DETECTION OF GASOLINE ADULTERATION USING AN ULTRASONIC MEASUREMENT METHOD

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Abstract: The aim of this study is to identify the possible changes in gasoline fuel using ultrasonic parameters of attenuation and propagation velocity. The test samples used in this study were the mixtures of gasoline and ethanol anhydrous in concentrations of gasoline varying from 100.0 to 52.3% by mass; and a commercial fuel gasoline bought from a local distributor. The correlation coefficient between gasoline concentrations and ultrasonic propagation velocity was 0.93, and the maximum combined uncertainty was 0.81 $m.s^{-1}$; contrastingly, for attenuation, the correlation coefficient was 0.90, and the maximum combined uncertainty was 0.066 $dB.cm^{-1}$.

Key words: Gasoline, adulteration, attenuation and propagation velocity.

1. INTRODUCTION

Gasoline is a mixture of volatile and flammable liquid hydrocarbons (paraffinic, olefinic, naphthenic and aromatic) and a lower amount of oxygen and sulfur products. These hydrocarbons have different structures in different proportions, generally compounds ranging from four thirteen carbon atoms in the molecule and a boiling point between 50 and 225 ° C. Being a mixture of hydrocarbons, the final composition of gasoline depends on the nature of oil used in refining, petrochemical process used to obtain them and the different currents petrochemicals used in their manufacture. These different characteristics, properties, composition and proportions of the hydrocarbons present exert influence on physicochemical characteristics that determine the quality of gasoline.

Gasoline Type C is the most common type for this is popularly known as gasoline, is formed by a mixture of 75% of the gasoline that comes from the refinery or petrochemical plant and 25% of anhydrous alcohol. All gasoline sold in Brazil have anhydrous ethanol. The content currently is 25% and may vary by Law 20 to 25%, with its own variation of a percentage point.

The characteristics of Brazilian gasoline are specified by Resolution n º 38, December 9, 2009 the National Petroleum Agency (ANP) [1] and the content of Ethyl Alcohol Anhydrous to be added to their compositions must be in agreement with the specification set by the Ministry of Agriculture, Livestock and Supply which currently has the addition of the level of 25 ± 1% of Ethyl Alcohol Anhydrous. However, what has happening so often in Brazil is the adulteration this fuel.

In the case of gasoline, the most common adulteration method is the addition of ethanol to the gasoline in amounts that are more than what is specified in the legislation, resulting in an off-specification product that is thereby unsuitable for use as a fuel. The immediate victim of adulteration is the consumer who supplies fuels his car with the adulterated fuel. However, the adulteration practice is interest of all, as this leads to a reduction of tax revenue and damages the whole society. Due to several problems in ensuring the quality of fuel used in Brazil, it is necessary to use a robust, accurate and non-destructive method, such as ultrasound, that can be applied in the process line. [2]

Ultrasound has been used recursively in several stages of a chemical process: to accelerate the reaction [3]; to separate the compounds [4] and to identify and analyze the compounds [5]. The ultrasound is also suitable for other related activities such as flow measurement, as a physical principle of process execution. However, from the metrological point of view, there is still some work to be done. Metrology is essential to support and demonstrate scientifically the advantages and applications of ultrasound in sonochemistry and to control chemical processes.

The physical properties of a medium can be determined from the measurement of acoustic parameters as well as from other parameters, such as propagation velocity, impedance, attenuation and scattering. From ultrasound can calculate the density, viscosity, degree of homogenization of a mixture, and concentration of solid particles in a liquid [6]. At present, the chemical industries, such as the petrochemical and pharmaceutical industries, have a considerable demand for measuring instruments that perform the characterization and discrimination of liquids with high sensitivity and precision. Additionally, automation of the processes often requires "in line" measurements. For this purpose, the use of ultrasound technique can be applied to the process line [7,8]

The aim of this paper is to provide a fast, inexpensive and feasible method to identify the possible fuels adulteration through ultrasonic measurements of attenuation and sound propagation velocity, using the methodology

implemented in the Laboratory of Ultrasound (Labus) of the Brazilian Institute of Metrology (Inmetro) [9]. The uncertainties were assessed according to the Guide to the Expression of Uncertainty in Measurement (GUM) [10].

2. MATERIAL AND METHODS

The samples used for measuring the attenuation were poured into a glass cylinder of 80 mm height and 35 mm diameter, and sealed with a PVC film. The reference sample contained only distilled water, and the sample to be analyzed contained: a mixture of gasoline and ethanol anhydrous in concentrations of gasoline varying from 100.0 to 52.3% by mass, a commercial gasoline and pure gasoline obtained in the research center of CENPES. These percentages were chosen based on Resolution ANP n º 38, December 9, 2009 the National Petroleum Agency and Ministry of Agriculture, Livestock and Supply which currently has the addition of the level of 25 ± 1% of the anhydrous ethanol.

In a transmission/reception scheme, an arbitrary waveform generator model 33250A (Agilent Technologies, CA, USA) was used to excite the transmission transducers with 20 V peak-to-peak 20cycle ultrasonic sine bursts for each tested frequency. The signal from the reception transducer was digitized with an oscilloscope model DSO6032A (Agilent Technologies, CA, USA). One pair of identical transducers of a resonance frequency of 15 MHz (Panametrics-NDT Olympus Corporation, Japan) was used to generate and capture the ultrasonic signal. The temperature was monitored throughout the measurements with a calibrated digital thermometer, model 34970A (Agilent Technologies, CA, USA). See Figure 1.

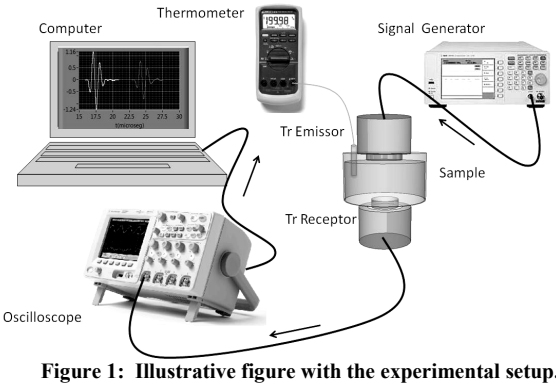

Figure 1: Illustrative figure with the experimental setup.

2.1. EXPERIMENTAL ATTENUATION

Experimental attenuation (AT_E) for the gasoline/ethanol sample was calculated according to equation **Erro! A origem da referência não foi encontrada.**, where V_{wat} is the water attenuated waveform effective (RMS) amplitude (reference signal), V_A is the sample gasoline/ethanol attenuated waveform RMS amplitude (sample signal), and x_e is the sample thickness or the transmission path length in centimeters.

$$AT_E = \frac{20\log\left(\frac{V_{wat}}{V_A}\right)}{x_e} \quad \left[\mathrm{dB \cdot cm^{-1}}\right] \tag{1}$$

According to equation **Erro! A origem da referência não foi encontrada.**, AT_E is the excess ultrasonic attenuation in gasoline/ethanol sample relative to attenuation in water. The sample thickness x_e (equation **Erro! A origem da referência não foi encontrada.**) was calculated as a function of the transmission delay Δt_{wat}, in s, measured with the oscilloscope using water as the attenuation medium and the propagation velocity in pure water c_{wat}, in $\mathrm{m \cdot s^{-1}}$, which was corrected for the temperature according to [11] (equation **Erro! A origem da referência não foi encontrada.**), where T is the temperature, in $^{\circ}\mathrm{C}$. The positioning system was used to move the transmission transducer away and back to the same position to adjust the distance when the gasoline/ethanol sample was used.

$$x_e = 100 \cdot c_{wat} \cdot \Delta t_{wat} \quad \left[\mathrm{cm}\right] \tag{2}$$

$$c_{wat} = 1.40238744 \times 10^{3} + 5.03836171\,T - 5.81172916 \times 10^{-2} T^{2} + 3.34638117 \times 10^{-4} T^{3} - 1.48259672 \times 10^{-6} T^{4} + 3.16585020 \times 10^{-9} T^{5} \quad \left[\mathrm{m \cdot s^{-1}}\right] \tag{3}$$

The samples of gasoline/ethanol and distilled water were poured into glass cylindrical tubes with diameters of 35 mm. The tubes' bottoms were sealed with PVC film. Measurements were repeated five times at the frequency of 15 MHz, and the attenuation medium (water and gasoline/ethanol samples) was changed between successive measurements.

2.2. PROPAGATION VELOCITY OF THE ETHANOL/WATER SAMPLE

Propagation velocity (c_A) was calculated according to equation **Erro! A origem da referência não foi encontrada.**.

$$c_A = \frac{x_e}{\Delta t_A} \quad \left[\mathrm{m \cdot s^{-1}}\right] \tag{4}$$

where x_e is the same distance of the transmission path length of water, in m, and Δt_A is the transmission delay with the gasoline/ethanol sample, in s.

2.3. UNCERTAINTIES MODELS

Type A uncertainties were calculated for the experimental measurement, and Type B uncertainties were assessed for other means than of measurement, such as information taken from the manual of the equipment used. To combine both Type A and Type B uncertainties for a single frequency, the highest value of Type B was selected. Uncertainty in the experimental approach was calculated according to the

Guide to the Expression of Uncertainty in Measurement (GUM). [10] Details of uncertainty assessment can be found in the cited literature.

2.4. STATISTICAL ANALYSIS

With the final result created a linear correlation of the data, leading to a function for attenuation and another for propagation velocity. Statistical tests were performed to validate the method and to analyze the concentration range of ethanol that can be used in the gasoline fuel.

3. RESULTS

Using the parameters as defined in equation **Erro! A origem da referência não foi encontrada.** and equation 4, the experimental results for attenuation and propagation velocity are given in Table 1.

Table 1. Experimental results for attenuation and propagation velocity with their respective uncertainties.

(%)	Attenuation		Propagation Velocity	
	Mean ($dB.cm^{-1}$)	Combined uncertainty ($dB.cm^{-1}$)	Mean ($m.s^{-1}$)	Combined uncertainty ($m.s^{-1}$)
52.3	0.968	0.021	1136.99	0.52
55.2	1.003	0.039	1141.76	0.63
58.0	1.048	0.045	1144.86	0.81
62.4	1.075	0.045	115150	0.40
65.4	1.102	0.032	1155.85	0.73
68.5	1.132	0.033	1157.07	0.21
72.2	1.163	0.031	1159.49	0.72
75.5	1.181	0.033	1160.86	0.31
80.3	1.228	0.057	1168.27	0.29
Commercial Gasoline	1.224	0.042	1164.88	0.79
Gasoline 100%	1.713	0.066	1212.27	0.49

Figure 2 shows the scatter plot between attenuation and different concentrations of gasoline/ethanol with respective combined uncertainties. The triangle represents commercial fuel. Correlation coefficient between attenuation and the gasoline/ethanol concentration was 0.90 with a maximum uncertainty of 0.066 dB.

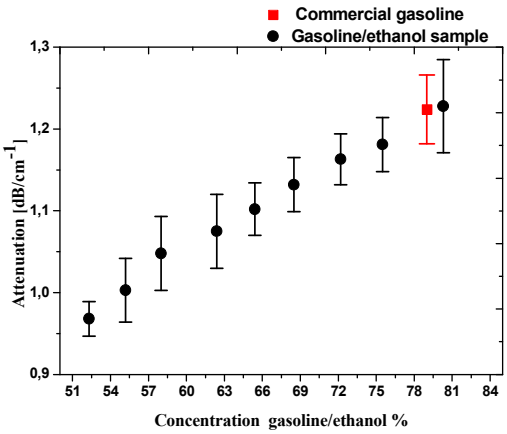

Figure 2. The scatter plot between attenuation and different concentrations of gasoline/ethanol with respective combined uncertainties. The triangle represents commercial fuel. Correlation coefficient between attenuation and the gasoline/ethanol concentration was 0.90 with a maximum uncertainty of 0.066 dB.

Figure 3 shows the scatter plot between propagation velocity and different concentrations of gasoline/ethanol with respective combined uncertainties. The triangle represents commercial fuel. The correlation coefficient between attenuation and the gasoline/ethanol concentration was 0.93 with a maximum uncertainty of 0.81 $m.s^{-1}$.

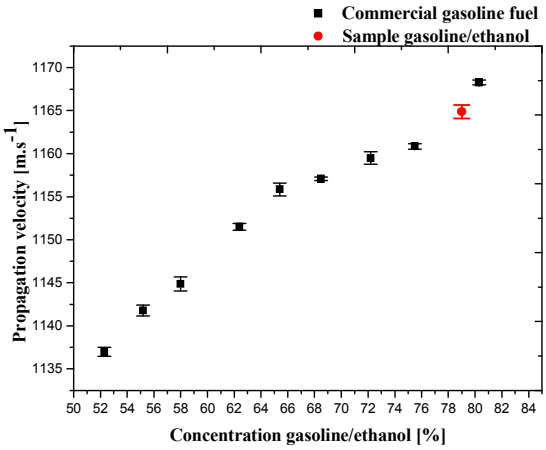

Figure 3. The scatter plot between propagation velocity and different concentrations of gasoline/ethanol with respective combined uncertainties. The triangle represents commercial fuel. The correlation coefficient between attenuation and the gasoline/ethanol concentration was 0.93 with a maximum uncertainty of 0.81 $m.s^{-1}$.

4. DISCUSSION AND CONCLUSION

Two ultrasonic parameters were measured for different concentrations of gasoline and ethanol. The concentration until 75% of gasoline was selected to be the value minimum of de gasoline permissible in the Brazilian regulation.

Experimental attenuation ($dB.cm^{-1}$) shows a maximum combined uncertainty of 0.066 $dB.cm^{-1}$ and a correlation coefficient of 0.90, whereas ultrasonic propagation velocity

shows better results, with a maximum combined uncertainty of 0.81 $m.s^{-1}$and a correlation coefficient of 0.93 (in modulus).

In Table 1 are shown the results of the attenuation and of the propagation velocity of samples of gasoline / ethanol at different percentages, commercial gasoline and pure gasoline, where can to observe that the propagation velocity also increases with increasing concentration of gasoline, because the gasoline is more viscous than ethanol and the higher the viscosity the greater the speed of ultrasonic propagation.

As gasoline and ethanol has a very low attenuation that increases with frequency, a relatively high ultrasonic frequency of 15 MHz is selected for the experiments. The instability of ultrasonic propagation at high frequencies can lead to higher uncertainties, and, thus, extra precaution should be taken in the experimental setup. Alternatively, low frequencies would lead to low sensitivity in the attenuation curve.

The results show that the ultrasonic parameters have statistically different outcomes for the concentrations closer to and lower than the permissible limit (75%) specified in Brazilian regulation. For attenuation, the lower concentration was statistically 65.4%, which differs from 75.5% ($p < 0.02$, $\alpha < 5\%$). Similarly for propagation velocity, the concentration is 68.5% ($p < 0.002$, $\alpha < 5\%$). This result indicates that this parameter seems to be reliable to detect concentration within the permissible limits imposed by the Brazilian regulation.

In this study, the experiments were conducted in a laboratory under controlled temperature conditions with a variation of less than 1.0°C. The liquid temperature has a remarkable influence on the viscosity, which is one of the main parameters that affect attenuation and propagation velocity. Therefore, for outdoor application, precaution should be taken to avoid basic errors due to temperature variation.

The methodology implemented in the present work can be used to identify adulteration in gasoline fuel. The efficiency of this methodology is demonstrated by the experimental uncertainties lower and the high correlation coefficients. The ultrasonic parameters used to analyze commercial fuel were tested within the Brazilian fuel regulations with different concentrations of ethanol in gasoline. The propagation velocity showed an overall better result than the ultrasonic attenuation. One should keep in mind that the proposed method is to be used as a survey, and precision of the method is not comparable to other analytical methods used in chemistry.

The described methodology can be used as a tool to identify fuel adulteration, and the assessment can be performed "in line" by controlling some environmental variables.

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