

Application of the surface plasmon resonance phenomenon to controlling suspensions

A.V. Fedorenko¹, N.V. Kachur¹, H.V. Dorozinska², G.V. Dorozinsky¹, V.P. Maslov¹, O.V. Sulima², T.O. Rudyk²

¹V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine
41, prosp. Nauky, 03680 Kyiv, Ukraine

²National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute"
37, prosp. Peremohy, 03056 Kyiv, Ukraine
Corresponding author e-mail: natalykachur@gmail.com

Abstract. Represented in this paper are the results of investigations aimed at checking up the capabilities of devices based on the surface plasmon resonance (SPR) phenomenon to be applied for studying the properties of water suspensions. As an example, the authors used here the suspensions of tooth pastes Sensodyne and Colgate in distilled water. For measurements, we used the SPR device Plasmon-71 operating in the near infrared spectral range. Results of these measurements were compared to those obtained using the spectrophotometric ones. The measured values of the sedimentation velocity obtained using both the applied methods confirmed availability to efficiently apply SPR devices for studying the opaque multi-component suspensions.

Keywords: surface plasmon resonance, infrared spectral range, spectrophotometer, suspension, tooth paste.

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1. Introduction

Plasmonics is now the field of promising investigations, the technological base of which offers variety of specific measuring devices – spectrometers based on the phenomenon of surface plasmon resonance (SPR). Majority of these devices are designed using the Kretschmann optical scheme [1]. In this scheme, it is usually used a fixed wavelength of polarized light in the configuration of angle scanning, which is necessary to observe disturbance in total internal reflection at the interface “dielectric–studied substance”. SPR-devices can operate in various spectral ranges, and among them, one of the promising is the near infrared range (NIR) [2].

Application of the SPR method in various investigations is rather universal way, which enables to reach a high accuracy in determining parameters of liquid and gas-like substances when measuring their optical refraction coefficients. Using the SPR devices makes it possible to study various multi-component mediums and to measure their separate components. In the work [3], for instance, the authors modeled the possibility to determine the glucose content in the human blood. Besides, these devices enable to study suspensions, ascertain the size of nanoparticles as well as their size distribution [4, 5].

When producing goods from ceramics, the slip process is widely used. To produce qualitative and highly-reliable goods, it is necessary to make slip control (*i.e.*, to watch over the following slip parameters: homogeneity and size of particles). From the technological viewpoint, the slip is a suspension with the water content approximately 30%. Therefore, in industry the slip density is monitored the most often [6]. For example, there exists a capacitive sensor that enables to measure the suspension flow density within the range of volume fractions 0...29% for the solid substance [7].

The lack of this method is that it provides only the possibility to study suspensions with a small content of solid particles and to measure only integrated values of mixture capacitance, which does not enable to determine the size distribution of particles. At the same time, there are optical methods for studying the size, for instance, represented in the work [8] is the way to study drops of slime by using the method for digital holographic microscopy. This method allows measuring the concentration and size distribution of solid particles having the dimensions close to one micrometer in suspension. Since the SPR method can help to study behavior of nanoparticles, is fast and has a high accuracy, it seems very promising to provide effective investigations in this field.

The tooth paste is an example of suspension, because beside an abrasive material it contains a set of chemical admixtures and, in some cases, nanoparticles [9]. It means that the paste is rather complex multi-component substance to be analyzed. Composition of these tooth pastes is usually indicated by producer, and scientific investigation of them in most cases concerns directly their influence on the human organism and teeth. For instance, it is known the work [10], where abrasive properties of tooth paste were investigated using a profilometer. As an experimental sample, the tooth paste was already used earlier [11].

In this paper, we have reported results of applying the infrared SPR-spectrometer Plasmon-71 to investigate suspensions based on the tooth pastes of two kinds.

2. Materials and methods

Two tooth pastes of the sorts Sensodyne and Colgate were acquired in the ordinary shop. To perform measurements, we used the spectrophotometer Mapada UV-1600 and the SPR-device Plasmon-71 operating in the infrared spectral range in accord with the Kretschmann scheme. Its main technical characteristics are as follows: the operation wavelength $\lambda = 850$ nm, angle resolution for the incident light beam – 10 ang. sec, maximum range of scanning angle – 17°, availability to use two measuring channels simultaneously. The used prism is made of glass F1 and has the refraction index 1.61. Besides, we used a glass plate with the gold layer of the thickness 50 nm. To reduce possible errors caused by the influence of external medium as well as heating the elements with time, the measurements were performed simultaneously in both channels with two different samples.

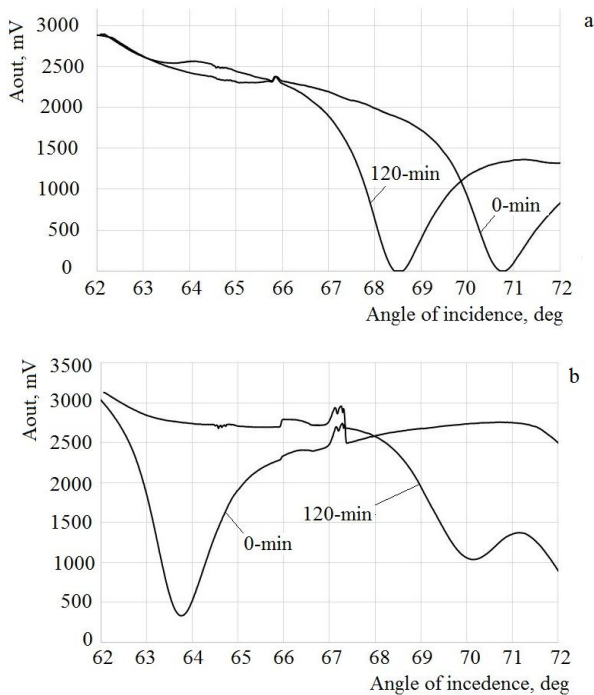


Fig. 1. SPR curves for the tooth pastes Sensodyne (a) and Colgate (b).

3. Results and discussion

Unlike other substances, for example, turbid water [12], for which measurements are available due to their partial transparency [12], toothpaste is not transparent in the visible spectral range. However, the SPR device is suitable for measuring these opaque suspensions. Given in Fig. 1 are the SPR curves for Sensodyne (a) and Colgate (b) pastes.

The tooth pastes were simultaneously deposited onto the gold layer of sensor plate and measured in ambient air. The moisture from the pastes was evaporated with time, and their composition was changed. It caused respective changes in their SPR characteristics and a considerable shift of reflection minimum positions. The changes in these positions with time are added in Fig. 2.

As can be seen from the plots, behavior of these two pastes is different. From the very beginning, the SPR characteristic of Sensodyne was shifted only by 2° to the side of lower angles, and then remained unchanged. It may be indicative of availability of hydrophilic components in its composition. The Colgate characteristic, though being at its beginning close to the left side of measuring range, started to quickly change, *i.e.*, the angle of minimum reflection shifted to higher values up to the limit of measuring range. At the same time, we observed a decrease in the value of SPR minimum depth.

To increase the transparency of tooth paste, the latter should be diluted with distilled water, which enables measurements of its spectral characteristics. The transmission spectrum of the paste diluted in the ratio 1:5 is shown in Fig. 3. At the same time, the paste suspension becomes more suitable for pumping through the cuvette, which makes it possible to simpler measure the kinetics of substitution in a closed volume.

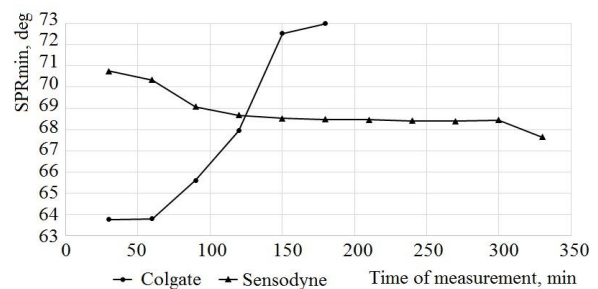


Fig. 2. Changes in the SPR minimum positions with time.

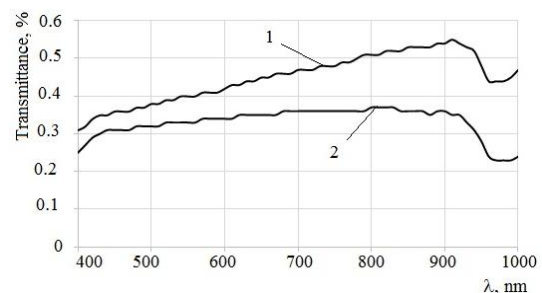


Fig. 3. Transmission spectra of tooth pastes Colgate (1) and Sensodyne (2) diluted in distilled water in the ratio 1:5.

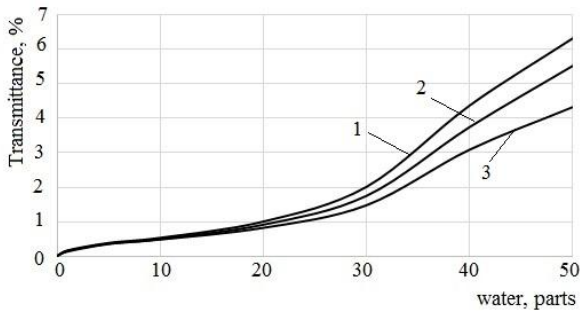


Fig. 4. Plot of dependence for the transmittance of tooth paste Sensodyne for various ratios of dilution with distilled water. The wavelengths of measurements: 1 – 700 nm, 2 – 600 nm, 3 – 500 nm.

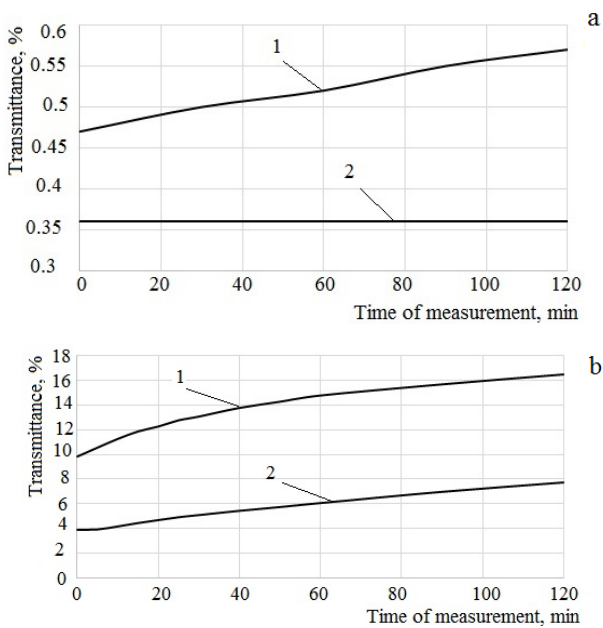


Fig. 5. Transmittance at the wavelength 700 nm for the pastes Colgate (1) and Sensodyne (2) with time running (a – diluted ratio 1:5, b – diluted ratio 1:50).

With account of the spectral dependence for the transmission of diluted tooth paste, it is possible to choose the wavelength that allows better measuring its transparency. It is clearly seen that with transfer to the near-infrared range the transparency increases, and sensitivity grows, too. If at the wavelength 500 nm the difference between these two pastes is equal to 16%, then at the wavelength 700 nm it reaches already 24%. Besides, at further dilution of the tooth paste with distilled water, this difference only enhances (Fig. 4).

It means that the measurements of transmittance for the studied suspension are reasonable to perform within the spectral range 700...900 nm.

Being diluted in water, the tooth paste as a multi-component complex system can undergo sedimentation onto the sensitive element of SPR device. It implies that weighty and sizeable particles of the fraction will have a larger influence on the obtained SPR characteristic.

We measured changes of transmittance with time at the wavelength 700 nm for both pastes (Fig. 5) diluted in the ratio 1:5 (a) and 1:50 (b), respectively.

When dilution was 1:5, the paste Sensodyne did not change its transparency, while the paste Colgate became more transparent with the velocity 0.05%/hour. For the dilution ratio 1:50, both pastes underwent sedimentation, and their transmittance was increased with the velocities: for Sensodyne 1.92%/hour, and Colgate 3.32%/hour. It is indicative of complexity in studying and monitoring the diluted pastes by using spectrophotometry.

When investigating the kinetics of substitution of tooth paste suspension with the other ones of different concentrations, we obtained the following results: the plots of substituting the distilled water with the tooth paste suspensions in comparison to the distilled water in the reference channel: Sensodyne – Fig. 6, Colgate – Fig. 7.

In the kinetics of substitution for the paste Sensodyne, it is observed the shift of SPR curve minimum, which increases after completion of substitution. It is indicative of the sedimentation processes. In this case, the higher is the distilled water content in this mixture, the more prolonged is the process itself. The velocity of the angle shift for various dilutions was as follows: 1:5 – 0.497 deg/hr, 1:20 – 0.35 deg/hr, 1:50 – 0.285 deg/hr. Besides, some definite amount of particles in the form of sediment remains on the gold layer and cannot be washed out with the flowing distilled water. This is confirmed by the difference of reflections in the measuring and reference channels.

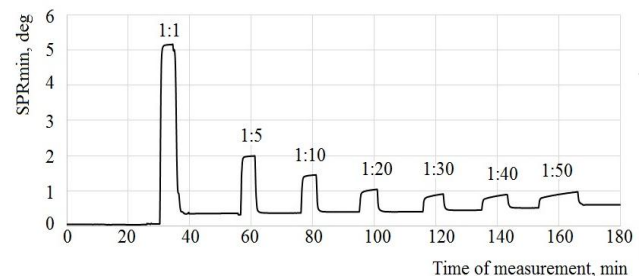


Fig. 6. Kinetics of substituting the distilled water with the Sensodyne suspension of various dilutions.

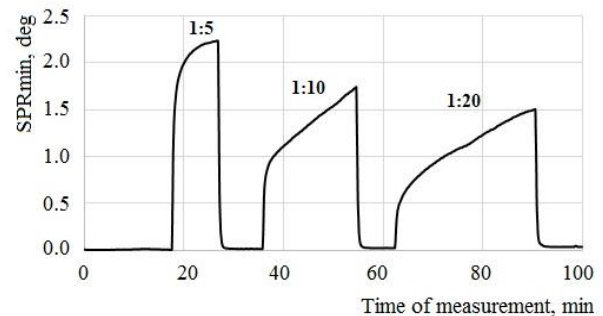


Fig. 7. Kinetics of substituting the distilled water with the Colgate suspension of various dilutions.

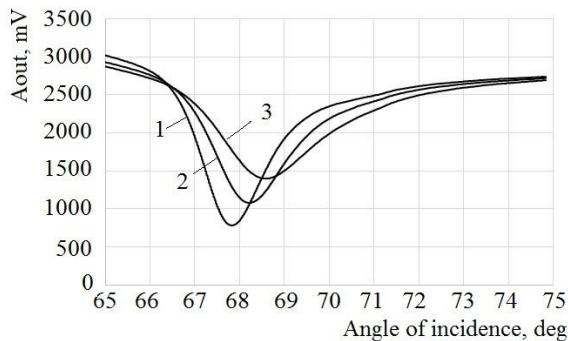


Fig. 8. SPR curves for the paste Colgate: 1 – at the beginning of drift; 2 – in the middle; 3 – at the end of drift after substitution.

In the case of Colgate paste, the shift velocity of the SPR curve minimum after substitution is considerably higher even at lower concentrations. So, for the dilution 1:5, it is 3.02 deg/hr, but for the dilution 1:20 – 2.213 deg/hr. For this paste, the sediment was washed out with the distilled water practically in full. The change of SPR characteristic inherent to the paste Colgate for the dilution 1:20 at the very beginning, in the middle and at the end of drift are adduced in Fig. 8.

As the plot shows, there observed is not only the shift of SPR curve, but the depth of its minimum is decreased, too. The similar processes were observed in Fig. 1b, when this paste was dried. But in this case duration of the process is approximately 10 min, contrary to 120 min in the former one. Due to strong dilution (1:20), one can observe mostly the processes of sedimentation of solid particles from the suspension.

4. Conclusions

The performed investigations have shown the capabilities and perspectives to apply the devices based on the SPR phenomenon and operating in the near infrared range to study sedimentation processes in suspensions with low transparency (for example, tooth pastes diluted with distilled water). This method allows one to carry out the dynamical measurements, which enables to obtain information about behavior of solid particles in these mediums.

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Authors and CV



Artem Fedorenko, PhD, researcher of the Department of sensor systems at the V. Lashkaryov Institute of Semiconductor Physics, NASU. Received his master's degree at the National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute". The area of his scientific interests includes IR photodetectors and laser ranging.

E-mail: aaartemaa@gmail.com,
<https://orcid.org/0000-0001-6201-6129>



Nataliya Kachur got her degree MS in Physics and Techniques at the National Aviation University of Ukraine, Mechanical faculty in 2006. She is PhD student at the V. Lashkaryov Institute of Semiconductor Physics, NASU. The area of her scientific interests includes physics of surfaces, development and design sensors for applying in control of quality of transparent materials.

<https://orcid.org/0000-0001-6868-8452>



Hanna Dorozinska, PhD, assistant at the NTUU “Igor Sikorsky Kyiv Polytechnic Institute”. She is the author of 33 publications and 8 patents of Ukraine. Her research interests in optical metrology and development as well as design of chemical sensors and biosensors for application in industry and ecology.

E-mail: annakushnir30@ukr.net,
<https://orcid.org/0000-0002-9352-3761>



Glib Dorozinsky, PhD, Senior Researcher of the Department of sensor systems at the V. Lashkaryov Institute of Semiconductor Physics. Author of more than 56 publications and 34 patents of Ukraine. The area of his research interests in physics of surfaces, development and design of chemical sensors and biosensors.

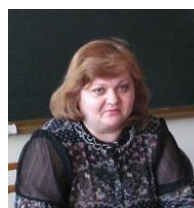
E-mail: gvdorozinsky@ukr.net,
<https://orcid.org/0000-0002-7881-2493>



Volodymyr Maslov, Doctor of Materials Science, Leading Researcher of the Department of sensor systems at the V. Lashkaryov Institute of Semiconductor Physics. Honored inventor of Ukraine. Author of more than 156 publications and more than 400 patents of Ukraine and author’s certificates of USSR. His research interests include several topics of optical engineering and physical behavior of functional materials as well as phenomena of surface plasmon resonance with its application in medicine and ecology. E-mail: vpmaslov@ukr.net,
<https://orcid.org/0000-0001-7795-6156>



Olga Sulima, PhD, associate professor of the Department of Mathematical Physics and Differential Equations. She has been working at the NTUU “Igor Sikorsky Kyiv Polytechnic Institute” since 1989. Her main scientific interests: analytical and ecological instrumentation, formation of mathematical competence of students of the technical university. E-mail: olgasulimakpi@gmail.com,
<https://orcid.org/0000-0002-5811-7717>



Tatiana Rudyk, PhD, associate professor of the Department of Mathematical Physics and Differential Equations. She has been working at the NTUU “Igor Sikorsky Kyiv Polytechnic Institute” since 1989. Her main scientific interests: theory of optimal control, applied mathematics, methods of teaching higher mathematics at a technical university. E-mail: ru58@ukr.net,
<https://orcid.org/0000-0003-1121-4963>

Authors’ contributions

Fedorenko A.V.: investigation, writing – original draft (partially).

Kachur N.V.: investigation, writing – original draft (partially), writing – review & editing.

Dorozinska H.V.: formal analysis, investigation, data curation.

Dorozinsky G.V.: investigation, investigation, data curation, writing – review & editing.

Maslov V.P.: conceptualization, methodology, supervising.

Sulima O.V.: conceptualization, methodology, writing – review & editing.

Rudyk T.O.: formal analysis, data curation, visualization.

Застосування явища поверхневого плазмонного резонансу для контролю суспензій

А.В. Федоренко, Н.В. Качур, Г.В. Дорожинська, Г.В. Дорожинський, В.П. Маслов, О.В. Суліма, Т.О. Рудик

Анотація. У статті наведено результати досліджень, спрямованих на перевірку можливості застосування приладів на основі явища поверхневого плазмонного резонансу (ППР) для вивчення властивостей водних суспензій. Як приклад, автори використовували розчини зубних паст Sensodyne і Colgate у дистильованій воді. Для вимірювань використовувався ППР-прилад Plasmon-71, що працює у ближньому інфрачервоному діапазоні спектра. Результати цих вимірювань порівнювали з отриманими за допомогою спектрофотометра. Виміряні значення швидкості осадження, отримані обома застосованими методами, підтвердили можливість ефективного застосування приладів ППР для дослідження непрозорих багатокомпонентних суспензій.

Ключові слова: поверхневий плазмонний резонанс, інфрачервоний спектральний діапазон, спектрофотометр, суспензія, зубна паста.