Measurement of Water Content
of Crude Oil Using Quartz Crystal Microbalance

Yan Wang,* Chong Li, and Baorui Zhao

School of Electrical Engineering and Information, Southwest Petroleum University, Chengdu 610500, China

The water content of crude oil is an important parameter in oilfield development. It plays an important role in determining the water production of oil wells and the location of the oil layer, in estimating crude oil production, and in evaluating the value of production. The problem of inaccurate measurement of the high and low water cuts has always existed in oilfield development. In this paper, a systematic method of applying quartz crystal microbalance (QCM) liquid phase detection technology to the water content measurement of crude oil is proposed, and the water content of six standard glycerol solutions is measured. The results show that the error between the theoretical and experimental values is very small (<3%) and that the magnitude of the error hardly increases at low and high water contents (increase <1%). Repeated experiments also verify the effectiveness of the method. Finally, the field measurement results of water content of crude oil confirm the applicability of the model. This method will help improve the measurement accuracy of the water content of crude oil over a wider range of water content, which is of great significance for the application of the QCM in oilfield development.

1. Introduction

A quartz crystal microbalance (QCM) is a mass balance of quartz crystal resonator (QCR) under converse piezoelectric effect, which was first developed in the early 1960s. Because of its high sensitivity, low cost, real-time accuracy, and ease of use, it has attracted wide attention and in-depth research by researchers. In the past few decades, the QCM has been widely used in various sensor research applications, from initial thin-film thickness detection[1,2] to electrochemistry,[3,4] biomedicine,[5,6] materials science,[7,8] environmental monitoring,[9,10] and many other fields.

In recent years, QCM detection technology has been used in the petrochemical industry. The water content of crude oil is an important technical indicator in oil exploitation. Its accurate measurement plays an important role in improving the production efficiency and predicting the development life of oil wells, and in the secondary high-efficiency exploitation of old wells. At present, the development of most oilfields has gradually entered the high water cut or even ultrahigh water cut. With the recent decrease in oil output and the increasing difficulty of

exploitation, the petroleum industry urgently needs a high-precision and low-cost system for measuring the water content of crude oil.

At present, the conventional methods for detecting the water content of crude oil include the distillation method,[11] Karl Fischer titration,[12] capacitance method,[13] near-IR spectroscopy,[14] terahertz time-domain spectroscopy,[15] and microwave resonance.[16] Compared with them, the density method has the advantages of high accuracy, easy implementation, and low cost for a high water content, but its resolution is low for a low water content, which leads to large errors. Therefore, this method is generally not suitable for the water cut measurement of oil wells with water cut below 20%. In recent years, many researchers have improved and optimized the density method. As one approach, technical improvements in the structure of differential pressure sensors and in temperature compensation have minimized the error caused by external factors. As another approach, the BP neural network model of multi-sensor information fusion is used to predict the water content of crude oil, which can obtain the complete information of various factors affecting the water content of crude oil, thus realizing the accurate characterization of the water content of crude oil. These approaches can indeed reduce certain errors, but they do not solve the key problem of how to improve the accuracy and resolution of measurement, especially for a low water cut. The frequency signal output by QCR is very sensitive to the change in surface mass load, and its response sensitivity reaches Hz/ng. In this paper, we propose a method of applying a QCM to water content detection. It has been demonstrated by theory and experiment that this new method can show extremely high accuracy and precision, regardless of the water content.

2. Measurement Principle

The density method is based on the oil and water two-phase model, which uses the different density characteristics of oil and water to measure the water content of crude oil. Suppose the density and volume of an oil–water mixture are ρ and V, the density and volume of the oil phase contained in the oil–water mixture are ρ_o and V_o, and the density and volume of the water phase are ρ_w and V_w, respectively. Then the following formulas hold:

$$D_V = \frac{V_w}{V} = \frac{\rho - \rho_o}{\rho_w - \rho_o},$$

(1)

$$D_M = \frac{\rho_w V_w}{\rho V} = \frac{\rho_w(\rho - \rho_o)}{\rho(\rho_w - \rho_o)},$$

(2)

where D_V is the volume water content of crude oil and D_M is the mass water content of crude oil. The densities of oil and water are known constants; thus, the water content of crude oil can be calculated by measuring its density using a sensor. From Eq. (2), the absolute error and relative error of the water content are

$$\Delta D_M = \frac{1}{\rho^2} \cdot \frac{\rho_w \rho_o}{\rho_w - \rho_o} \Delta\rho, \tag{3}$$

$$\frac{\Delta D_M}{D_M} = \frac{\rho_o}{\rho - \rho_o} \cdot \frac{\Delta\rho}{\rho}. \tag{4}$$

The error of the water content is inversely proportional to $\rho - \rho_o$, which also explains why the error of the density method formula increases when the water content is low and the density of crude oil is close to that of pure oil. At the same time, if the accuracy of the sensor is approximated by $\Delta\rho/\rho$, then the error of the water content calculation is directly affected by the accuracy of the instrument. Obviously, these two problems can be reduced by improving the measurement accuracy, i.e., the higher the measurement accuracy of the sensor, the smaller the water content error.

A QCR is usually composed of metal electrodes on the upper and lower sides and an AT-cut piezoelectric quartz wafer sandwiched between them. Its schematic is shown in Fig. 1. The quality factor Q and mass sensitivity of the QCR with the n–m-type electrode are greatly improved compared with those of the QCR with the m–m-type electrode. Therefore, we used an n–m-type electrode QCR in this experiment. The most widely used formula for the frequency shift of a QCM in the gas phase is the classical Sauerbrey equation:[17]

$$\Delta f = -\frac{2 f_0^2}{A \sqrt{\rho_q \mu_q}} \Delta m, \tag{5}$$

where f_0 is the fundamental frequency of the QCM, A is the effective piezoelectric area of the working electrode, and ρ_q and μ_q are the density and piezoelectric shear modulus of the quartz crystal, respectively. The Sauerbrey equation was the first equation to reveal the linear relationship between the resonant frequency of the QCR and the change in mass on the electrode, which laid the theoretical foundation for the application of a piezoelectric quartz crystal in the gas phase, and its theoretical model is still in use today. However, for the application of QCM in the liquid phase, the Sauerbrey equation will lead to large errors between the experimental results.

In practical applications, the surface of the QCM electrode usually adsorbs a local or uneven mass, and the resulting frequency change is given by[18]
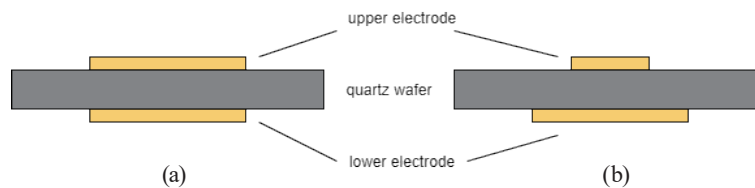

Fig. 1.   (Color online) Schematic diagram of typical QCR with different electrodes. (a) m–m-type electrode. (b) n–m-type electrode.

$$\Delta f = -\frac{1}{\pi r_d^2} \int_0^{2\pi} \int_0^{r_d} S_f(r,\theta) m(r,\theta) r dr d\theta, \tag{6}$$

where $S_f = (r, \theta)$ is the mass sensitivity function, $m(r, \theta)$ is the additional effective mass on the electrode, r_d is the radius of the effective mass load on the electrode, and r and θ are the distance and angle of the local mass from the center of the electrode in the polar coordinate system, respectively. If the attached mass is a uniform layer covering the surface of the electrode, using calculus, Eq. (6) can be simplified to

$$\Delta f = -\frac{\Delta m}{\pi r_d^2} \int_0^{r_d} 2\pi r S_f(r) dr. \tag{7}$$

This is the QCM mass sensitivity integral average detection model.[19] Compared with the Sauerbrey equation, this model not only considers the distribution characteristics of the mass sensitivity function, but also introduces factors such as the material, size, and thickness of the metal electrode, which can more accurately reflect the relationship between the frequency shift and the quality of the QCM in practical applications. The mass sensitivity distribution function is expressed as[20]

$$S_f(r) = \frac{|A(r)|^2}{2\pi \int_0^\infty r |A(r)|^2 dr} C_f, \tag{8}$$

where $A(r)$ is the QCM particle displacement amplitude function and C_f is the Sauerbrey sensitivity constant. $A(r)$ is the solution of the particle displacement amplitude equation[20,21]

$$r^2 \frac{\partial^2 A}{\partial r^2} + r \frac{\partial A}{\partial r} + \frac{k_i^2 r^2}{N} A = 0, \tag{9}$$

where $k_i^2 = (w^2 - w_i^2)/c^2$, where $i = E, P, U$, (E, P, and U respectively represent the full electrode region, partial electrode region, and non-electrode region), c is the acoustic wave velocity in the crystal, and N is a material constant that depends on the quartz crystal. $A(r)$ can be obtained from the boundary conditions of the QCM electrodes, and then the mass sensitivity distribution function $S_f(r)$ of the QCM is obtained from Eq. (8).

Taking the QCR (5 MHz fundamental frequency, AT-cut type, n–m-type gold electrode) used in our experiment as an example, the diameter and thickness of the quartz wafer are 2.54 cm and 331 μm, and the electrode parameters of thickness, inner diameter and outer diameter are 1000 Å, 6.6 mm and 12.9 mm, respectively. The radial distribution of its mass sensitivity function is calculated by the above analysis and is shown in Fig. 2. It can be seen that the mass sensitivity distribution of the QCR is not constant: it is maximum at the center of the electrode and decreases exponentially with increasing distance from the electrode center.
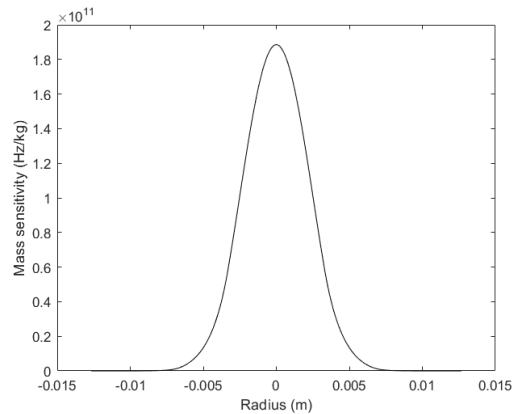
Fig. 2.   Mass sensitivity distribution for AT-cut 5 MHz fundamental QCM.

When the center of the QCM electrode is loaded with a tiny droplet, its thickness shear wave penetrates into the droplet and decays rapidly through viscous damping. The decay length of the shear wave depends on the viscosity and density of the liquid:[22,23]

$$\delta = \sqrt{\frac{\eta}{\pi f_0 \rho}}.$$ (10)

Therefore, the effective mass and QCM frequency shift caused by the effective mass can be respectively expressed as[24]

$$\Delta m = \frac{1}{2} r_d^2 \sqrt{\frac{\pi \rho \eta}{f_0}},$$ (11)

$$\Delta f = -\sqrt{\frac{\pi \rho \eta}{f_0}} \int_0^{r_d} S_f(r)\, r\, dr.$$ (12)

In conclusion, if the viscosity of crude oil is known, the liquid detection technology of the QCM can be used to accurately measure its density, and its water content can be accurately calculated by combining Eqs. (1) and (2).

3.   Materials and Methods

An experiment was carried out at room temperature (about 20 °C) using the setup shown in Fig. 3. In this study, glycerol was selected as the measurement medium. With the volume water content (V_{water}/V_{total}), six glycerol solutions with different water contents (0, 20, 40, 60, 80, and 100%) were prepared by adjusting the volume ratio of glycerol to water and the total volume of each solution is 100 ml. A droplet of 10 μL was loaded at the center of the QCR (QCM25) electrodes with a pipette (TP-10) for each measurement. The droplet radius was measured with
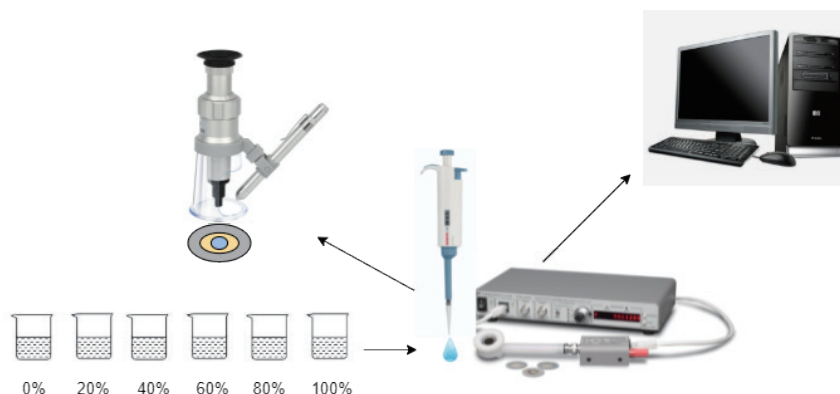
Fig. 3.   (Color online) Schematic diagram of the experimental setup.

an optical magnifier (GP-2009) while the real-time frequency on the QCM digital controller (QCM200) and the frequency shift curves on the LabVIEW were obtained. Before and after each test drip, the surface of the quartz wafer was cleaned with an ultrasonic cleaner (JP-020S) for 30 min, and then an electric blower (DHG-101) at 50 °C was applied for 30 min to dry the wafer, to ensure that there were no impurities on the surface of the wafer, which would affect the experimental results.

The glycerol was purchased from Tianjin No. 3 Chemical Plant Co., Ltd. (Tianjin, China). The QCM system was purchased from Stanford Research Systems (California, USA). The pipette was purchased from DLAB Scientific Co., Ltd. (Beijing, China). The optical magnifier was purchased from Kunshan Gaopin Precision Instrument Co., Ltd. (Jiangsu, China). The rotary viscometer was purchased from Shanghai Lichen Instrument Technology Co., Ltd. (Shanghai, China). The ultrasonic cleaner was purchased from Shenzhen Jiemeng Ultrasonic Cleaning Equipment Co., Ltd. (Shenzhen, China), and the electric blower was purchased from Shaoxing Supo Instrument Co., Ltd. (Zhejiang, China).

4.   Results and Discussion

4.1   Confirmatory experiment of glycerol solution

The densities of glycerol and water are 1.22×10^3 and 0.99125×10^3 kg/m^3, respectively. The theoretical density of the well-configured glycerol solution was calculated using the volume water content formula, then the viscosity η of each solution was measured with a rotary viscometer (NDJ-1), and finally, the theoretical frequency shift Δf_t was calculated using Eq. (12). The frequency of the QCM at the time of unloading was measured and recorded as f_1, then a tiny droplet was loaded at the center of the QCM electrodes. The droplet radius was measured and the frequency f_2 of the QCM at this time was recorded. The frequency response curve of the QCM is shown in Fig. 4.

The actual frequency shift is expressed by Δf_e ($\Delta f_e = f_1 - f_2$), and the relative error between the actual frequency shift and the theoretical frequency shift is expressed by E [$E = (\Delta f_e - \Delta f_t) / \Delta f_t$] The experimental results are shown in Table 1. The difference between the

(a)   (b)

(c)   (d)

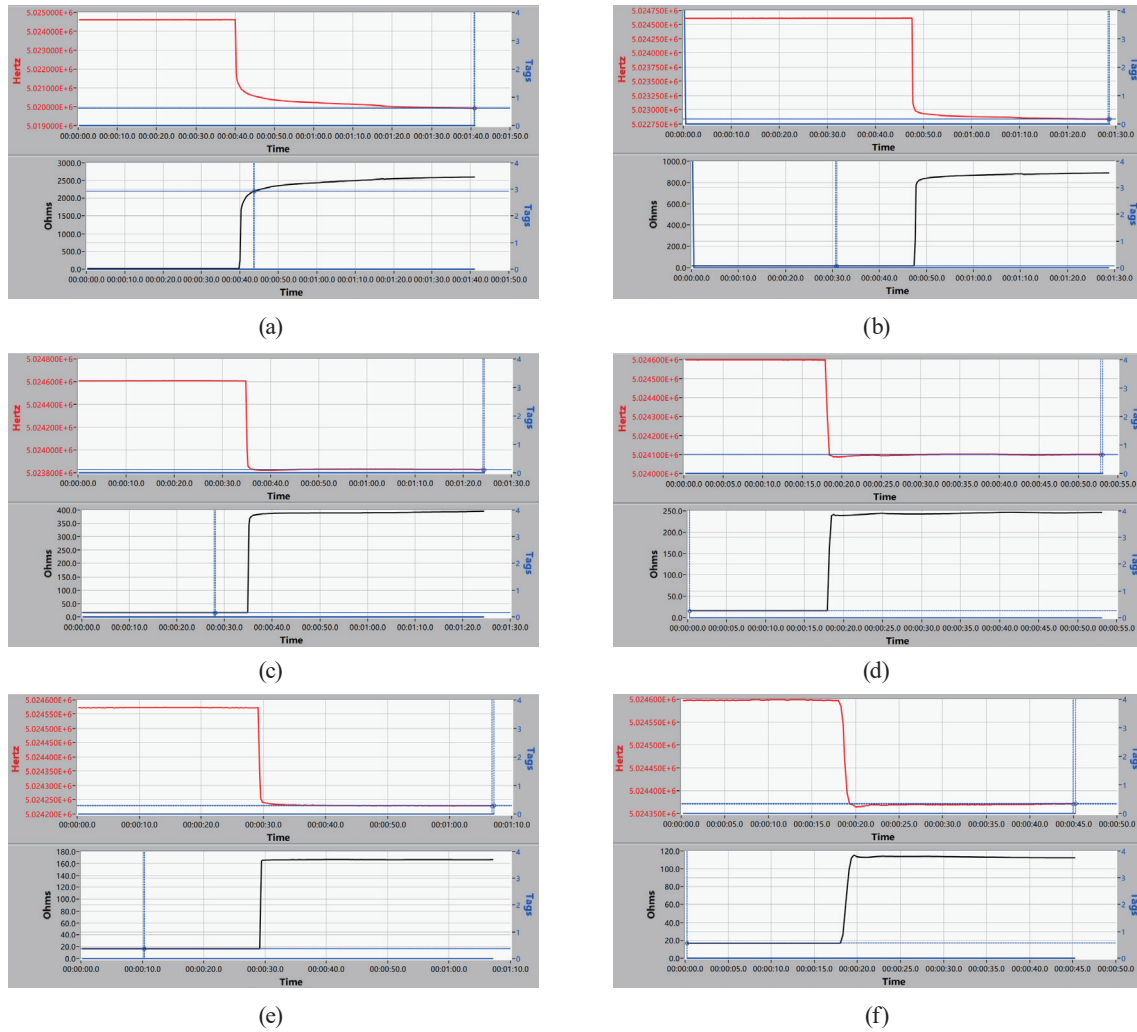(e)   (f)

Fig. 4.   (Color online) QCM frequency response (red lines) and resistance response (black lines) of glycerol droplets with different water contents; (a)–(f) show the results for water contents of 0, 20, 40, 60, 80, and 100%, respectively.

Table 1
Experimental results and theoretical values of glycerol solutions.

Water content (%)	Δf_e (Hz)	Δf_t (Hz)	E (%)
0	−4689	−4747	−1.22
20	−1761	−1776	−0.84
40	−777	−770	+0.91
60	−495	−489	+1.23
80	−340	−335	+1.49
100	−228	−223	+2.24

actual frequency shift and the theoretical frequency shift of the six solutions is very small, and the errors are all within 3%. Therefore, the experiment confirms the correctness of the theoretical derivation. It can also be seen that the error between the experimental results and theoretical values increases very little (by less than 1%) at high and low water contents, which shows that this model is applicable to the measurement of high and low water contents.

4.2 Repeatability of confirmatory experiment

The repeatability of a QCM refers to the consistency of the results obtained by the same method for the same measuring medium under the same conditions. Repeated measurements were performed on glycerol solutions with water contents of 40, 60, and 80%. The results are shown in Fig. 5.

It can be seen that the error between the theoretical frequency shift and the actually measured frequency shift in this experiment is very small. For the glycerol solutions with water contents of 40, 60, and 80%, the largest relative errors are 3.68, 3.56, and 3.26%, respectively, as shown in Fig. 5(d). These results indicate that the model has good repeatability.

4.3 Field measurement of water content of crude oil

The confirmatory experiment of glycerol solution confirmed the correctness of the theoretical model. In addition, the field measurement of water content of crude oil was carried out. Owing
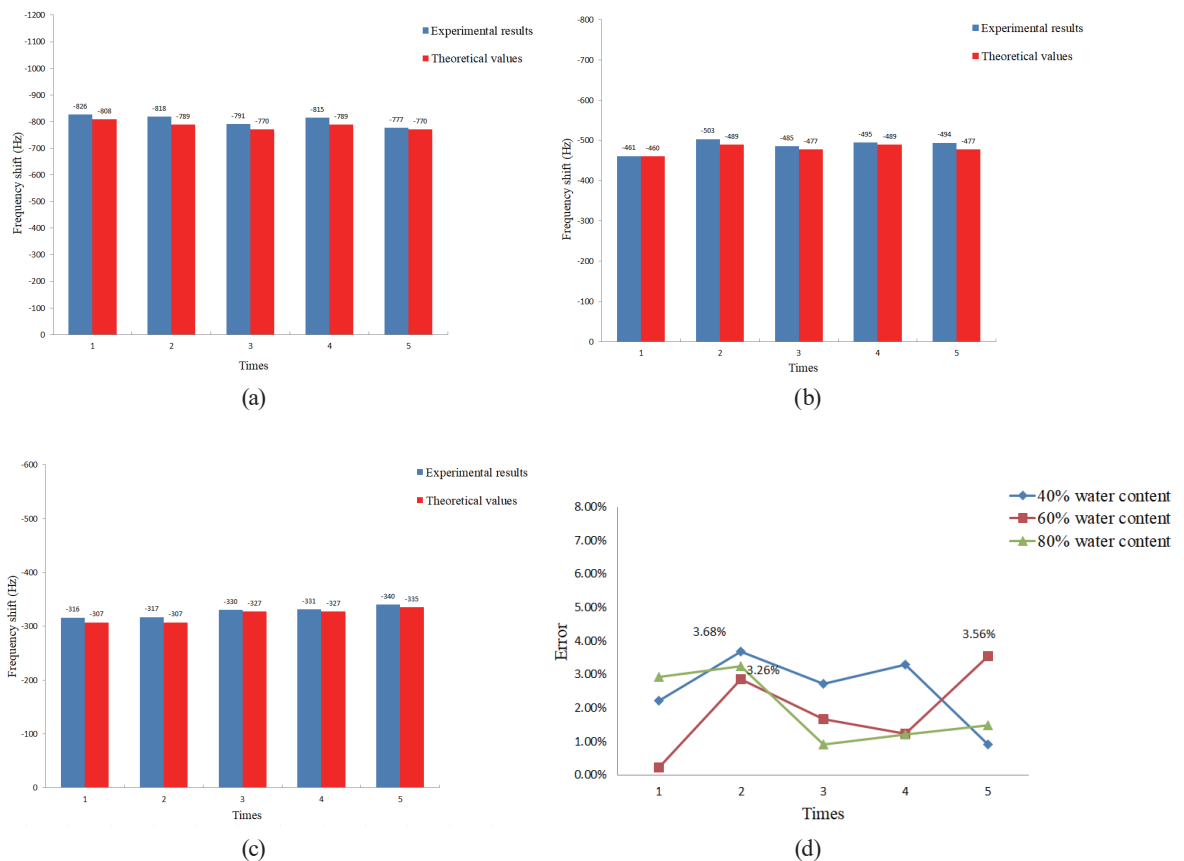

Fig. 5.　(Color online) Experimental results and theoretical values of five experiments; (a)–(c) represent the frequency change of the QCM for the glycerol solutions with water contents of 40, 60, and 80%, respectively, and (d) shows the error of each experiment for the three glycerol solutions.

Table 2
Experimental results and theoretical values of crude oil.

Water content	Δf_e (Hz)	Δf_t (Hz)	E
	−2046	−2076	−1.45
	−2343	−2463	−4.87
Crude oil	−2240	−2319	−3.41
	−2169	−2203	−1.54
	−2236	−2282	−2.02

to the uncertainty of the water content of crude oil in practical on-field measurements, a method of replacing the theoretical density calculated using the actual water content with the density (0.808×10^3 kg/m^3) measured with a precision electronic balance (JMA3002) was adopted. The crude oil was provided by the State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation of Southwest Petroleum University, and the precision electronic balance was purchased from Zhuji Chaoze Weighing Equipment Co., Ltd. (Zhejiang, China). The experimental frequency shift of the water content of crude oil was measured five times continuously, and Table 2 shows the comparison results between the experimental and theoretical values.

As shown in Table 2, the absolute value of the maximum relative error between the experimental and theoretical values is 4.87%, which confirms the applicability of the frequency response model in the field measurement of the water content of crude oil. There may be several reasons for these errors: first, the center of the droplet does not completely coincide with the center of the QCM electrode; second, slight changes in the indoor temperature and humidity will change the QCM frequency; third, the rounding error of MATLAB in the theoretical calculation; fourth, the error of the system used to measure the droplet radius with the optical magnifier; fifth, the different fundamental frequencies and electrode structures of the QCR will affect the accuracy of the measurement results. However, the errors in the above experiments are all within 5%, which demonstrates the effectiveness of the theoretical model of the water content of crude oil and verifies the high repeatability of the model.

5.　Conclusions

This paper presents a systematic method to accurately measure the water content of crude oil by using the liquid phase detection technology of a QCM in oil exploitation. The correctness and effectiveness of the theory for water content detection are verified by measuring glycerol solutions with different water contents. Theoretical analysis and experimental results show that the method has a very wide application range, and can be used for the entire range of water contents, overcoming the problems of a large error and low resolution of measurements for a low water content in the traditional density method. The field measurement results of water content of crude oil also confirm the applicability of the model. To improve the accuracy and repeatability of future water content measurement experiments, we will use a quartz wafer with a larger fundamental frequency and richer electrode structure to obtain a mass sensitivity curve with greater absolute mass sensitivity and a more uniform distribution. Because the QCM has a

simple structure and low price, the proposed new technology will be helpful to improve the measurement accuracy of the water content of crude oil over a wide range of water contents, and has broad application prospects in oilfield development.

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About the Authors

Yan Wang was born in Shandong, China, in 1986. She received her Ph.D. degree in detection technology and automatic equipment from the University of Electronic Science and Technology of China. She joined Southwest Petroleum University in 2013 and is now an associate professor. She has been engaged in the development of crystal oscillators and crystal filters.

Chong Li received his B.S. degree from Chongqing Technology and Business University, China, in 2020, and he is studying for his M.S. degree at Southwest Petroleum University. His research interest is the application of the quartz crystal microbalance to liquid phases.

Baorui Zhao received his B.S. degree from Southwest Petroleum University, China, in 2020, where he is now studying for his M.S. degree. His research interest is quartz crystal sensors.