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Determination of octane numbers for clean gasoline using dielectric spectroscopy

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ABSTRACT

In this work, dielectric spectroscopy (DES) in association with partial least squares (PLS) multivariate calibration method was employed to determine octane numbers (research octane number or RON and motor octane number or MON) of clean gasoline samples. The factor number included in PLS model was obtained according to the lowest sum of squares of predicted residual error (PRESS) in calibration set. The performance of the final model was evaluated according to PRESS and correlation coefficient (R). The optimal factor numbers are 9 in both RON and MON PLS calibration models, which were achieved with PRESS = 2.74 and $R = 0.9598$ in RON calibration set and the lowest PRESS = 2.72 and $R = 0.8983$ in MON calibration set. In validation set, PRESS = 1.00 and $R = 0.9552$ for RON and PRESS = 0.47 and $R = 0.9105$ for MON were obtained. Results indicated that PLS multivariate calibration models based on DES data were proven suitable as a practical analytical method for predicting octane numbers of clean gasoline.

1. Introduction

Octane numbers (RON and MON) are important properties to evaluate the anti-knock performance of gasoline. Currently both RON and MON are still measured in a standardized single cylinder, internal combustion engine (Cooperative Research Fuel-CFR engine), following the standard methods ASTM D2699 (RON) and ASTM D2700 (MON), respectively. In China, GB/T5487-1995 (RON) and GB/T503-1995 (MON) are adopted equivalent to ASTM D2699 (RON) and ASTM D2700 (MON). As all the standard methods are time-consuming, complicated, relatively expensive and of poor environmental performance, fast, easy and accurate determination of octane numbers is important for refiners and quality inspectors as optimization of refining process and quality control at a reasonable cost is ever-increasing requirement. Very soon scientists began to look for a correlation between the tendency of hydrocarbon-based fuels to knock and the composition of these fuels to calculate the octane numbers indirectly and rapidly [1].

There are various existing analytical techniques to obtain gasoline compositional data from which calculation of octane numbers (RON and MON) can be done. The main disadvantages of most of them are either their limiting details in terms of the compositional data they can provide or their testing and instrument cost. For example, gas phase chromatography (GC) and nuclear magnetic resonance (NMR) can provide detailed compositional data but the cost of testing or instrument is too high and the analysis procedure is too time-consuming to be applied widely, especially for online testing. The analytical techniques such as fluorescent indicator adsorption (FIA), near infrared (NIR) can provide only limited compositional information, corresponding to structural groups such as aromatics, olefins and saturates. For example, currently a large number of anti-knocking agents including organic ashless such as oxygen-containing organic compounds, commonly known as 'oxygenates' (methanol, ethanol, methyl *tert*-butyl ether or MTBE and *tert*-amyl methyl ether or TAME) and metallic ash additives such as manganese-containing organic compounds (methylcyclopentadienyl manganese tricarbonyl or MMT and cyclopentadienyl manganese tricarbonyl or CMT) are added to most of the gasolines to boost octane performance and to reduce exhaust emission levels of carbon monoxide. But the compositional information of most of these anti-knock agents, especially the metallic ash additives, cannot be obtained by NIR or FIA satisfactorily.

Dielectric spectroscopy (DES) is an analytical technique on the interaction between dielectric materials and electromagnetic energy in the radio-frequency and microwave range, which is a powerful structural detection technique for dielectric materials. What DES studies is the dependence of materials' dielectric properties on wavelength or frequency. DES' frequency ranges from 10^{-7} Hz to 3×10^{13} Hz. At the present time, DES technique enables researchers to make sound contributions to contemporary problems in modern physics such as the scaling behavior of glass transition and dynamics of molecules in confined space [2]. DES for agriculture application has been carried out by Nelson [3,4], and he found that DES can be employed to quality sensing application of agricultural products such as moisture content. DES technique

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has also excellent performance on evaluating the insulation system of most power transformers which consists oil and cellulose [5,6].

Dielectric spectroscopy measures the dielectric properties of a medium as a function of frequency. It is based on the interaction of an external field with the electric dipole moment of the sample. There are a number of different dielectric mechanisms, connected to the way a studied medium reacts to the applied field. Each dielectric mechanism is centered around its characteristic frequency, which is the reciprocal of the characteristic time of the process. In general, dielectric mechanisms can be divided into relaxation and resonance processes. The most common, starting from high frequencies, include electronic polarization, atomic polarization, dipole relaxation, ionic relaxation and dielectric relaxation. Dielectric relaxation as a whole is the result of the movement of dipoles (dipole relaxation) and electric charges (ionic relaxation) due to an applied alternating field, and is usually observed in the frequency range 10^2–10^{10} Hz. Relaxation mechanisms are relatively slow compared to resonant electronic transitions or molecular vibrations, which usually have frequencies above 10^{12} Hz. So in this article the frequency range from 5×10^3 to 1.6×10^7 is utilized and observed and the response signals collected by the instrument DSAP stand for the relaxation information.

Petroleum products are all typical dielectric materials, whose dielectric properties such as dielectric constant and conductivity have widely been applied in testing and analysis field. For example, Jin et al. [7] have developed a portable instrument to measure octane numbers of gasoline on dielectric constant. But dielectric constant can only provide limited information so that this method cannot work well when gasoline additives are added. Bardetsky [8] has invented a method to evaluate properties of a working fluid using dielectric spectroscopy. In his patent, the permittivity of the working fluid as the temperature is varied is measured and then a mathematical model is established to evaluate the degree of contamination or degradation. Furthermore, dielectric spectroscopy can be used to classify Engine lubricating oil classification by SAE grade and source [9]. However, quantitative determination of petroleum product's properties on DES data has not been paid much attention to all the time. DES is indeed a novel method for fuel analysis.

Gasoline is a mixture of hydrocarbons. The bulk of a typical gasoline consists of hydrocarbons with between 5 and 12 carbon atoms per molecule. The hydrocarbons consist of a mixture of *n*- and *iso*-paraffins, naphthenes, olefins and aromatics which have different octane numbers. Naphthenes, olefins and aromatics, which have high octane numbers, increase the octane rating of the gasoline whereas the *n*-paraffins have the opposite effect which have lower octane number. It is interesting that there is a relatively good linear correlation between the octane numbers and the dielectric constants ε of the components of gasoline: the greater dielectric constants are, the higher those octane numbers are. So the Chinese GB/T 18339-2001 has been developed which is a testing method for motor gasoline octane number based on dielectric constant [10].

Compared with optical analysis techniques such as NIR, the main advantage is its relative simplicity and low-cost: the stimulating source and measured signals of DES are both electro-signals while those of NIR are both light-signals which must be followed by signal detector between light-signal and electro-signal. Both light source and signal detector will degrade and will be abandoned in the end. For optical spectroscopy analytic technique, some parts' deterioration of the instrument over time will produce changes in the instrument response function. The aging of sources, probes, and detectors may lead to instability of the signal over time (drift) or non-linearities in the spectra. For example, NIR data may be additionally problematic due to differences in pathlengths of optical probes and wavelength registration shifts. Furthermore, the instrument's environment changes will influence the reliability of the instrument. For example, temperature and humidity variations can have a strong influence on measurement values of NIR data by causing shifts in absorption bands and non-linear changes in absorption intensities on the spectra. All the influence factors are not so crucial for DES. Therefore, DES instrument is more stable and reliable than NIR instrument.

In this work, calculation of octane numbers (RON and MON) has been done on the basis of DES data coupled with partial least squares (PLS) multivariate calibration method. This study has demonstrated the feasibility of using DES as a non-invasive, non-destructive and fast method to analyze petroleum products. The major challenges in this work are the small amount of samples.

2. Experimental

2.1. Apparatus and methods

A Dielectric Spectroscopy Analyzer for Petroleum (DSAP) instrument made by Logistical Engineering University (LEU) was employed to obtain the DES data. DES measurements are usually performed using an instrument system which can generate sinusoidal signals with different desired frequencies and the voltage or current values through the sample can be measured when the sinusoidal signals are applied to the sample. On the basis of the voltage or current values measured by the instrument, the complex dielectric constant can be obtained through complicated calculation. As for the application of DES to the petroleum qualitative and quantitative testing and analysis, it is dispensable that the voltage or current values through the sample be transformed into complex permittivity, which can be utilized directly and regarded as the dielectric response values of the sample. This is also the main principle of DSAP. According to DSAP, signals through the sample are amplified, filtered, rectified in turn and input into the 12 bits A/D converter in the end. So the values DSAP measures called 'response signal' are non-dimensional numbers and range from 0 to 4096. Besides the sine wave, another two wave forms can be generated from DSAP. The main parameters of DSAP are:

Wave form: 1. sine wave, 2. square wave, 3. triangle wave.
Amplitude range: -10 V to +10 V.
Frequency range: 50 kHz–16 MHz.
Temperature held: 30 ± 1 °C.
Analysis time for one sample: about 3 min.

The main principles of the DSAP instrument operation can be shown in Fig. 1.

As for dielectric spectroscopy measurement, the sample material is usually mounted in a sample cell between two electrodes forming a sample capacitor. In the article, the gasoline sample is deposited on the interdigital electrodes, which is very similar to the parallel plate capacitor. The electrodes of an interdigital capacitor are coplanar so that very low signal to noise ratio will be gotten. In order to get a strong signal the electrode pattern is be repeated many times, which leads to the structure known as the interdigital structure.

A voltage $U0$ with a fixed frequency $\omega/2\pi$ is applied to the sample capacitor. If the system under test (SUT) is linear, $U0$ causes a current $I0$ at the same frequency in the sample. In addition, there will generally be a phase shift between current and voltage described by the phase angle φ. On the other hand, if the SUT is non-linear, the response signal will not have the same frequency with the generator excitation frequency $\omega/2\pi$ but contains addi-