approach is taken in further evaluating the repeatability of the resulting models, see Section 2.6.2.

2.2. IR spectroscopy

A Nicolet Protegé 460 Fourier Transform (FT) IR Spectrometer with an Attenuated Total Reflection (ATR) measuring cell, equipped with a diamond crystal, has been used for obtaining FT-IR spectra of the oils. All measurements were made at room temperature. One drop of oil is placed on the crystal, and 32 spectra are measured. The spectra are then averaged, giving a master spectrum for the oil. 5 master spectra have been measured for each oil, in case the homogenization is poor, and the average of the resulting 5 master spectra has been calculated. Background correction was done prior to investigating a new oil. All spectra are in Reflectance form.

2.3. Permittivity measurements

The permittivity, ϵ , was measured over the frequency range from 100 kHz to 1 GHz using the experimental set-up and procedure described in [13] and illustrated in Figs. 1 and 2. An oil sample was inserted between the inner and outer conductor of a 20 cm long coaxial measurement cell. In the low frequency range (below 20 MHz) the

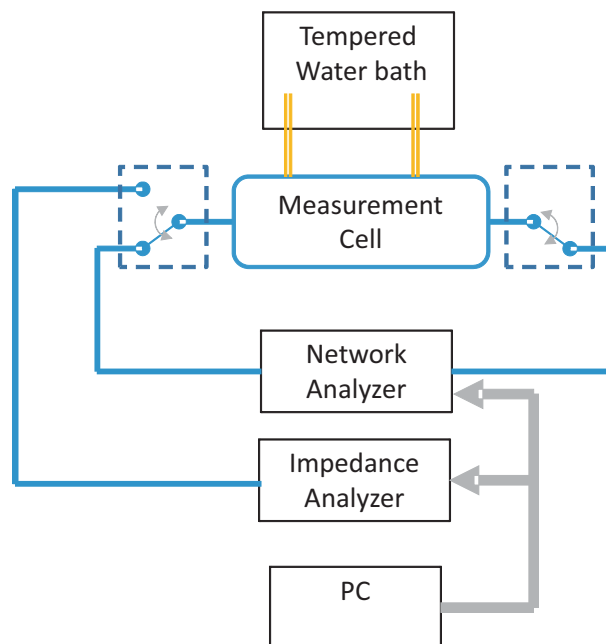


Fig. 1. The permittivity measurement setup. The details of the measurement cell are shown in Fig. 2.

impedance of the measurement cell was measured as a function of frequency using an impedance analyzer (Hewlett Packard 4294). The permittivity was calculated from the impedance using a linear, frequency dependent model. The model was calibrated with measurements of n-decane, toluene and n-heptane. Systematic errors in the imaginary part of the permittivity were corrected with n-heptane measurements. At frequencies above 50 MHz, a network analyzer (Hewlett Packard HP8722C and Rohde & Schwarz ZVL-13) was used to measure the reflection and transmission coefficients of the measurement cell, and a bilinear calibration method [14,15] was used to calculate the permittivity. In the intermediate frequency range (50–150 MHz) the permittivity was calculated from reflection measurements and in the highest frequency range (above 150 MHz) the permittivity was calculated from transmission measurements. The bilinear calibration method requires three calibration fluids, and in this work n-decane, toluene and n-heptane were used. The dielectric measurements were done at 20 °C.

2.4. Cole–Cole modeling

The Cole–Cole model [1] of relative permittivity ϵ is given by

$$\epsilon = \epsilon_{\infty} + \frac{\epsilon_s - \epsilon_{\infty}}{1 + (j\omega\tau)^{1-\alpha}}, \quad (1)$$

where ϵ_{∞} is the infinite frequency permittivity, ϵ_s is the static permittivity, τ is the macroscopic relaxation time, α is an empirical factor ($0 \leq \alpha < 1$), and ω is the angular frequency.

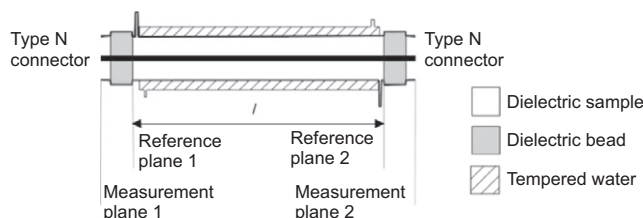


Fig. 2. The permittivity measurement cell.

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