Sensor for the evaluation of dielectric properties of sulfur-containing heteroatomic hydrocarbon compounds in petroleum based liquids at a microfluidic scale

Cite as: AIP Advances 10, 025006 (2020); https://doi.org/10.1063/1.5141482
Submitted: 06 December 2019 . Accepted: 15 January 2020 . Published Online: 04 February 2020

Mykhailo Kutia , Nikolay Mukhin , Hanna Petrova , Aleksandr Oseev , Liubov Bakhchova , Marc-Peter Schmidt, Alexander Aman, Stefan Palis, Sergey Tarasov, and Soeren Hirsch

ARTICLES YOU MAY BE INTERESTED IN

Proton radiation effects on carrier transport in diamond radiation detectors
AIP Advances 10, 025004 (2020); https://doi.org/10.1063/1.5130768

Alfvenic perturbations with finite Larmor radius effect in non-Maxwellian electron-positron-ion plasmas
AIP Advances 10, 025002 (2020); https://doi.org/10.1063/1.5141891

Cooperative torus mode emission of O-ring lasers
AIP Advances 10, 025007 (2020); https://doi.org/10.1063/1.5134832
Sensor for the evaluation of dielectric properties of sulfur-containing heteroatomic hydrocarbon compounds in petroleum based liquids at a microfluidic scale

Cite as: AIP Advances 10, 025006 (2020); doi: 10.1063/1.5141482
Submitted: 6 December 2019 • Accepted: 15 January 2020 • Published Online: 4 February 2020

Mykhailo Kutia,1,a) Nikolay Mukhin,2,3 Hanna Petrova,1 Aleksandr Oseev,1 Liubov Bakhchova,1 Marc-Peter Schmidt,1,5 Alexander Aman,1 Stefan Palis,1 Sergey Tarasov,3 and Soeren Hirsch5

AFFILIATIONS
1 Institute for Automation Engineering, Otto-von-Guericke-University Magdeburg, Magdeburg 39106, Germany
2 Institute for Micro and Sensor Systems, Otto-von-Guericke-University Magdeburg, Magdeburg 39106, Germany
3 Department of Photonics, Saint Petersburg Electrotechnical University LETI, Saint Petersburg 197376, Russia
4 FEMTO-ST Institute, CNRS UMR-6174, Université de Bourgogne Franche-Comté, 15B, Av des Montboucons, Besançon 25030, France
5 Department of Engineering, University of Applied Sciences Brandenburg, Magdeburger St. 50, 14770 Brandenburg an der Havel, Germany

a) Author to whom correspondence should be addressed: mykhailo.kutia@ovgu.de

ABSTRACT
Desulfurization of hydrocarbons is an important step in the processing of petroleum products, which requires an accurate and robust method for the sulfur-containing component evaluation. On the other hand, sulfur-containing heteroatomic hydrocarbon additives are harmful for people and the environment. Therefore, it is advantageous to conduct laboratory tests at low volumes to reduce doses of exposure of sulfur-containing vapors to the personnel. Microfluidics is an emerging platform that provides an advantage to operate with low volumes. The microfluidic dielectric spectroscopy approach is proposed in the current contribution as a platform for determination of the concentration of polar heteroatomic components in binary mixtures. The presence of heteroatomic components in petroleum products leads to a perceptible change in the dielectric properties of the blend. This paper shows the technological aspects for the microfluidic sensor chip design. It was successfully used to determine the concentration of thiophene (as a typical sulfur-containing hydrocarbon) in gasoline. We compare the commercially available solution with the developed microfluidic sensor. We demonstrate the developed microfluidic sensor chip that has a comparable sensitivity as a macroscopic commercial measurement cell but at the microscale. It is able to operate at 103 times reduced volume of liquid analyze, providing stable control of the sulfur-containing additive concentration. The obtained results are intended to be applied for lab monitoring of sulfur-containing components in petroleum products.

© 2020 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1063/1.5141482

I. INTRODUCTION

Petroleum is a complex mixture of hydrocarbons that includes paraffins, naphthenes, aromatic compounds, unsaturated hydrocarbons, and heteroatomic compounds in the form of components containing atoms of sulfur, oxygen, or nitrogen. There are sulfur compounds thiols, sulfides, cyclic sulfides, disulfides, thiophenes, benzothiophenes, dibenzothiophene, and naphthobenzo thiophenols in petroleum. Compounds containing oxygen may be present as alcohols, phenols, ethers, carboxylic acids, esters, ketones, and furans. Compounds containing, in their composition, a nitrogen atom in petroleum mixtures are represented as molecules of pyrrole,
indole, carbazole, benzo carbazole, pyridine, quinoline, indoline, and benzoquinolines and their metal components. Detection and determination of the exact concentration of these components is necessary for the entire petroleum production and processing cycle: to set the initial data for the design of petroleum inflow, for petroleum preparation for transport, and for deep petroleum refining. To create a qualitative mathematical model of the inflow, it is necessary to know the exact composition of petroleum. Heteroatomic components can significantly affect the properties of the hydrocarbon mixture, so determining their content is an important task for petroleum engineers.  

A. Approaches to evaluate heteroatom compounds in petroleum blends

Sulfur is the most common heteroatom in petroleum and petroleum products. Its content in petroleum can reach 14%. Petroleum, committed devoid of sulfur, does not exist. The determination of sulfur in petroleum and its removal are of great importance since sulfur compounds adversely affect the quality of petroleum products and pollute the environment. There are different methods of analyzing petroleum and petroleum products to control heteroatomic components that can be used to determine the concentration of sulfur compounds.

One of the most effective laboratory methods for analyzing the petroleum component composition is gas and high-performance gas chromatography. Gas-liquid chromatography is also demonstrating high measurement accuracy and can separate components that are very similar in their physical and chemical properties. However, preparation and preliminary separation of the sample into narrow fractions requires a long time. Separation of analytes occurs in columns (tubes) filled with a solid porous sorbent, with a liquid non-volatile stationary phase on the surface of the sorbent. A vapor of analytes that are mixed with carrier gas is moved through the column. In this case, multiple equilibrium is established between the mobile gas and liquid stationary phases due to the repetition of the dissolution and evaporation processes. Substances that dissolve in the stationary phase better have retained longer in the column. As a next step, an analyzed mixture is divided into separate components and all of them are left in the column separately and registered at the output. As a result, it can be concluded that with the help of these methods it is possible to achieve high resolution of the analysis. However, the high cost of equipment, large dimensions, and complexity of the analysis process limit the industrial application of chromatographic methods.

Methods of spectral analysis are also widely used to determine the properties of liquid hydrocarbons and gases. Raman spectroscopy makes it possible to obtain spectra with characteristics of different components in complex mixtures. This method has been successfully used to measure a suspension of carbon particles in an aqueous solution of carbohydrates. In addition to Raman spectroscopy, infrared (IR) spectroscopy and near-infrared (NIR) spectroscopy are widely used. A comparison of NIR, IR, and Raman spectroscopy for analyzing the component composition of petroleum was carried out in Ref. The results of the study showed that IR spectroscopy provides an acceptable analysis of heavy petroleum fractions. The use of Raman spectroscopy is limited due to fluorescence in consequence of fractions of heavy petroleum. However, Raman spectroscopy can be used for narrow fractions of petroleum with a low boiling point.

Most of the methods listed above are difficult to apply for flow online analysis, which can create difficulties in using them to monitor the content of sulfur-containing heteroatomic components in real time.

The simplest and most effective method to control heteroatomic petroleum-based products is to measure dielectric properties, evidenced by a large number of works devoted to the study of various types of fuel by the method of dielectric impedance spectroscopy. In Ref. 14, the authors show the possibility of using a sensor system to study complex three-component mixtures of gasoline, ethanol, and water. Similar work on the study of bioethanol fuels by the method of impedance spectroscopy is described in Ref. 15. Since thiophene, like ethanol, is soluble with petroleum fractions, does not form emulsions, and its molecule is polar, we used a similar approach during the current research. Another important advantage of impedance spectroscopy is the ability to be realized as a compact microfluidic sensory system. It allows gaining sensitivity at reduced dimensions and performs a multiparametrical testing on a miniature platform.

B. The dielectric properties of petroleum

Investigations of the dielectric properties of liquid systems make it possible to obtain extensive information about their molecular structure, intermolecular interactions, kinetics, and mechanisms of molecular processes. It is necessary to find a solution for these problems to understand and manage chemical and technological processes regarding the vast majority taking place in liquid phases. In this way, dielectric properties of fluids are interesting for a wide range of professionals, who work in different fields of physics, chemistry, biology, and medicine.

In the petroleum and gas industry, the study of dielectric spectra can provide an opportunity for the flow online determination of the presence of heteroatomic components and water in the petroleum products.

The presence of heteroatomic components containing sulfur, oxygen, or nitrogen in crude petroleum can reach 10% or more. These compounds can pose a threat to the environment and equipment. Therefore, it is crucially important to be able to control their content at all stages of the petroleum refining process. Dielectric spectroscopy provides a great opportunity for point and flow analyses of flow ability and transport properties of petroleum.

Any petroleum product is a mixture, which includes a large number of components that differ in the length of the carbon chain and in the presence of atoms other than carbon and hydrogen. Petroleum and hydrocarbon mixtures obtained from petroleum are good dielectrics. However, it can be noted that the dielectric permittivity grows insignificantly, depending on the number of carbon atoms in the molecule. So, for hexane with the formula C\textsubscript{6}H\textsubscript{14}, the dielectric permittivity is equal to 1.90, in the case of heptane C\textsubscript{7}H\textsubscript{16}, the dielectric permittivity is equal to 1.927, for octane C\textsubscript{8}H\textsubscript{18} it is equal to 1.976, etc.

The presence of heteroatomic components leads to a significant change in the dielectric permittivity of the mixture, because of the presence of sulfur, oxygen, or nitrogen atoms (typical atoms that form heteroatom compounds of hydrocarbons), which changes the
polarizing properties of hydrocarbon molecules. For example, the dielectric permittivity for the least polar cyclic heteroatomic component of thiophene is 2.73. For non-cyclic heteroatomic hydrocarbon compounds, such as mercaptans, alcohols, and disulfides, the value of dielectric permittivity can be more than ten times higher than the standard one for alkanes, which prevail in most petroleum fractions.

In recent years, a significant quantity of articles shows the possibility of using dielectric spectroscopy for the analysis of petroleum products. It was shown that it is possible to determine a large number of parameters for liquid hydrocarbons by using dielectric spectroscopy. The authors prove the possibility of determining the percentage of ethanol in gasoline, the octane number of gasoline, the volume of biodiesel, and others. Using microfluidic technologies for dielectric spectroscopy of hydrocarbons provides the development of “lab-on-the-chip” measurement systems.

Dielectric spectroscopy for measurements in fine-dispersed systems attains great interest nowadays. Some of the most known examples of such systems are water-in-petroleum emulsions and water-in-fuel emulsions. Usually, great attention is paid to the study of influence of different properties of gasoline-water emulsions on the change of the dielectric spectrum of mixtures. The relative volume of water and its drop sizes were detected by means of dielectric spectrum. These parameters determine the quality of water-based oils. On the other hand, dielectric spectroscopy can be used for flow on-line monitoring of the degradation degree of lubricating oils. Lubricating oils with different degrees of oxidation were proposed as a model dielectric medium for the study.

The dielectric permittivity of petroleum products, which are complex multicomponent mixtures of hydrocarbons of different structures, is a complex quantity consisting of the permittivity of the constituent components. The dielectric permittivity can be determined as follows:

\[ \varepsilon_r = X_{d.f.}\varepsilon_{d.f.} + X_{d.g.}\varepsilon_{d.g.} + X_{l.f.}\varepsilon_{l.f.} + X_{h.e.}\varepsilon_{h.e.}, \]

where \( X_{d.f.}, X_{d.g.}, \) and \( X_{l.f.} \) are the volume fraction of dissolved gaseous, light [boiling temperature (\( T_b \)) is less than 350°C], and dark petroleum fractions (\( T_b > 350°C \)); \( X_{h.e.} \) is the volume fraction of components containing polarizing heteroatomic elements; \( \varepsilon_{d.f.}, \varepsilon_{d.g.}, \) and \( \varepsilon_{l.f.} \) are the relative dielectric permittivities of dissolved gaseous, light (\( T_b < 350°C \)), and dark petroleum fractions (\( T_b > 350°C \)); and \( \varepsilon_{h.e.} \) is the relative dielectric permittivity of polarized heteroatomic elements.

The main goal of the present work is sensor development for the evaluation of the dielectric properties of sulfur-containing heteroatomic hydrocarbon compounds in petroleum based liquids at the microfluidic scale.

II. MATERIALS AND METHODS

The microfluidic sensor structure was developed and produced in Otto-von-Guericke University Magdeburg. In the current study, we examined our sensor structure for evaluating sulfur-containing heteroatomic hydrocarbons in gasoline with the help of Biologic SP-150 and Agilent 4395a. Raman spectroscopy and commercial dielectric cell Keysight 16452A Liquid Test Fixture were used as reference studies.

A. Samples choice

Thiophene is a representative of sulfur-containing components, which may be included in the composition of petroleum and its derivatives. The fact that thiophene completely dissolves in petroleum and derivatives without forming emulsions is also important. Therefore, it was chosen as a representative heteroatomic component for our experiments. Due to the fact that thiophene has a cyclic structure and its permittivity is 2.8, the polarizing sulfur atom significantly increases the permittivity, which will enable the best estimate of the resolving power of the method.

Gasoline with a boiling point of 100–140°C purchased from Sigma-Aldrich was used as a base solvent.

B. Experimental setup

The experimental setup is shown in Fig. 1. The experimental setup consisted of an impedance analyzer, a thermostat with a
temperature of 0°C, a control thermometer, and a sensor structure. In order to eliminate the influence of temperature, the measuring cell was placed inside a thermostat with a temperature of 0°C. The measurements were carried out after cooling the solution in the cell to +0.5°C. Since the experiment used the narrowing fraction of gasoline with a boiling point of 100°C–140°C, we do not expect the appearance of frozen paraffins. Liquid was supplied at a low flow rate of 5 ml/min with pre-cooling in a heat exchanger. The liquid circulation is organized by means of a pump to create a constant pressure and differential pressure during all measurements, which prevents deformation of the channel.

C. Technological stages of microfluidic sensory structure formation

The technology based on the SU-8 polymer is used by us to create a microfluidic sensor structure. As a basis for the sensor, SU-8 polymer layers of various thicknesses are used, which form almost the entire structural material. This approach allows us to create a sensory structure in which the same material forms microfluidic channels and is also used as an insulating material, which greatly simplifies the process.

For the development of a multilayer microfluidic sensor structure most commonly used are patterning electrodes on two different plates and further anodic compound with the intermediate polymer layer. When developing the sensor, it was clarified that it was necessary to keep the surface flat after structuring the microfluidic channels and the use of solid-state glass plates as the basis, which complicates the creation of one-sided structures. The application of the bonding polymer layer using TMMF and hot-roll lamination eliminates the need for substrate alignment. However, this approach is still poorly suited for high-frequency measurements.

The investigated sensory structure multichannel sensor is based on silicon/SU8 that was created by Institute for Micro and Sensor Systems, Otto-von-Guericke-University Magdeburg with top/bottom electrode design. All the contact pads, as signal shield contacts and ground electrodes, are positioned on the same chip side for the flip-chip attachment by the solder process. The sensor chip includes four fluidic channels to analyze multicomponent mixtures using simultaneous measurements at different frequencies. The multichannel sensor is demonstrated in Fig. 2.

In the technological process of an impedance sensor combined with a microfluidic structure, the following materials were used: SU8 photoresist as the main structural and insulating material, Cu (500 nm)—electrode material, and Ti (30 nm) as an adhesive sublayer for copper. As shown in Fig. 2(b), two fragments of the sensor were obtained on different glass substrates (Pyrex) and brought to a complex structure by adhesive bonding. Pyrex glass wafers were purified in piranha etch solution. In the case of the first fragment, the electrode material was sputtered directly onto the glass and insulated with a 5 μm SU8 layer. Once the insulation for the electrode was performed, another SU8 layer was spin-coated on top of it and microfluidic channels of 40 μm height were structured by a photolithography process. For the second fragment, a 40 μm SU8 layer was applied to a pre-coated Omnicoat glass substrate. Once the cross-linking of SU8 was finished, the electrode Ti/Cu was sputtered and isolated with a 5 μm thick SU8 layer (Fig. 3).

For the bonding process of two polymer layers, a necessary condition is incomplete polymerization. This provides the presence of the functional groups of polymer chains on the surface. Adhesive bonding for this structure was carried out with an intermediate polymer layer (5 μm, SU8), which was exposed after the soft bake step and directly before bonding with an exposure dose of 250 mJ/cm². Bonding was performed over one hour in a SUSS SB6e substrate bonder at a pressure of 3000 mbar and a temperature of 120°C without any leakage of SU8 in the microfluidic channel, as shown the Fig. 1(b). Once the bonding was performed, the top glass wafer was released by the etching of the Omnicoat layer in a MF319 developer.

Two fragments of the structure were bonded without any leakage in the microfluidic channel, as shown the Fig. 1(b). This appears as a challenging part of microfluidic impedance sensor manufacturing. As mentioned above, to complete the bonding process, it is necessary to have at least one layer of photosist SU8 not fully polarized. After two final fragments’ alignment appears a shadow area, created by the metal electrodes. Photosist in that part cannot be completely polarized. Therefore, the optimal parameters for exposure of the photosist were found before the alignment, to provide enough functional groups and keep the material polarized.

To ensure electrical contact with the upper and lower electrodes, 40 μm and 90 μm holes were etched in the SU8 layers. Dry etching was performed with the presence of an aluminum mask and in O2/SF6 ICP plasma. The etching rate was 0.9 μm/min.

The performed four-channel microfluidic chip has dimensions 20 mm × 55 mm. Top and bottom copper electrodes with titanium sublayer have sizes 3.15 mm × 26 mm and 4.05 mm × 30.2 mm, respectively.

![Image of a sensor structure](image_url)
III. RESULTS AND DISCUSSION

The initial studies with sensor structure were aimed at the possibility of determining the presence and concentration of heteroatomic hydrocarbons in petroleum using a multichannel microfluidic sensor. For this purpose, mixtures of gasoline with thiophene were used.

Studies have been carried out in the frequency region from 0.03 MHz to 5 MHz. Low-frequency measurements from 0.03 MHz to 1 MHz [Fig. 4(a)] were performed using Biologic sp-150. Measurements in a higher frequency region (up to 5 MHz) were performed using Agilent 4395a. As can be seen from Fig. 4, the capacities of pure gasoline, thiophene, and thiophene showed a significant difference in the spectra. As expected, we see a shift in the spectrum of the total cell capacity with increasing thiophene concentration. Measurements performed in the low-frequency range show linear values of the change in capacitance with increasing concentration of thiophene. The high-frequency region [Fig. 4(b)] shows the differences between all solutions; however, the increase in the value of the capacitance is nonlinear.

Figure 5 shows the experimental results of dielectric spectroscopy of a gasoline mixture with thiophene. The specimens were prepared with thiophene content from 0% to 5%. The graphic shows that the spectral shift is depending on the concentration of thiophene. It is possible to track the displacement linearity of the curves depending on the concentration.

The behavior of mixtures of gasoline with sulfur-containing components was taken into account when conducting dielectric spectroscopy in microfluidic channels. When the concentration of thiophene changes, the drugs show some similar dynamics. Figure 5(b) shows the equivalent circuit due to which the values of parasitic resistance and capacitance were calculated (2). Next, dielectric permittivity parameters were calculated for mixtures of gasoline with thiophene (3–4). The dielectric constant for...
a frequency of 500 kHz is shown in Fig. 5(b).

\[
\begin{align*}
R_p\omega C_p Z'_{\text{air}} + Z''_{\text{air}} &= 0, \\
-Z'_{\text{air}} + R_p\omega C_p Z''_{\text{air}} &= -R_p,
\end{align*}
\]

where \( R_p \) is the parasitic resistance, \( \omega = 2\pi f \) is the circular frequency, \( C_p \) is the parasitic capacitance, \( Z'_{\text{air}} \) is the real part of the impedance for an empty sensor structure, \( Z''_{\text{air}} \) is the imaginary part of the impedance for an empty sensor structure, \( C_p \) is the total capacity, \( Z'_0 \) is the real part of the impedance for the sensor structure field by the measured liquid, \( Z''_0 \) is the imaginary part of the impedance for the sensor structure field by the measured liquid, \( Z'_p \) is the real part of the impedance after subtracting the parasitic resistance and capacitance, \( Z''_p \) is the imaginary part of the impedance after subtracting the parasitic resistance and capacitance.

Due to the fact that the molecules of the selected sulfur-containing compounds are sufficiently large and weakly polarized, as well as they are completely soluble in gasoline, it was expected to obtain a linear displacement of the graphs of the dielectric spectra, which was observed experimentally. A similar behavior of the graphs, namely, the linear change in impedance depending on the number of heteroatomic compounds, was demonstrated in Ref. 26.

The main disadvantage of the method used in this study is the determination of the concentration for only one additional component in the mixture. With a simultaneous change in the concentration of several components in the solution, the obtained data can be interpreted using methods of mathematical statistics. Similar work was done by the authors in Ref. 27, where methods of mathematical statistics were applied simultaneously with methods of dielectric spectroscopy.

A dielectric cell Keysight 16452A Liquid Test Fixture was chosen as a standard reference device to verify our results. The measurements correspond to the cell manufacturer’s recommendations and were carried out as follows: the Keysight 16452A Liquid Test Fixture was washed with ethanol before measurement and then left for 60 min in a fume hood until ethanol evaporated completely. In the next step, the inductance and the resistance were measured during a short circuit at a frequency of 1 MHz. It was determined that the influence of external factors is negligible, because the measured inductance did not exceed 20 nH, and the resistance was less than 0.5 Ω. The reference values for capacity \( C_0 \) and resistance \( R_0 \) were measured by air measurements, which were necessary for further subsequent calculations. After this step, the measuring cell was placed inside a thermostat, where it was cooled for 5 min. Then, the cell was filled with the sample and was cooled down to 0.5 ºC, after which the spectra of \( C_p \) and \( R_p \) were taken.

The dielectric permittivity is calculated from the following equation:

\[
\varepsilon = \frac{Z'_0}{C_p 2\pi f |Z_0|},
\]

Comparing the main solutions with a zero concentration of thiophene, we clearly see the difference between the spectra of the capacity of the petroleum fractions as a result of different values of the dielectric constant for mixtures of hydrocarbons. As expected, the graphs in Fig. 6(a) show a gradual decrease in capacity with increasing frequency, regardless of the main component and thiophene concentration. The addition of thiophene leads to an increase in the capacity of the solutions.

With changing concentration of thiophene in the base solutions, a gradual increase in capacity was expected, which was confirmed. We can observe such an effect as a result of a noticeable increase in the permittivity of solutions with a change in the content of the polarizing sulfur-containing component with a higher value of the permittivity.

The permittivity was calculated from the capacitance spectra shown in Fig. 6(a). To check the dynamics of the growth of the
permittivity, graphs of changes in the permittivity obtained at a frequency of 500 kHz are shown in Fig. 6(b). The graphs clearly show the difference between the different fractions of petroleum. It shows the dependence of the permittivity on the concentration of thiophene in solutions. The dynamics of changes in permittivity suggests that the type of base solution does not significantly affect the overall measurement results.

Comparing the data obtained between our and commercial cells, we came to the conclusions written below. The deviation between permittivity dependencies shown in Figs. 5(b) and 6(b) is not higher than 2%. We estimated the sensitivity of the sensors as a change in their capacitance with the addition of 1% thiophene into gasoline. The sensitivities of the developed microfluidic sensor structure and Keysight 16452A Liquid Test Fixture were 0.8% and 0.3%, respectively.

To compare the sensitivity of capacitive measurements with the sensitivity of optical methods, we used Raman spectroscopy. The results of the measurements are presented in Fig. 7.

The measurements were carried out by a Raman spectrometer “Enspectr R532” to estimate the lower limit of measured concentration that can be found by this method. The measurements carried out with pure thiophene showed the presence of a characteristic peak at a Raman shift of 3121 cm$^{-1}$. The increase of thiophene concentration causes an intensive fluorescence. Due to this, the resolution of the measurements decreases. The thiophene’s characteristic peak begins to appear with an increase in its concentration of 2% and higher. In this case, Raman measurements with low concentrations of thiophene are limited and give way to the capacitance method.

IV. CONCLUSIONS

In the current work, we have demonstrated a novel microfluidic sensor for the monitoring of sulfur compounds in petroleum products. Gasoline mixtures with thiophene as a typical sulfur-containing heteroatomic hydrocarbon were investigated using this sensor. The results show that the developed microfluidic cell provides a stable response and sufficient sensitivity to the variation of thiophene. We compared the commercially available solution with the developed microfluidic sensor. We demonstrated that the developed microfluidic sensor chip has a comparable sensitivity as a macroscopic commercial measurement cell but at the microscale. It is able to operate at $10^3$ times reduced volume of liquid analyte, providing stable control of sulfur-containing additive concentration. The obtained results are intended to be applied for lab monitoring of sulfur-containing components in petroleum products.

ACKNOWLEDGMENTS

This work was supported by the Federal Ministry of Education and Research (BMBF) within the MicroSens (Grant No. 03IPT518A) project and by the Ministry of Education and Science of the Russian Federation under the project of the state task in the field of scientific activity (Project No. 16.1750.2017/4.6).

The authors declare no conflict of interest.
REFERENCES

1. L. P. Dake, The Practice of Reservoir Engineering. Revised ed. (Elsevier, Burlington, 2001), ISBN: 9780080574431.

2. J. G. Speight, The Chemistry and Technology of Petroleum, 3rd ed. (Marcel Dekker, New York, 1999), ISBN: 082470409X, rev. and expanded.

3. J. G. Speight, Handbook of Petroleum Analysis (Wiley, New York, Chichester, 2001), ISBN: 0-471-13870-2.

4. M. Kutka, M. Fyk, O. Kravchenko, S. Palis, and I. Fyk, "Improvement of technological-mathematical model for the medium-term prediction of the work of a gas condensate field," East. Eur. J. Enterp. Technol. 5, 40–48 (2016).

5. D. H. Desty and R. H. F. Whymann, "Application of gas-liquid chromatography to analysis of liquid petroleum fractions," Anal. Chem. 29, 320–329 (1957).

6. F. S. Wolffenbuttel, J. Visser, R. Soltis, and R. F. Wolffenbuttel, "Multi-domain spectroscopy for composition measurement of water-containing bio-ethanol fuel," Appl. Spectrosc. 69, 224–228 (2012).

7. S. Aman, A. Aman, W. Hintz, M. Trüe, P. Veit, and S. Hirsch, "The exfoliation of graphite particles in the vibratory disk mill," Chem. Ing. Tech. 89, 1185–1191 (2017).

8. H. Chung and M. S. Ku, "Comparison of near-infrared, infrared, and Raman spectroscopy for the analysis of heavy petroleum products," Appl. Spectrosc. 54, 239–245 (2000).

9. F. Opekar, R. Cabala, and T. Kadlecová, "A simple contactless impedance probe for determination of diesel/biodiesel blends and potential dielectric approaches for biodiesel content assessment," Fuel 88, 1453–1459 (2009).

10. L. M. Middelburg, G. de Graaf, A. Bossche, J. Bastemeijer, M. Ghaderi, F. S. Wolffenbuttel, J. Visser, R. Solits, and R. F. Wolffenbuttel, "Multi-domain spectroscopy for composition measurement of water-containing bio-ethanol fuel," Fuel Process. Technol. 167, 127–135 (2017).

11. E. P. Santos, "Determination of electrical properties of crude oil and its influence on the performance of the oil reservoir," Ph.D. thesis, Federal University of Santa Catarina, 1999, in English.

12. I. G. G. Speight, Handbook of Petroleum Analysis (Wiley, New York, Chichester, 2001), ISBN: 0-471-13870-2.

13. J. G. Speight, The Chemistry and Technology of Petroleum, 3rd ed. (Marcel Dekker, New York, 1999), ISBN: 082470409X, rev. and expanded.

14. M.-P. Schmidt, A. Osev, C. Engel, A. Brose, A. Aman, and S. Hirsch, "A novel design and fabrication of multichannel microfluidic impedance spectroscopy sensor for intensive electromagnetic environment application," Proc. Eng. 87, 88–91 (2014).

15. L. Guan, X. L. Feng, G. Xiong, and A. L. Brandes Marques, "A simple and fast method to determine water content in biodiesel by electrochemical impedance spectroscopy," Talanta 79, 753–759 (2010).

16. L. P. Dake, The Practice of Reservoir Engineering. Revised ed. (Elsevier, Burlington, 2001), ISBN: 9780080574431.

17. J. G. Speight, Handbook of Petroleum Analysis (Wiley, New York, Chichester, 2001), ISBN: 0-471-13870-2.

18. L. P. Dake, The Practice of Reservoir Engineering. Revised ed. (Elsevier, Burlington, 2001), ISBN: 9780080574431.