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Water content of water-oil mixtures by the speed of sound measurement

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Abstract
Ultrasonic meters are calibrated for flowrate measurement of pure oil flows. However, the indicated oil flow rate is greater than its true value when water is mixed with oil in the flow, as usual in pipeline flows. A methodology was developed to measure the water content of water-oil mixtures, using the already measured speed of sound by installed intrusive or non-intrusive (clamp on type) ultrasonic meters for flowrate measurement, together with the previously determined speed of sound and density of pure water and oil as a function of temperature, thus avoiding additional meters. The paper shows a reduction of the uncertainty of measurement when the meter indicated water-oil mixture speed of sound is directly related to the traceable measurements of water content and temperature of previously prepared water-oil mixtures, what turns out to be the meter calibration for water content measurement. Water content uncertainty value of 0.0020 is obtained when curve fitting de data in the 0-0.025 range, that covers the fiscal measurement range (< 0.01)

Keywords
Water content of water-oil mixtures; speed of sound; fiscal flowrate measurement

Introduction
Ultrasonic meters are calibrated for flowrate measurement of pure oil flows. However, the indicated oil flow rate is larger than its true value when water is mixed with oil in the flow. A maximum of 1 % water content of the fluid, for example, is required for fiscal measurement operations. By sampling the fluid in the pipe flow, it is possible to measure in a laboratory the water content of the fluid, and, thus, to calculate the true oil flowrate, The US patents [1] and [2] show that the water content of the oil mixture is a function of the speed of sound. In this paper, an expression was theoretically developed, using the previously measured speed of sound and density of pure water and pure oil, for calculating online, the water content of the oil mixture from its measured speed of sound, without sampling the fluid and taking it to a laboratory for analysis. The methodology was experimentally verified with the measured speed of sound by two types of flow meters, (a) Eight (8) acoustic path intrusive ultrasonic flow meter, and, (b) Two (2) acoustic path non-intrusive (clamp on) ultrasonic flow meter. A methodology was also developed to correlate directly the water content to the measured fluid speed of sound for several previously prepared mixtures of water and oil, using diesel as a fluid, thus reducing the propagation of the uncertainty of measurement from pure fluid measured properties. The methodology is detailed in [3]

Methodology
The water content of a water-oil mixture (*f*) is defined as the ratio between the mass of water (m_{water}) and the total mass of the mixture (m), which can be calculated as the sum of the mass of water (m_{water}) and the mass of oil (m_{oil}), Eq. (1). The specific volume of either water (v_{water}) or oil (v_{oil}) can be calculated as the ratio between the volume (V) and the mass (m), respectively for water (v_{water}= V_{water}/m_{water}) and oil ($v_{oil}=V_{oil}/m_{oil}$). Density is calculated as the inverse of the specific volume, for either water (ρ_{water}) or oil (ρ_{oil}). Thus, the following equations can be written for the water content (*f*) and specific volume of the mixture (v)

$$f = \frac{m_{water}}{m} = \frac{m_{water}}{m_{water} + m_{oil}} \quad (1)$$

$$v = v_{oil} - f\ (v_{oil} - v_{water}) \quad (2)$$

The speed of sound in a fluid (c), can be defined in terms of the partial derivative of the pressure (P) with respect to its specific volume (*v*), at constant entropy (s)

$$c = \sqrt{\left.\frac{\partial P}{\partial \rho}\right|_s} = \frac{1}{\rho}\sqrt{-\left.\frac{\partial P}{\partial v}\right|_s} \quad (3)$$

From Maxwell relation and using Eq. (3),

$$\left.\frac{\partial v}{\partial P}\right|_s = 1/\left.\frac{\partial P}{\partial v}\right|_s = -\,1/(\rho\ c)^2 \quad (4)$$

Substituting v, ρ and c for, respectively, v_{water}, ρ_{water} and c_{water}, Eq. (4) is valid for water. Likewise, substituting v, ρ and c for, respectively, v_{oil}, ρ_{oil} and c_{oil}, Eq. (4) is valid for oil.

Taking the partial derivative of Eq. (2) with respect to P, at constant entropy (s),

$$f = \frac{\left[\frac{1}{(\rho.c)_{oil}^2} - \frac{1}{(\rho.c)^2}\right]}{\left[\frac{1}{(\rho.c)_{oil}^2} - \frac{1}{(\rho.c)_{water}^2}\right]} \qquad (5)$$

Equation (5) shows that the water content (f) of the fluid mixture can be calculated from the measured speed of sound (c) if both density and speed of sound have been determined for pure water and pure oil before measurement. The mixture density can be calculated, solving Eqs. (5) and (6), which was derived from Eq. (2), relating

$$\rho = \frac{\rho_{oil}}{1 - f\left(1 - \frac{\rho_{oil}}{\rho_{water}}\right)} \qquad (6)$$

Both density and speed of sound for pure fluids are function of temperature and pressure. Therefore, in absence of further experimental data, the available correlation should be used. The API methodology [4] calculates the density of Petroleum products to within 0.25 % up to 200 ºF (93,3 ºC). The speed of sound (c) can be calculated by Eq. (8) using the isentropic bulk modulus (β), which was defined by Eq. (7)

$$\beta = \rho \left.\frac{\partial P}{\partial \rho}\right|_s \qquad (7)$$

$$c = \sqrt{\beta/\rho} \qquad (8)$$

Menon [5] suggests the ARCO formula for calculating the isentropic bulk modulus for crude oils from temperature, pressure and density (expressed in API units). Nikolic et allii [6] obtained experimentally an expression for the speed of sound in diesel fuel as a function pressure, at 19.85 ºC. The speed of sound difference between the two methodologies was calculated in this research to be at most 1 % in the 0-10 MPa.range.

Several water density expressions are available in the literature as a function of temperature and pressure. For nearly atmospheric pressures, the National Metrology Institutes recommends Tanaka et allii expression [7]. The distilled water speed of sound was measured by [8] at nearly atmospheric pressures. Several expressions, [9], [10], [11], [12] and [13], are available for the speed of sound in seawater, as a function of salinity and pressure (water depth). They were used to estimate the uncertainty of measurement in tap water used in the experiments.

This paper deals with the validation of the theory, using as a fluid the diesel fuel at nearly atmospheric pressure. As a first step, the accuracy of the speed of sound measurement was verified. Then, expressions were experimentally obtained for the speed of sound in diesel and water as a function of temperature. Then, the speed of sound was measured in several previously prepared water-oil mixtures, as a function of temperature, and used to calculate the water content by Eq. (5), determining the uncertainty of results. Finally, aiming the reduction of the uncertainty of measurement, the measured speed of sound data were correlated directly with temperature and water content, thus reducing the propagation of the uncertainty of measurement in the speed of sound and density of pure water and pure oil in Eq. (5). The results were analyzed and compared.

Experimental Procedure

A loop was built to measure the water content in the oil-water mixture. It consists of a 3" acrylic vertical tube, with two pairs of clamp on flow meter sensors installed outside on its center position. The speed of sound of either oil or water was measured, after having introduced into the tube a certain amount of fluid, maintained at a specified temperature outside the loop. The water content measurement was measured by preparing a mixture with measured amounts of oil and water, which was maintained outside the tube at a specified temperature, and introduced into the loop. A circulating pump and an agitator was used to circulate and to homogenize the fluid.

The fluid temperature was calculated as the average value measured by two platinum resistance thermometers (Pt100), which were positioned at the ends of the speed of sound measuring tube section. They were calibrated against a standard platinum resistance thermometer inserted into the reservoir of a temperature controlled calibrating bath. The uncertainty of the fluid temperature measurement is estimated in 0.18 ºC (95.45 %).

The uncertainty of the water content measurement in the prepared mixture was estimated in 0.000062 (95.45 %) for f = 0.05 (5 %).

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The repeatability of the speed of sound metering device for water was, calculated by its measurement at eigtheen nominal temperature values in the 0-35 ºC range. A data acquisition system was used to measure both temperature and speed of sound every 6s, during about 10 minutes, Therefore, 1839 sets of temperature and speed of sound values were used for fitting the speed of sound versus temperature curve for water in the 0 – 35 ºC range. The following expression was obtained,

$$c_{water} = -0.03993\,T^2 + 4.502\,T + 1{,}406.92 \qquad (9)$$

The repeatability (95.45 %) of calculating the speed of sound from temperature measurement, following ISO GUM [14], is in the range of 0.80 m/s (3,5 ºC) to 0.50 m/s (33.4 ºC), or 0.056 % to 0.032 % range, respectively. Those values represent the spread (95.45 %) of many measurements taken every 6s. However, if those measurements are grouped into sets of *n* measured values, the spread of the average set values is reduced by a factor of $\sqrt{n}$ [14], what makes them closer to each other, thus improving the repeatability of the results. Thus, the average of about 100 measured values, of speed of sound and temperature, taken at every 6s, for each water content value, was used to predict the water content in the water-oil mixture.

A measuring device works with the principle of relating a measured transducer property to a physical quantity, usually represented by a reference meter. However, both the intrusive and non-intrusive (clamp on) meters were are not supposed to be calibrated directely for speed of sound measurement. Instead, the value of the indicated speed of sound by the meter was related to values of water content, by measuring traceable amounts of water and oil, and temperature, what is considered to be an indirect meter calibration. The meter repeatability was determined as before.

Even though, the meter accuracy for speed of sound measurement was accessed by comparing the meter indicated value with the available results in the literature for the same temperature. Reference [8] has reliable values for distilled water. However, the experiments of this paper used tap water. Five (5) additional references, [9], [10], [11], [12] and [13] show expressions for the speed of sound in seawater for zero salinity and zero depth (sea surface) values. The systematic error was calculated using 1839 measured values of speed of sound for each reference equation in the 0 ºC to 35 ºC range, resulting, respectively, as a root mean square differences of 9.2 m/s, 5.2 m/s, 5.0 m/s, 5.0 m/s, 4.9 m/s and 4.9 m/s. Reference [8] results differ from the rest of the references, showing that the fluid cannot be considered, probably, as distilled water, The average of all other 5 values is 5,1 m/s, or 0,34 %, and was chosen as the speed of sound systematic error and should be considered with the meter repeatability for estimating the uncertainty of measurement, if desired.

Results and Discussion

The validation of Eq. (5) was conducted at nearly atmospheric pressure and temperature (25 ºC) temperature. An expression for the speed of sound in water and oil was determined from measurements in the 0-35 ºC range. Water density was calculated by [7]. Oil density was calculated by [4]

$$c_{water} = -0.033467\ T^2 + 4.336\ T + 1{,}407.48 \quad (10)$$

$$c_{oil} = -0.01213\ T^2 - 3.1274\ T + 1{,}469.28 \quad (11)$$

Measurements of speed of sound and temperature were made at each previously prepared and homogenized water-oil mixture. The true water content value was calculated by Eq. (1), using the measured amounts of water and oil in the mixture. The mixture density was calculated by Eq. (6).

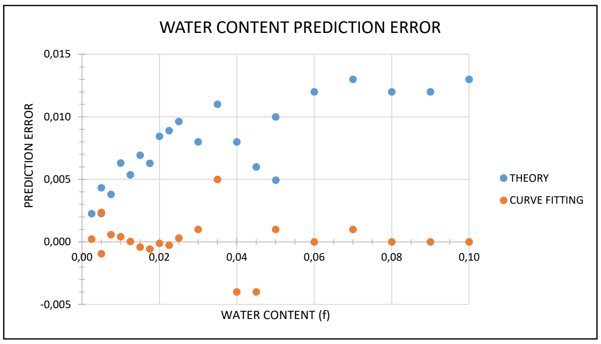

Figure 1. Water content prediction error

The water content value was predicted by two methodologies, (I) Theory, Eq. (5), calculating the pure water speed of sound by Eq. (10), and the pure oil speed of sound by Eq (11). Water and oil densities were respectively calculated by [7] and [4], (II) Curve fitting directly by the least square method [3], the measured mixture speed of sound (c) as a function of water content (*f*) and temperature (T) by Eq. (12), thus reducing the uncertainty propagation of the expressions used to calculate the speed of sound and density for both pure water and pure oil on the predicted water content.

$$c = A + B\,f \quad (12)$$

$$A = A_1 + A_2\,T + A_3\,T^2 \quad (13)$$

$$B = (B_1 + B_2\,T + B_3\,T^2) \quad (14)$$

Table 1. Curve Fitting Coefficients

	WATER CONTENT RANGE		
	0-0.025	0.05-0.20	0.80-1.00
A_1	1,604.09	-3,023.60	-79,270.9
A_2	-13.4419	360.653	6,442.72
A_3	0.185719	-7.37095	-128.722
B_1	15,240.7	27,805.9	98,135.3
B_2	1,206.43	-2,238.5	-7,834.98
B_3	-23,6499	45.1594	156.608

Three water content ranges were used for the curve fitting. For fiscal flow rate measurement, the first range (0.00-0.025) in Tab. 1, is of interest to control if the maximum allowed water content value of 0.01 (1 %) is achieved. The second range (0.05-

0.20) can also be used for non-fiscal measurement. Finally, the third range (0.80-1.00) was used to check the accuracy of the model when the water content is high.

Figure 1 shows that the prediction error is high for the first methodology (theory), justifying the use of a curve fitting. The prediction error starts from 0.0025 (0.25 %) and increases almost linearly to 0.006 (0.6%) for water content values of 0.01(1%), Therefore, is not still accurate to measure low water content values. The error levels off to around 0.012 for water content values above 0.02 (2 %). The curve fitting reduces the prediction error to less than 0.001 (95.45 %)..

The uncertainty of predicting the water content was estimated by propagating the uncertainty of curve fitting, temperature and speed of sound [3], resulting, respectively, in 0.0020 (0-0.025 range), 0,0036 (0.05-0.20 range) and 0.018 (0.80-1.00 range), for 95.45 % confidence level. For each measured water content value of the previously prepared water-oil mixture, the average values of temperature and speed of sound, together with their fluctuations were taken into account for processing the curve fitting and estimating the uncertainty of predicting the water content in the mixture by speed of sound measurement.

Conclusions

A methodology was developed to calculate the water content of a water-oil mixture from temperature and speed of sound measurements, using previously determined pure water and pure oil properties as a function of temperature. The propagation of the uncertainties in the determination of the properties is reduced by curve fitting directly the measured values of water-oil mixture speed of sound as a function of temperature and water content. A uncertainty value of 0.0020 (95.45 %) was obtained in the range of interest to fiscal measurement (< 0.01). The measurement system is calibrated by relating the meter indicated speed of sound to traceable values of temperature and water content of previously prepared mixtures.

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Responsibility Notice

The authors are the only responsible for the paper content.

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