



Fast determination of 2-ethylhexyl nitrate in diesel oils by infrared spectrometry



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HIGHLIGHTS

- ATR–FTIR method for the determination of 2-EHN in diesel fuel was developed.
- Validation of the method was performed.
- Ten real samples of diesel fuel analysed by means of 2-EHN content.
- ATR–FTIR method founded as a faster alternative to previously developed GC/MS method.

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ABSTRACT

In this study a rapid and easily applicable method for the quantification of 2-ethylhexyl nitrate (2-EHN) in diesel fuel was developed and validated. This method employs Fourier transform infrared spectrometry with attenuated total reflectance (ATR–FTIR). Before the determination of 2-EHN content, could be made to be necessary to analyse the fatty acid methyl esters (FAME) content in diesel fuel in order to prepare the appropriate background solution. Based on the matrix assisted calibration method, the limit of detection was found to be 0.009% w/w for 2-EHN and the limit of quantification 0.025% w/w. The method is linear over the range 0.025–0.300% (w/w), with a correlation coefficient over 0.9998 with satisfactory accuracy, repeatability, and reproducibility. The ATR–FTIR method has been applied to quantify 2-EHN in ten samples of real diesel fuel. Relative standard deviations for all fuel samples were lower than 10%.

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1. Introduction

Automotive diesel fuels are complex mixtures whose composition depends on the sources of the crude petroleum, methods of separation, and the purification techniques used. Diesel fuel must satisfy a wide range of engine types, different operating conditions, and duty cycles as well as variations in fuel system technology, engine temperatures, and fuel system pressures. By controlling specifications and properties, it is possible to satisfy the requirements of millions of compression ignition engines with a single grade of diesel fuel. Guidelines have been established internationally for diesel fuel quality by the American Society of Testing and Materials (ASTM), while some countries have their own standards, which may slightly vary from ASTM property limits. The ASTM standards are continuously reviewed and updated [1].

An important descriptor of diesel fuel is its cetane number (CN). It is an indicator of the time delay between injection and spontaneous ignition of fuel in a standard diesel engine running under

specified conditions; the shorter ignition delay means the higher CN [2]. The ignition quality of the diesel fuel depends on its composition. The CN decreases with an increase in the content of aromatic hydrocarbons (requiring higher temperatures and pressures to ignite), and increases with an increase in the content of the n-paraffins and olefins (able to ignite in a diesel engine with relative ease) [3,4]. Diesel fuels have a CN in the range 40–60, depending on the country where it is distributed. In Europe, the EN 590 standard requires a minimum cetane rating of 51 [5,6].

The CN scale uses two standard compounds, cetane (n-hexadecane) which has very good ignition quality and was assigned the CN of 100, and 2,2,4,4,6,6,8,8-heptamethylnonane (sometimes called HMN or isocetane) with poor ignition quality, which was assigned a CN of 15 [5]. The CN of a diesel fuel is defined by ASTM as the volume percentage of normal cetane in a blend with isocetane, which matches the ignition quality of the diesel fuel being rated under the specified test conditions. This implies that $CN = \% (n\text{-cetane}) + 0.15 (\% \text{ HMN})$. The ASTM D-613 method involves running the fuel in a single cylinder compression-ignition engine, with a continuously variable compression ratio under a fixed set of conditions [7].

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A very important group of additives used in the diesel fuels are cetane improvers which enhance the cetane quality of diesel fuels by reducing the delay between injection and ignition when fuel is sprayed into a combustion chamber. The chemicals most commonly used as cetane improvers are nitrates and certain peroxides [8]. Among the various alkyl-nitrates (e.g. fatty acid glycol nitrates [9], nitrate derivatives of triglycerides [10], etc.), 2-ethylhexyl nitrate (2-EHN) is the most widely used improver commercially [3].

2-EHN is the nitric ester of 2-ethylhexan-1-ol. In refineries, 2-EHN is usually added to diesel fuel in the concentration range of 0.03–0.3% w/w. Refineries have a set level of cetane improver for base fuel to meet the legislative requirements for fuel quality (according to quality standard), which is monitored as CN according to the ASTM D-613 using the test engine method. Monitoring of the cetane improver content is sufficient to indirectly control of the cetane number. The concentration of 2-EHN in the Czech Republic is determined using the standardized EN ISO 13759 method [11]. This method is based on the hydrolysis of 2-EHN using a strong acid solution and the released nitric acid reacts with 2,4-dimethylphenol. The reaction product is extracted by 2,2,4-trimethylpentane followed by addition of sodium hydroxide. Color intensity of the established yellow salt solution is measured using spectrophotometry at wavelength of 452 nm.

The standardized method contains several disadvantages such as requiring large solvent volumes, significant time consumption, and relatively high values of relative standard deviations for repeatability and reproducibility. To solve these problems, an alternative method was developed using a static headspace-GC/MS for the quantification of 2-EHN in diesel fuel [12]. The developed GC/MS method removes the above mentioned disadvantages of the standardized method, however, it requires specific instrumentation, not available everywhere.

The aim of this work was to find an alternative method for the determination of 2-EHN in diesel fuel, comparable with the reported GC/MS method including conditions such as low solvents and time consumption, repeatability, and reproducibility. The method was developed using ATR-FTIR (attenuated total reflectance Fourier transform infrared spectrometry), and was found to be comparable with the GC/MS method. The ATR-FTIR method was faster than GC/MS method, and also uses a less solvent. 2-EHN was determined in two diesel fuel types available in the Czech Republic: B7, with a FAME content of no greater than 7% (v/v) (according to the EN 590 [6]); and B30, containing a minimum of 30% (v/v) of FAME (according to the ČSN 65 6508 [13], which is specific standard applied in the Czech Republic, since there does not exist as of yet a European standard for blend of diesel oil and FAME labelled as B30 yet).

2. Materials and methods

2.1. Reagents

2-EHN (97%) and 2-nitrotoluene (99%) were purchased from Sigma-Aldrich (Steinheim, Germany). Nitrates-free diesel fuel

and fatty acid methyl esters (FAME) were provided by Paramo, a.s. (Pardubice, Czech Republic).

Stock solution of 2-EHN was prepared by dissolving of appropriate amount in nitrates-free diesel oil at concentration of 10% w/w. Control samples S1, S2, S3 and S4 were prepared by spiking nitrate-free diesel with 2-EHN at various levels (Table 1).

Diesel fuel samples were collected at petrol pumps situated around the city of Pardubice. All samples and solutions were stored in a dark location at laboratory temperature.

2.2. Instrumentation and methods

2.2.1. Fourier transform infrared spectrometry

The FTIR spectrometer, model Equinox 55 from Bruker (Rheinstetten, Germany) equipped with ATR accessories, was employed for all FTIR analyses.

Characteristic absorption bands of 2-EHN were identified in the range of 4000–600 cm^{-1} by comparing spectra of nitrates-free diesel fuel with 2-EHN containing diesel fuel (air as background). Calibration samples were prepared at concentrations ranging from 0.005 to 0.300 mg/kg and measured with background correction in the wavenumber range from 2000 to 1000 cm^{-1} . Areas and heights of the absorption bands were integrated and plotted against the concentration of 2-EHN. This was the chosen optimum calibration for the determination of 2-EHN (see Section 3.1).

2.2.2. Gas chromatography/mass spectrometry

A gas chromatograph, model GC-17A, coupled with mass spectrometry detector QP 5050A (Shimadzu, Kyoto, Japan) and Pal-Combi auto-sampler (CTC Analytics AG, Zwingen, Switzerland) were employed for all GC/MS analyses. The GC/MS system was equipped with a capillary column DB5-MS with length 30 m, 0.25 mm inner diameter and 0.25 μm film thickness (J&W Scientific, Folsom, CA, USA). Helium 5.0 (Linde Gas, Prague, Czech Republic) was used as the carrier gas at a constant linear velocity of 30 cm/s. Methane 3.5 (Linde Gas) was used as a reaction gas for negative chemical ionization. The injector and the interface temperature were maintained at 280 and 230 $^{\circ}\text{C}$, respectively. The column temperature was programmed as follows: the initial temperature was 100 $^{\circ}\text{C}$ (10 min), then increased at a rate of 25 $^{\circ}\text{C}/\text{min}$ up to 280 $^{\circ}\text{C}$ (13 min). o-Nitrotoluene was selected as the internal standard. The samples were incubated in an agitator at 60 $^{\circ}\text{C}$ for 30 min to allow the volatile compounds to achieve the equilibrium between gaseous and liquid phases. The headspace analysis was performed with a 2.5 mL gas tight syringe that was preheated at 37 $^{\circ}\text{C}$. A 500 μL headspace aliquot was injected at a split ratio of 1:100. After each analysis, the syringe was flushed with nitrogen for 2 min. Analyte detection was performed in selected-ion monitoring (SIM) mode and quantification of 2-EHN was performed by the internal standard calibration method. [12].

2.2.3. Method validation

The linearity was evaluated in the selected concentration range, with spiked blank diesel fuel (free of 2-EHN and FAME), see

Table 1
Comparison of the results obtained by measurement of control samples S1–S4.

Sample	Spiked concentration of 2-EHN (mg/kg)	Concentration of 2-EHN by ATR-FTIR (mg/kg), $n = 3$			
		Cal-1 ^a	Cal-2	Cal-3	Cal-4
S1	304	300 ± 29	321 ± 41	319 ± 16	290 ± 10
S2	458	470 ± 33	482 ± 20	447 ± 37	431 ± 13
S3	1203	1191 ± 60	1261 ± 50	1235 ± 21	1235 ± 29
S4	1820	1815 ± 12	1851 ± 54	1806 ± 23	1875 ± 20
The average relative difference from the true value (%)		1.3	4.3	2.7	4.0

^a Cal-1 – area at 1626 cm^{-1} , Cal-2 – height at 1626 cm^{-1} , Cal-3 – area at 1276 cm^{-1} , Cal-4 – height at 1276 cm^{-1} .

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