Sensibility of hydrous ethanol adulteration detection using ultrasonic parameters validated in a metrological base

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The aim of this study is to identify possible changes in fuels, in this case hydrous ethanol, through ultrasonic parameters such as attenuation and propagation speed. The system setup and method were implemented at Inmetro’s Laboratory of Ultrasound. Experiments and method uncertainties were assessed accordingly to ISO/IEC Guide 98 1:2009 (Uncertainty of measurement – Part 1: Introduction to the expression of uncertainty in measurement). Mixtures of ethanol and water varying from 90% to 94% of alcohol in mass were used as testing samples. Attenuation and propagation speed were accurately measured and uncertainties evaluated. The accordingly to Brazilian biofuel regulations, the concentration of water in hydrous ethanol can be accepted at a maximum concentration of 93.8 and minimum of 92.6 of alcohol in mass. To achieve that figure, a functional combination of tested parameters should be implemented. Those results could be used as a tool to identify adulteration of biofuel, even in analysis performed on site.
1- Introduction

Fuels produced from human grown biomass have high potential and one of the main advantages is reduction of emissions of greenhouse gases. Thus, this may be a safe fuel source, gradually reducing dependence on ex-submersed biomass, such as petroleum, developing a strategic reserve [1].

However, the activity of marketing of fuels, in all stages, the profit margins worked are relatively low. Some owners of gas stations or distributors choose as a solution to rapidly gain: the adulteration of fuels. In the case of ethanol, the most common adulteration of hydrated alcohol is the addition of more water to the formula, resulting in a product off-specification, therefore, unsuitable for use. The immediate victim of adulteration is the consumer who supplies his car with fuel adulterated. However, it is worth noting as everyone loses with tampering, since the fraud reduces tax revenue, which creates damage to the whole society.

Due to several problems found in ensuring the quality of biofuel used in Brazil, it is necessary to use robust, accurate and nondestructive methods that can be applied in the process line, such as the use of ultrasound.

Ultrasound has been used recursively in several stages of a chemical process, whether to accelerate the reaction [2], as the separation of compounds [3] or even in their identification and analysis [4]. Other related activities, such as flow measurement, they are also suitable for using the ultrasound as a physical principle of process execution. However, by the metrological point of view, there still is some homework to complete. It is essential to support and demonstrate scientifically the advantages and best applications of ultrasound in sonochemical and control of chemical processes widely.

The physical properties of a medium can be obtained through the measurement of acoustic parameters of the medium as well as from the measurement of parameters such as propagation velocity, impedance, attenuation and scattering. It can calculate the density, viscosity, degree homogenization of a mixture, the concentration of solid particles in a liquid, etc. [5] Currently, in the chemical industries, petrochemical, pharmaceutical, just referring to some well-known ones, require a considerable demand for measuring instruments that perform the characterization and discrimination of liquids with high sensitivity and accuracy. Moreover, automation of the process often needs to be measurement of process “in line”. To this purpose, the use of ultrasound techniques is interesting, because is a method robust, accurate, and non destructive and can be applied to the process line. [6, 7]

2- Objectives

The aim this paper is identify possible adulteration in fuels such as ethanol, through acoustic measurements such as attenuation and propagation speed using ultrasound, using the method implemented in the Laboratory of Ultrasound (Labus) Inmetro. And get the uncertainties of these measurements as described in the book GUM (Guide to the Expression of Uncertainty in measurement).
3- Experimental

The samples used for measuring the attenuation were inserted into a cylinder 80 mm in height and 35 mm in diameter, its lower end sealed by a PVC film. The reference sample contained only distilled water and sample to be analyzed contained a mixture of ethanol / water in the following proportions: 94.0%, 93.8%, 93.4%, 93.0%, 92.6%, 92.2%, 92.0%, 91.6%, 91.2%, 90.8%, 90.4% and 90%. These percentages were chosen because of the ANP Resolution nº36, de 6.12.2005- DOU 7.12.2005 [8], which specifies that the Hydrated Alcohol Fuel (HAF) must contain an alcoholic strength by ºINPM of between 93.8 to 92.6 and so we used that track specific and spread a bit more percentages to better analyze the results.

Each sample was analyzed in five repetitions for that be obtained for a statistical average. Chose to perform dilutions in ethanol, because this is a renewable fuel which developed national technology, while reducing imports petroleum. May thus provide a quality standard for Brazilian fuel.

In a transmission/reception scheme, an arbitrary waveform generator model 33250A (Agilent Technologies, CA, EUA) was used to excite the transmission transducers with 20 V peak-to-peak 20 cycles 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 resonance frequency of 15 MHz (Panametrics-NDT Olympus Corporation, Japan). Figure 1 illustrates the measurement setup. Software was developed in LabVIEWTM 8.5 (National Instruments Corporation, Austin, TX, USA) to automate the measurement, as well as to calculate attenuation and related uncertainties. Temperature was monitored throughout measurements with a calibrated digital thermometer model 34970A (Agilent Technologies, CA, USA).

To calculate attenuation, distilled water was used as reference liquid. For a given frequency, a fixed excitation signal was used firstly with water and then with mixture of ethanol / water, adjusting the same distance between transmitting and reception transducer for both mountings with a manual positioning system (Newport Corporation, Irvine, CA, USA).

![Figure 1](image.png)

**Figure 1.** Illustrative figure with the experimental setup, where “Tr Emissor” is the emitting transducer, “Tr Receptor” is the reception transducer, “Sample” is the container for samples of attenuations mediums, “Signal Generator”, “Computer”, “Thermometer” and “Oscilloscope” are accessories measuring instruments.

All parameters used in the method implemented in Labus were evaluated for their standard uncertainty Type A and Type B as well as the combined standard uncertainty. The aim of
classification Type A and Type B is to indicate the two different ways to evaluate the components of uncertainty. In the assessment of Type A, the method of evaluation of uncertainty is based on statistical analysis of a number of observations. In the assessment of Type B, the method of evaluation of uncertainty is based on means other than statistical analysis of a series of observations.

The combined standard uncertainty of a measurement result is the standardized uncertainty when this is obtained through the values of several other magnitudes, being equal to the square root of a sum of positive terms, being these the variance or covariance of these other magnitudes, weighted according with as the measurement result varies with variance in these magnitudes. [9]

4- Results:

The chart 1 shows the relationship of attenuation with different ethanol concentrations and their uncertainties. This uncertainty is the expanded uncertainty, where k = 2. [9]

Chart 1: Relationship of attenuation with different concentrations of ethanol / water and their uncertainties.

The chart 2 shows the relationship of speed with different ethanol concentrations and their uncertainties. This uncertainty is the expanded uncertainty, where k = 2. [9]
Chart 2: Relationship of the speed of propagation with different concentrations of ethanol / water and their uncertainties.

5- Discussion

The results of experimental attenuation in the different fractions of dilution of ethanol, given in [dB.cm\(^{-1}\)], where it can observe linearity in the results, since it was observed that the attenuation increases with increasing concentration of ethanol in the sample. And this occurs, due the difference of viscosity between the materials used in the mixture, then the higher the concentration of ethanol higher is the attenuation.

Because the viscosity is one of the main parameters that contribute to attenuation, it is noteworthy also talk that the viscosity is totally dependent on temperature, but the measurements that were carried in Labus, were with control the temperature at which the variation of measurements was between 1.2°C. Thus it can consider that the uncertainty due to temperature is inserted in uncertainty of the sample signal.

It can observe that the largest contribution to the uncertainty of measurement of attenuation is due to measurement of signal amplitude of the sample (ethanol / water), because this causes a certain instability in the sign of amplitude due to interaction between its molecules.

The results of the propagation speed in different fractions of dilution of ethanol using a pair of transducers at a frequency of 15 MHz where it can observe that the propagation speed decreases with increasing concentration of ethanol, because as higher resistance material the greater the time that the sound wave will take to traverse a given space.

It can observe that the largest contribution to the uncertainty of measuring the propagation speed is due to measurement of the thickness of the sample in case (ethanol / water). Yet the uncertainty remains small, allowing a measurement with accuracy. In Chart 2 it was observed a linear trend in the results of measurements of propagation speed.

It was noted that both the parameters used to identify adulteration in fuel ethanol were efficient, managed to distinguish a concentration of the other, but the parameter of attenuation has a value greater of uncertainty due to the instability of the samples.
5- Conclusion

It can be concluded that the methodology used to identify adulteration in fuel ethanol was efficient. And that through the study of uncertainties of measurements of attenuation and propagation speed can be observed that the combined standard uncertainty of measurements of propagation speed was much lower than the standard combined uncertainty in measurements of attenuation. But an analysis complements the other. And such analysis together is good parameters for identifying adulteration in fuels, because the results were consistent and of reliability and other important factor is that these assessments can be performed "in line".

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