



Full Length Article

Mobile compact ^1H NMR spectrometer promises fast quality control of diesel fuel



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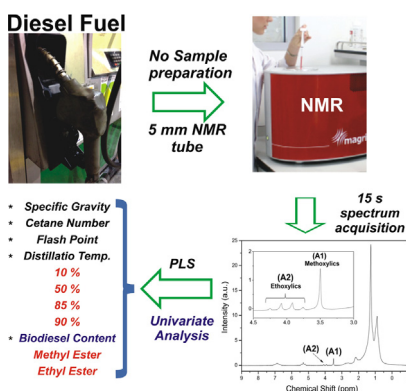
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HIGHLIGHTS

- Bench top NMR spectrometer to determine different quality parameters of diesel fuel.
- 9 important diesel fuel quality parameters determined in less than 1 min.
- Similar results compared to reference methods applied nowadays.
- Low field NMR spectroscopy as a powerful technique for police control of diesel fuel.

GRAPHICAL ABSTRACT



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ABSTRACT

To address the need for fast quality control of diesel fuel, this study introduces a compact ^1H NMR spectrometer to develop Partial Least Squares (PLS) regression models for rapidly determining several quality parameters of diesel fuel such as specific gravity, cetane number, flash point, and distillation temperatures to 10% and 50% of recovery. For all these quality parameters, the developed models showed margins of error better or comparable than reference analytical techniques. The compact NMR spectrometer was also applied for determining biodiesel content (methyl- and ethyl esters) in diesel fuel by using a univariate calibration curve. For all tested commercial diesel fuel samples, this new tool generated comparable results, within the tolerable margin of error, to those obtained with Mid-IR as a reference technique. Operation of the compact low-field NMR spectrometer is simple and fast: no sample pre-treatment or dilution in deuterated solvents is required, and the single-scan measurements take only 15 s per spectrum.

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1. Introduction

The ever growing worldwide demand for fuels and the recent enactment of restrictive environmental regulations on fuel quality have prompted the development of new analytical technologies to monitor the quality of fossil fuels. Not only does the production

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and fuel commercialization sectors benefit from this development but also policy control agencies, in particular, regarding fuels consumed in the transport of passengers and goods, where one can see adulterations that prejudice consumers and strain public coffers [1].

Nowadays diesel/gasoil ranks first in the list of global demand for refined products, considering all sectors of consumption [2]. For the worldwide scenario of demand, diesel fuel takes second place to gasoline. Particularly for Brazil, diesel is the most important fuel for the economy, since trucks transport the major part of Brazilian products. Moreover, the production of diesel fuel makes up about 40% of total Brazilian production of petroleum derivatives. Among petroleum derivatives, diesel fuel assumes first place in terms of import volume [3,4].

Thus, to ensure fuel quality and minimize illegal adulteration practices, the determination of quality parameters for diesel fuel is important in terms of the production chain and commercialization of this product [5]. In Brazil, the commercialization and government control of fuels are both conducted by the National Petroleum Agency (*Agência Nacional do Petróleo, Gás Natural e Biocombustíveis (ANP)*) which, in 2010, mandated the addition of 5% in volume of biodiesel to diesel fuel, a stipulation previously set at 3% [6]. The determination of several quality parameters of diesel fuel proposed by the ANP requires a large number of assays mainly based on physical methods proposed by the American Society for Testing and Materials (ASTM). These assays are normally time-consuming and require specialized technicians. Although these physical assays have a good accuracy and precision, several different instruments are needed for their implementation, a fact that considerably increases the time and cost of the analysis [7].

As alternatives to the conventional methods of diesel analysis, several approaches have been proposed, most of which are based on vibrational spectroscopy (Mid-IR, NIR, and Raman) [8–12]. These techniques provide a rich amount of chemical information about samples in their spectra, which is obtained in a simple and fast way. However, it is not always possible to resolve resonances at well defined frequencies since typically the signals of the different chemical groups in diesel samples overlap precluding their quantification by a simple integration procedure. The problem has been solved introducing chemometric tools to process the experimental data, where the Partial Least Squares (PLS) regression is mostly applied [5,7,13,14]. This approach has become a routine strategy for analyzing vibrational spectra leading to fewer required analytical tests which, in turn, reduces the associated costs and time for analysis [15].

Another spectroscopic technique, which has been considered for diesel analysis in the past is ^1H NMR spectroscopy [16–28]. It provides information of molecular conformation and its environment as well as molecular mobility, in a non-destructive way, by sensing the interaction of nuclear spins with magnetic fields. One of its advantages is the proportionality of the measured signal to the density of the sample under investigation. Moreover, since the typical sample preparation procedure consists of a dilution process in conventional solvents, and no calibration is required for different samples, the analytical quantification becomes direct and easy. Unlike optical spectroscopic techniques, NMR is characterized by low sensitivity and a high investment required to acquire and maintain a superconducting magnet. This fact has limited the use of ^1H NMR for quality control of fuels to research groups or fuel refineries which can afford the costs.

Nonetheless, recent magnet designs combined with efficient shimming techniques of magnetic fields have led to permanent magnets as alternative sources to superconducting ones for the magnetic field generation in compact NMR instruments, without losing the access to chemical shift information [29]. Although permanent magnets generate weaker magnetic field intensity, they

enable the construction of bench-top devices that can be directly applied to monitor a process inside a factory or at a government control point [29,30]. The feasibility of *in situ* measurements with an NMR spectrometer positions NMR as an alternative to vibrational spectroscopic techniques for monitoring process activities according to the modern concepts proposed by process analytical technology (PAT) [31].

This current study investigates the application of a compact high-resolution ^1H NMR device, built with permanent magnets, in order to rapidly determine different quality parameters of diesel fuel such as: specific gravity, cetane number, flash point, distillation temperatures to 10%, 50%, 85% and 90% of recovery and biodiesel content (methyl and ethyl esters) [32–37].

2. Materials and methods

2.1. Instrumentation

The ^1H NMR spectra were recorded on a bench-top NMR spectrometer (*Spinsolve*, Magritek) equipped with a permanent magnet generating a magnetic field of 1 T (43 MHz for the proton Larmor frequency), with homogeneity of 0.01 ppm (see [Supplementary material](#)). The instrument has dimensions of 58 cm × 43 cm × 40 cm and weighs about 55 kg. A high-field Bruker-400 MHz NMR spectrometer was used as a reference to the low-field *Spinsolve* NMR spectrometer.

2.2. Diesel samples

A set of 57 commercial diesel samples (named **Set 1**, composed of diesel fuel gathered as B5 at gas stations), collected from all over São Paulo state (Brazil), was investigated. For the whole sample set all the many quality parameters studied by NMR were determined prior to this work by standard methods of analysis by an accredited analytical laboratory, as regulated in Brazil by the ANP [38]. It is important to mention that the sampling strategy and sample stabilization were carried out by an accredited laboratory according to all the ASTM norms.

The ^1H NMR spectra measured at 1 T were generated without any dilution of the sample in specific solvents or utilization of reference compounds. For this purpose 0.9 mL of sample (used as received) was inserted in a 5 mm NMR glass tube. Each spectrum was acquired immediately after the application of a single 90° radio-frequency (RF) pulse. For each sample, only a single scan was used, and this procedure was performed in triplicate. All samples were brought to the magnet site 2 h before the measurement. Each spectrum was recorded 2 min after the insertion of the sample into the magnet bore. All these procedures were carried out to ensure temperature stabilization. The lab was maintained at a temperature of 25 ± 2 °C. For all the acquired spectra, baseline correction, zero-order phase correction, Lorentzian apodization window of 1 Hz and spectral normalization were applied. The normalization process was conducted by division of each spectrum by its maximum in the range of $\delta = 0$ to $\delta = 9$ ppm. The device was automatically shimmed after 15 spectra acquisition (5 different samples) and the complete shim procedure took no more than 3 min.

One sample of mineral diesel (without biodiesel), provided by a Brazilian distributor of fuel, was also studied. For this sample, both low-field and high-field spectra were acquired. This sample was used only for spectral elucidation and determination of the biodiesel content parameter. The high-field spectrum was acquired by diluting 25 mg of mineral diesel in 700 μL of CDCl_3 , and the low-field spectrum was acquired after the addition of 50 μL of tetramethylsilane (TMS) in the sample inside the NMR tube and subsequent shaking.

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