

Characterization of lubricity improver additive in diesel by gas chromatography–mass spectrometry

Michelle J.C. Rezende*, Carlos R. Perruso, Débora de A. Azevedo, Angelo C. Pinto

Departamento de Química Orgânica, Instituto de Química, Universidade Federal do Rio de Janeiro, Centro de Tecnologia, Bloco A, Sala 621, Ilha do Fundão, Rio de Janeiro-RJ 21949-900, Brazil

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Abstract

The characterization of lubricity improver additives by GC–MS–SIM is an important tool for the development and monitoring of new formulations as well as for quality control of additives in diesel. A simple method for the quantification of a linoleic oil additive derivative in diesel has been developed. Calibration is performed by analysis of standard solutions containing 2-hydroxy-ethyl linoleate with pentadecanoyl propanoate as the internal standard. The proposed method permitted the quantification of the linoleate ester at a concentration of 300 $\mu\text{g/mL}$ in the additived diesel. The recovery of additive and the repeatability of the quantitative results are evaluated.

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1. Introduction

Due to concern about environment preservation more restrictive emission levels for diesel vehicles have been introduced since the last decade. Thus, the refining industry has been producing purer sulfurless fuels through hydrotreatment. However, the desulfurization process also removes polyaromatic and polar compounds, such as oxygen- and nitrogen-containing molecules, which confers lubricating properties to the fuel [1,2]. Problems of wear in fuel-injection equipment are linked directly to the reduced lubricity of low sulfur fuels [3,4]. These problems could be overcome either by addition of lubricity improver additives to diesel fuel or by suitable modification of the engine design.

Several types of lubricity additives have been proposed, such as formulations involving fatty acid esters, unsaturated fatty acids dimers, aliphatic amines and long chain monocarboxylic acids [5–9]. In particular, mono-esters produced by the transesterification of vegetable oils with alcohols such as

1,2-ethanediol, 1,3-propanediol and 1,2,3-propanetriol [10], have found considerable use.

The identification of types and concentrations of lubricity improver additives is an important tool for the development and monitoring of new formulations with better performance, as well as for the quality control of these additives in diesel. As far as we know, there is no method in the literature which can identify or quantify lubricity improver additives in diesel. The objective of this work is the development of a method for the characterization of lubricity improver additives in diesel by gas chromatography–mass spectrometry (GC–MS) using the selective ion monitoring (SIM) mode. In this paper we present results obtained for a lubricity additive derivative from soybean oil and 1,2-ethanediol (Fig. 1), which is used commercially.

2. Experimental

2.1. Chemicals

Methyl linoleate and 1-pentadecanol were from Aldrich (>99%, USA). Propanoyl chloride was from Merck (USA).

* Corresponding author. Fax: +55 21 25627256.

E-mail address: michelle@iq.ufrj.br (M.J.C. Rezende).

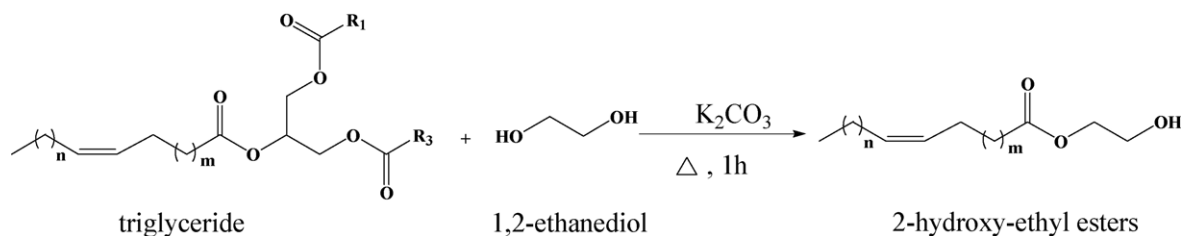


Fig. 1. Synthesis of the additive.

1,2-Ethanediol, potassium carbonate and sodium sulfate were from Vetec (Brazil). UV/HPLC spectroscopic grade solvents (hexane, ethyl acetate, methylene chloride) were from Vetec (Brazil). Diesel was obtained from a Brazilian refinery and was used as the base fuel. Soybean oil was obtained commercially.

2.2. Standard ester and lubricity additive synthesis

The standard ester, 2-hydroxy-ethyl linoleate, was prepared by the transesterification of methyl linoleate with the corresponding alcohol, 1,2-ethanediol, in a 10:1 molar ratio of alcohol-to-ester and in the presence of potassium carbonate at reflux for 1 h. The product was obtained after neutralization (pH 7) with a 10% hydrochloric acid solution, followed by extraction with ethyl acetate. The organic layer was washed with water and then dried over sodium sulfate. Finally, the solvent was evaporated under reduced pressure. The product was filtered on a silica gel column and eluted with different mixtures of *n*-hexane and ethyl acetate. The *n*-hexane:ethyl acetate (70:30) fraction was found to consist mainly of the standard ester. The standard purity was determined by gas chromatography analysis (GC–FID).

The lubricity additive was synthesized by the transesterification of soybean oil following the same procedure as for the standard synthesis. The amount of 2-hydroxy-ethyl linoleate in the additive was determined by GC–FID.

2.3. Internal standard synthesis

The internal standard (IS) was prepared by the esterification of propanoyl chloride with 1-pentadecanol in methylene chloride. The mixture was stirred at room temperature for 90 min. The solvent was then evaporated under reduced pressure and the product filtered on a silica gel column using *n*-hexane as eluent. The IS purity was determined by GC–FID.

2.4. Preparation of standard solutions

A standard stock solution of approximately 1000 $\mu\text{g/mL}$ was prepared by dissolving 10 mg of 2-hydroxy-ethyl linoleate in 10 mL ethyl acetate solvent. It was then stored at -20°C . Standard diesel solutions were prepared from this stock solution in the range of 60–360 $\mu\text{g/mL}$ of ester. The

standard diesel solutions were prepared by mixing a known volume (30, 60, 90, 120, 150, 180 μL) of the standard stock solution, 100 μL of diesel, 100 μL of a 2000 $\mu\text{g/mL}$ pentadecanoyl propanoate solution as IS and the volume completed to 500 μL with ethyl acetate solvent. Calibration graphs in SIM mode were built up with known amounts of 2-hydroxy-ethyl linoleate standard in diesel (60, 120, 180, 240, 300, 360 $\mu\text{g/mL}$) and IS at 400 $\mu\text{g/mL}$ in triplicate.

2.5. Recovery

Additive diesel samples were prepared at three concentration levels (500, 1000, 1400 $\mu\text{g/mL}$) by dissolving known weights of additive in diesel. The samples for analyses were prepared in a vial by the addition of 100 μL of the additive diesel, 100 μL of a 2000 $\mu\text{g/mL}$ IS solution and completed to 500 μL with ethyl acetate solvent. The entire procedure was carried out in triplicate in order to get the standard deviation and reproducibility.

External standard calibration curves were used for quantification of the additive diesel in addition to the IS.

2.6. Instrumentation and chromatographic conditions

GC–MS analyses were performed in a Hewlett Packard 5890 gas chromatography coupled to a Hewlett Packard 5972 MSD Instrument (Agilent Technologies, Avondale, USA) with electron impact ionization (70 eV ionization energy). A DB-1 capillary column (J & W, USA) with a 0.25 mm i.d., 15 m and 0.10 μm phase film diameter was used. The carrier gas was helium at a flow of 2.38 mL/min. The temperature program was 80–150 $^\circ\text{C}$ at a rate of 8 $^\circ\text{C}/\text{min}$, then increased to 200 $^\circ\text{C}$ at a rate of 4 $^\circ\text{C}/\text{min}$ and finally to 300 $^\circ\text{C}$ at a rate of 15 $^\circ\text{C}/\text{min}$ with a final isothermal period of 5 min. The injector and interface temperatures were held at 290 and 300 $^\circ\text{C}$, respectively, and the run time was 33 min. The sample volume of 1.0 μL and the split mode with a ratio of 1:10 was used. All samples were analyzed in SIM mode for quantification measurements of the ester and SCAN mode in the mass range of 40–500 u for confirmation of the spectral data.

GC–FID analyses were performed in a Hewlett Packard 5890 series II gas chromatography. The instrument was equipped with a flame ionization detector and a DB-1 capillary column (J & W, USA) with a 0.25 mm i.d., 15 m and

Table 1
Additive composition percentage analyzed by GC–FID

Esters	Area (%)
2-Hydroxy-ethyl palmitate	12
2-Hydroxy-ethyl linoleate	54
2-Hydroxy-ethyl oleate	28
2-Hydroxy-ethyl linolenate	3
2-Hydroxy-ethyl estearate	3

0.10 μm phase film diameter. The carrier gas was hydrogen at a flow of 1.5 mL/min. The temperature program was 100–240 °C at a rate of 10 °C/min with a final isothermal period of 5 min. The injector and detector temperatures were held at 290 and 300 °C, respectively, and the run time was 19 min. The sample volume of 1.0 μL and the split mode with a ratio of 1:20 was used.

3. Results and discussion

This method was developed especially for lubricity improver additive derivatives from linoleic oils. Thus, additives obtained by transesterification of vegetable oils such as soybean oil (53–55%), corn oil (57–60%), cottonseed oil (55–57%) and sunflower oil (68–73%) [11–13] can be analyzed by this method without changes in the conditions. The additive analyzed in this work was synthesized by the transesterification of soybean oil with 1,2-ethanediol. Therefore, 2-hydroxy-ethyl linoleate was selected for the quantitative determination by selective monitoring of its characteristic ions.

The standard and lubricity additive were synthesized by base-catalyzed transesterification in an excess of the alcohol and using potassium carbonate as catalyst [14,15]. This catalyst gives high yields of fatty acid esters and reduces the soap formation, which makes the reaction cleaner and the purification much easier. The standard ester purity (>99%) was determined by GC–FID and the lubricity additive analysis showed that 2-hydroxy-ethyl linoleate was 54% of the additive. The chromatographic conditions are described in Section 2.6 and the additive composition is summarized in Table 1.

Internal standard calibration was used for quantification of the selected ester in the diesel samples. Pentadecanoyl propanoate, having a retention time lower than 2-hydroxy-ethyl linoleate, has been chosen as the internal standard. It is different from any derived fatty acid ester, eliminating any possibility of its being formed in an additive originating from vegetable oil. In addition, it has the necessary characteristics for an appropriate internal standard, such as good stability and clear separation from the analyte we are trying to quantify. It could be easily synthesized and purified in the laboratory, the analysis by GC–FID showed the internal standard was more than 99% pure. The chromatographic conditions are described in Section 2.6.

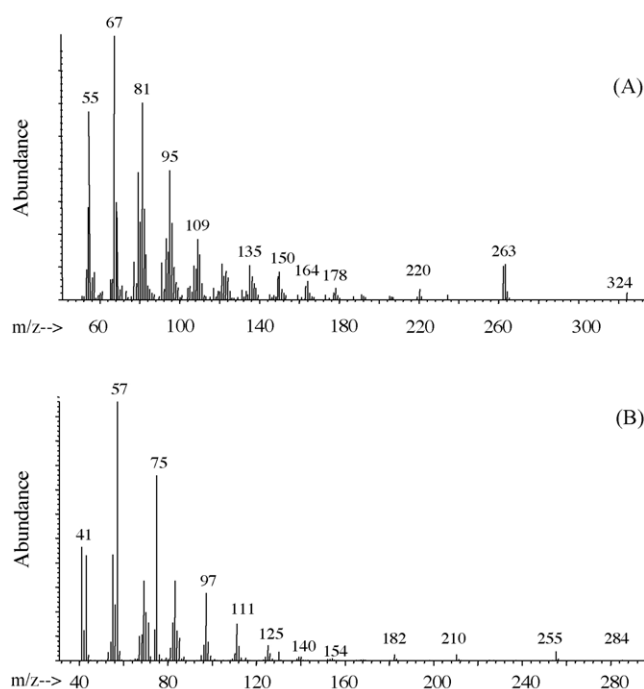


Fig. 2. Mass spectra of: (A) 2-hydroxy-ethyl linoleate and (B) pentadecanoyl propanoate.

Table 2
Retention time (t_R) and selected characteristic ions

Compounds	t_R (min)	Characteristic ions (m/z)
Pentadecanoyl propanoate	11.38	182/210/ 255
2-Hydroxy-ethyl linoleate	17.93	220/262/ 263

Ions for quantitative analysis are shown in bold.

3.1. Qualitative analysis

The mass spectrum of 2-hydroxy-ethyl linoleate is characterized by the presence of three signals: m/z 262, m/z 263 and m/z 324. For the internal standard, the selected ions were m/z 182, m/z 210 and m/z 255. The mass spectra are shown in Fig. 2. Qualitative mass chromatograms of these esters in diesel were obtained and the peak identifications were confirmed by injection at different concentrations. Table 2 presents the retention times, according to the temperature program used, and the characteristic fragments selected for qualitative and quantitative determinations.

3.2. Pure diesel analysis

After the peak identifications, pure diesel was analyzed by GC–MS–SIM. The purpose of this test was to detect compounds that could have the same ions chosen for the additive and internal standard in the matrix. In Fig. 3, the m/z 255 and m/z 263 mass chromatograms of pure diesel are presented. The analysis shows that diesel does not have compounds with these ions close to the retention time of pentadecanoyl propanoate and 2-hydroxy-ethyl linoleate. Thus, during the characterization of the additived formulations proposed, we

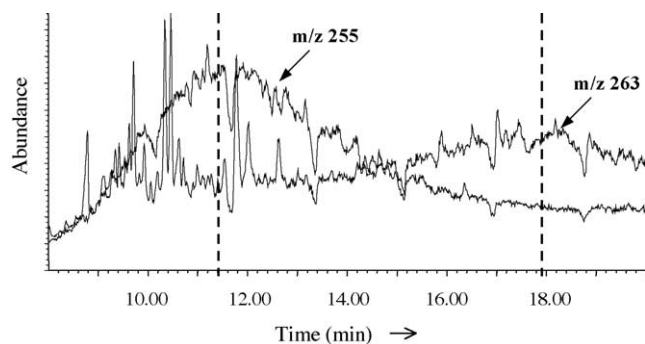


Fig. 3. GC-MS-SIM chromatogram, m/z 255 and m/z 263, of pure diesel.

are able to affirm that the registrations of the ions m/z 255 and m/z 263 in these areas only belong to the internal standard and 2-hydroxy-ethyl linoleate, respectively.

3.3. Calibration

The standard solutions were analyzed and the calibration graph was built in the range 60–360 $\mu\text{g/mL}$ using the ions m/z 255 and m/z 263 for the quantitative determination of pentadecanoyl propanoate and 2-hydroxy-ethyl linoleate, respectively. In Fig. 4, the m/z 255 and m/z 263 mass chromatograms are reported at three different concentrations. The standard calibration parameters are summarized in Table 3. The curve showed a linear relationship between the instrumental response and the analyte concentration. The quantification limit, calculated on the basis of a signal-to-noise ratio of 5:1, was 60 $\mu\text{g/mL}$. Considering that the diesel was diluted in the ratio of 1:5 to minimize the matrix effect, the quantification limit corresponds to a 2-hydroxy-ethyl linoleate concentration of 300 $\mu\text{g/mL}$ in added diesel. As a consequence, this method allows the quantification of additive in a minimal concentration of 550 $\mu\text{g/mL}$ in diesel, considering that the linoleate ester is present as 54% in the analyzed additive.

3.4. Quantitative results

For the evaluation of recovery, diesel from a Brazilian refinery used as reference (without additives) was spiked with known amounts of additive at different concentration levels. These were analyzed and the percentage recoveries were calculated comparing the quantitative results obtained by GC-MS-SIM analysis, using the external calibration equation presented in Table 3, and the actual concentra-

Table 3

Parameters of the standard solution calibration equation

Equation	$Y = 2.0054X - 0.0884$
R^2	0.9998
LQ ^a	60 $\mu\text{g/mL}$
LD ^b	50 $\mu\text{g/mL}$

^a Signal-to-noise ratio of 5:1.

^b Signal-to-noise ratio of 3:1.

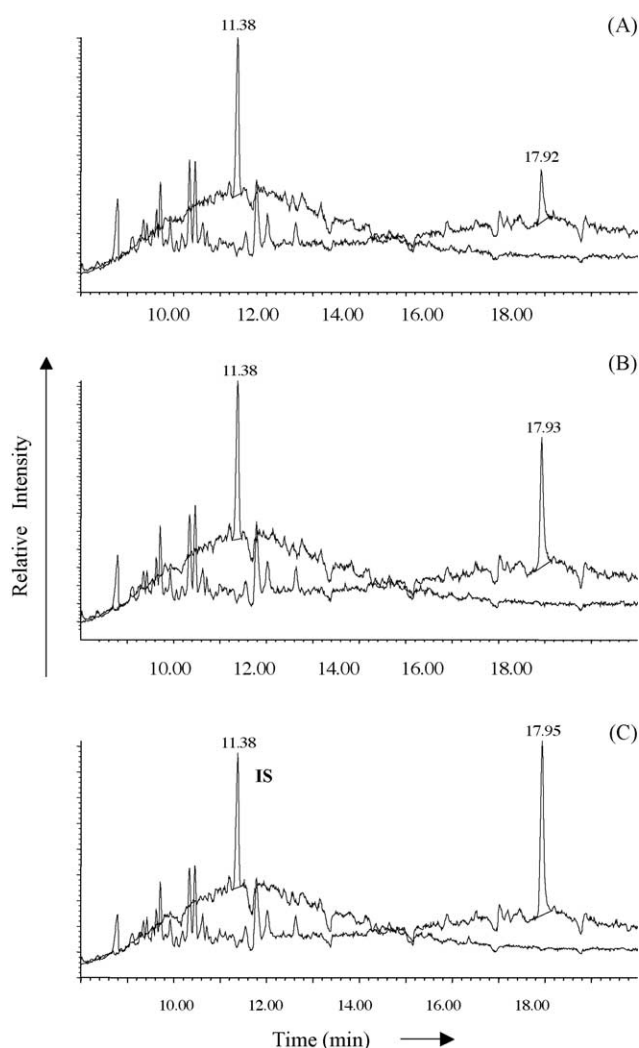


Fig. 4. GC-MS-SIM chromatograms, m/z 255 and m/z 263, of the additive diesel at different concentrations: (A) 120; (B) 240 and (C) 360 $\mu\text{g/mL}$. IS at concentration of 400 $\mu\text{g/mL}$.

tions of the compounds. The analysis showed an acceptable recovery even at the detection limit. The results are given in Table 4.

In order to check the precision of the method, a sample of additived diesel was prepared and consecutively analyzed three times. Additionally, nine samples of the additived diesel in three different concentrations were prepared and analyzed by GC-MS-SIM. The repeatability of the quantitative determination was evaluated and the results are summarized in Table 5. The data indicate the good repeatability of the quantitative results obtained by this method. Due to simple sample

Table 4

Average recovery ($n = 3$) for 2-hydroxy-ethyl linoleate at three concentration levels of additive diesel

Concentration ($\mu\text{g/mL}$)	Recovery (%)
54	108
108	125
180	101

Table 5

Repeatability of the quantitative results obtained by consecutive injections ($n=3$) and by repeated complete analysis including sample preparation ($n=9$)

Analysis	Concentration of 2-hydroxy-ethyl linoleate ($\mu\text{g/mL}$)			
	Consecutive injections	Complete analysis		
1	179	59	146	217
2	183	58	148	208
3	178	61	137	217
Mean	180.0	59.3	143.7	214.0
S.D.	2.6	1.5	5.8	5.2
R.S.D. (%)	1.4	2.5	4.0	2.4

preparation (comprising addition of the internal standard and dilution in the 1:5 ratio with solvent), the reproducibility of the quantitative results obtained by the methodology is as good as that obtained by consecutive injection of the same sample.

Finally, we would like to point out that this method is useful for the measurement of other hydroxy esters, for ex-

ample 3-hydroxy-propyl and 2,3-dihydroxy-propyl linoleate, which are also used commercially. They have different retention times in the established chromatographic temperature program and they can be monitored by the same ions (m/z 262 and m/z 263), according to the mass spectra illustrated in Fig. 5.

4. Conclusions

In a single GC–MS–SIM run, the proposed method provides qualitative and quantitative information about lubricity improver additive derivatives from linoleic oils. High reliability, simple instrumentation and sample preparation, short analysis time and the possibility of complete automation make this method well suited for the quality control of these additives in diesel fuel.

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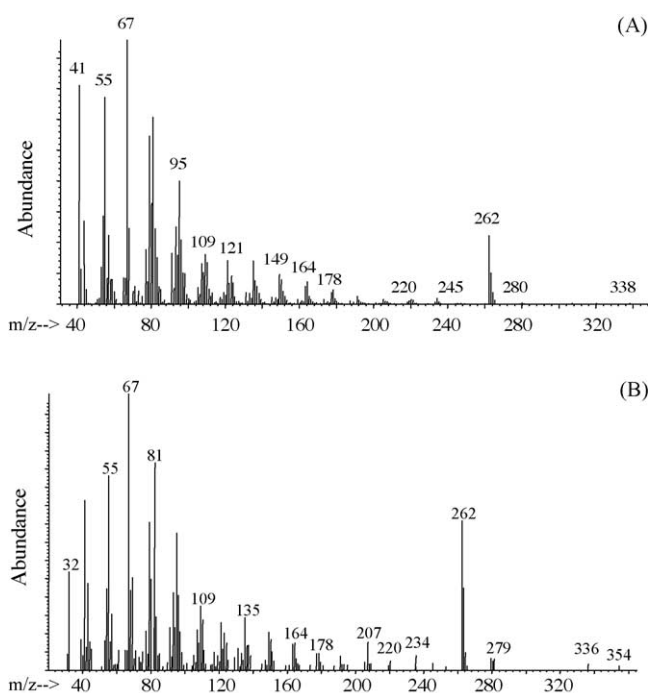


Fig. 5. Mass spectra of: (A) 3-hydroxy-propyl linoleate and (B) 2,3-dihydroxy-propyl linoleate.