



## Full Length Article

# Quantification of detergent-dispersant additives in gasoline by size-exclusion chromatography and thermogravimetry



Amanda Pereira Franco dos Santos<sup>a,b,\*</sup>, Kissya Kropf da Silva<sup>b</sup>, Jo Dweck<sup>a</sup>, Luiz Antonio d'Avila<sup>a,b</sup>

<sup>a</sup>Engineering Program in Chemical and Biochemical Processes, Escola de Química, Universidade Federal do Rio de Janeiro, 21941-909 Rio de Janeiro, RJ, Brazil

<sup>b</sup>Fuel and Oil Product Laboratory, Escola de Química, Universidade Federal do Rio de Janeiro, 21941-909 Rio de Janeiro, RJ, Brazil

## ARTICLE INFO

## Article history:

Received 13 October 2016

Received in revised form 28 December 2016

Accepted 4 January 2017

Available online 10 January 2017

## Keywords:

Additives

Gasoline

Chromatography

Thermogravimetry

## ABSTRACT

The use of detergent-dispersant additives in gasoline helps keep engines clean, inhibits the formation of gum and sludge in the combustion process, and reduces emissions of contaminants to the atmosphere. Although the composition of detergent-dispersant additives is a trade secret, it is known that their average molecular weight is higher than that of gasoline. As such, we propose a method for the quantification of these additives in gasoline using the atmospheric distillation technique for the pre-concentration of the additives, and then their analysis by size exclusion chromatography with a conventional refractive index detector. When a commercial gasoline is analyzed, the type of additive it contains must first be characterized before its concentration can be calculated, and thermal analysis proved to be a simple, effective alternative for this procedure. Standard samples were prepared to obtain calibration curves, and verification samples were used to test the proposed method. The results obtained proved satisfactory when compared with the nominal value of each verification sample. The relative error obtained was less than 8.5%.

© 2017 Elsevier Ltd. All rights reserved.

## 1. Introduction

Auto gasoline is basically composed of hydrocarbons, whose composition and properties are critical for the performance of engines and the amount of pollution generated in the combustion process [1,2].

In Brazil, auto gasoline is divided into regular and premium. Gasoline A is free of oxygenated components, while gasoline C is produced by blending gasoline A with anhydrous ethanol [3]. There is also a gasoline C that is additized with detergent-dispersant additives, which enhance the performance of the engine, keeping the solids suspended and finely dispersed and thus preventing them from forming unwanted deposits, while also reducing emissions of pollutants [2–4].

Detergent additives act via polar terminal groups and generally contain nitrogen. They adhere to metal surfaces, forming a protective film that prevents the build-up of residues on the internal surfaces of engines. Dispersant additives contribute to the dispersion of the particles that enter the engine via the air, fuel, or lubricant,

keeping them suspended as solids and finely dispersed, thereby preventing the build-up of deposits [1]. The benefits of using these compounds include a 3% reduction in fuel consumption, a 60–70% reduction in deposit formation, a 50–60% reduction in carbon monoxide and hydrocarbon emissions, and a 20% reduction in nitrogen oxide emissions [1,4].

Environmental concerns about gas emissions have driven improvements in the quality control of fuels. Following the example of other countries, including the USA, which in 1996 introduced the requirement for detergent additives to be added to gasoline to reduce emissions of pollutants from automotive vehicles, the Brazilian oil and gas industry regulatory agency, Oil, Gas and Bio-fuels National Agency (ANP), passed a regulation in 2013 (ANP Resolution 40/2013) that sets the specifications for gasoline for phase L-6 of the Automotive Vehicle Air Pollution Control Program (PRO-CONVE) and the rules for the use of detergent-dispersant additives in this fuel as of July 2017 [3,4].

The use of additives in all gasoline has been the target of research by working groups coordinated by ANP, because although additized regular gasoline C has been on sale in the domestic market for years, there is no reference method published by ANP or in the literature for the qualitative and quantitative analysis of the additives. This situation is compounded by the fact that the exact composition of the additives used in the fuel is not known, since

\* Corresponding author at: Centro de Tecnologia, Bloco K02, LABC0M, Cidade Universitária, Rio de Janeiro 21941-909, Brazil.

E-mail addresses: [apfranco@eq.ufrj.br](mailto:apfranco@eq.ufrj.br) (A.P.F. dos Santos), [kissyakropf@gmail.com](mailto:kissyakropf@gmail.com) (K.K. da Silva), [dweck@eq.ufrj.br](mailto:dweck@eq.ufrj.br) (J. Dweck), [davila@eq.ufrj.br](mailto:davila@eq.ufrj.br) (L.A. d'Avila).

they are sold by manufacturers as additive packages whose composition is a trade secret. According to Colaiocco and Lattanzio (1995), Silin et al. (2012), and Danilov (2015), the active ingredients of detergent additive packages may include amines, amides, amine-amides, alkenyl succinimides, polybutene amines, or other compounds, dissolved in mineral oils [5–7]. Even so, it is known that detergent-dispersant additives are added to gasoline by distributors, that their average molecular weight is greater than that of gasoline, and that the concentration of the additives depends on their effectiveness, but that the maximum concentration is 5000 mg kg<sup>-1</sup>, or 0.5 mass% [2]. As such, if the use of additives is to be mandatory, analytical methods must be developed for determining their concentration in gasoline if the law is to be enforced.

Although there are a great many patents for detergent-dispersant additive packages for fuel, there are few methods in the literature and few patents that cover the identification and quantification of these additives in gasoline. Medeiros (2009) has used vibrational spectroscopy (FT-IR and FT-NIR) in association with chemometric techniques and the pre-concentration of the fuels to quantify three additives in regular gasoline (type C) [1]. Pimentel et al. (2015) have developed a method for identifying and quantifying four detergent-dispersant additives in gasoline that involves concentrating them using the ring oven technique then using near-infrared hyperspectral imaging for their analysis [2]. Silva et al. (2014) have proposed a methodology which uses infrared spectra in the medium and near region (MIR and NIR) of the residue of distillation for classification of gasoline samples into two groups: with or without detergent/dispersant additives [8]. Pinto et al. (2016) have used the Nuclear Magnetic Resonance spectroscopy of hydrogen (<sup>1</sup>H NMR) along with principal component analysis (PCA) and Soft Independent Modelling of Class Analogies (SIMCA) to differentiate between common (CG) and additive gasoline (AG) [9]. Colaiocco & Lattanzio (1995) have described a method for identifying and quantifying amide detergents using size-exclusion chromatography [5]. Santos and d'Avila (2012) and Santos (2012) have used size-exclusion chromatography to identify and quantify detergent-dispersant additives in Brazilian gasoline [10,11]; indeed, this research formed the basis for the present study. Finally, patents CN1673737A, PI0400082-0A, and CA2132806A1 propose methods for separating and identifying detergent-dispersant additives in gasoline by thin-layer chromatography, liquid chromatography, and size-exclusion chromatography [12–14], while patent WO2014/075158A1 describes a quick, simple, easily executable, reliable way of identifying detergent-dispersant additives in fuels and lubricating oils in the field [15].

While the composition of detergent-dispersant additives may be a trade secret, it is known that their average molecular weight exceeds that of gasoline. This feature suggests they could be analyzed using size-exclusion chromatography and pre-concentrated by the atmospheric distillation (ASTM D86/11b) [16] of the additized gasoline, making the use of a refraction index detector feasible. For the analysis of commercial gasoline, the type of additive used has to be characterized first for the respective concentrations to be calculated, for which thermal analysis has also been found to be a simple, effective alternative.

## 2. Materials and methods

### 2.1. Preparation of samples

In the absence of any reference materials for additives and additized gasoline, reference samples of regular gasoline C were prepared to produce the calibration curves. Four additives of unknown composition (since this is a trade secret) provided by

ANP were used, named G, T, W, and Y, and the samples were prepared at concentrations of approximately 60, 100, 200, and 400 mg kg<sup>-1</sup>. For the 400 mg kg<sup>-1</sup> reference samples, approximately 0.4 g of each additive was weighed for every 1000 g of regular gasoline C. To obtain the lower concentrations, dilutions were made from the 400 mg kg<sup>-1</sup> samples. Additionally, verification samples were prepared of other concentrations than the ones used for the calibration curves (150 and 300 mg kg<sup>-1</sup>) for the purposes of evaluating the proposed method.

### 2.2. Pre-concentration of additives

The ASTM D86/11b standard test can be conducted using manual or automated equipment. A 100 mL sample of gasoline is measured using a graduated cylinder and then transferred to a special glass distillation flask, which is heated under controlled conditions for distillation to occur. Upon heating, the vapors of the product enter a condenser tube and are collected in a 100 mL glass cylinder. Normally, the temperatures that are recorded are the initial boiling point, the temperatures at which 10%, 50%, and 90% was collected, and the final boiling point, and the volume of residue at the end of distillation is also measured [16].

The ASTM D86/11b standard method for the distillation of petroleum products at atmospheric pressure, which is mandatory for the monitoring of gasoline quality and is thus available in any fuel testing laboratory, was used to concentrate the additives present in the residue obtained at the end of distillation [16]. The automated distillation tester used was the TANAKA AD-6 (Tanaka Scientific Ltd., Tokyo, Japan) and tetrahydrofuran, analytical grade (Tedia Inc., Fairfield, USA) was dissolved with the residue to obtain a final volume of 5 mL, making its concentration 20 times higher than that of the additive originally present in the gasoline.

### 2.3. Quantification by size-exclusion chromatography (SEC)

The pre-concentrated gasoline samples prepared in this research were analyzed using size-exclusion chromatography. The equipment used was an UltiMate 3000 quaternary pump (Thermo Scientific, Massachusetts, USA), a Shodex RI-101 refractive index detector (ECOM, Czech Republic), and an UltiMate WPS-3000 SL autosampler with a 250 µL sample loop. A Phenomenex (Torrance, USA) column 300 mm in length with a 7.8 mm internal diameter was used with a Phenogel 50 (GPC) phase (Phenomenex) with a particle size of 5 µm, pore diameter of 50 Å, and molecular weight ranging from 100 to 3000 (according to the manufacturer's catalogue). The mobile phase was composed of pre-filtered tetrahydrofuran, analytical grade (Tedia). Total analysis time was 14 min, conducted at 40 °C (column heater temperature) at a constant flow of 1 mL min<sup>-1</sup> with 250 µL injection volume. The samples were injected in duplicate to assess repeatability. The chromatograms were analyzed using Chromeleon<sup>®</sup> chromatography management software, version 6.80 SR11 (Dionex, USA), with manual integration.

### 2.4. Thermal analysis for the characterization of the type of additive in the gasoline

The residues obtained from the atmospheric distillation (ASTM D86/11b) of the verification samples were analyzed by derivative thermogravimetry (DTG) to characterize the type of additive used, so that the concentrations of the additives could be calculated in the SEC analysis. The equipment used for this was the TA Instruments Q600 (TA Instruments, New Castle, USA). Samples with masses of around 7 mg were placed in Tzero hermetically sealed aluminum pans (TA Instruments) with laser-cut pinholes in the lid in order better to separate out the volatilization and/or pyroly-

Download English Version:

<https://daneshyari.com/en/article/6475437>

Download Persian Version:

<https://daneshyari.com/article/6475437>

[Daneshyari.com](https://daneshyari.com)