

ГОДИШНИК НА УНИВЕРСИТЕТА ПО АРХИТЕКТУРА, СТРОИТЕЛСТВО И ГЕОДЕЗИЯ – СОФИЯ

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SURFACE PHOTO-CHARGE EFFECT: APPLICATIONS FOR FLUIDS

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Research area: field-matter interactions

ABSTRACT

The methods for fluid characterization based on the surface photo-charge effect (SPCE) are described for the cases of some practical applications as liquid identification, monitoring of octane factor, liquid level measurement, milk and water quality control, etc. Experimental setups and approaches are discussed as well as the main advantages and potential of the SPCE-based sensors for on-line and/or in situ control. The study reflects the priority of contemporary scientific research for the improvement of the quality of life.

1. Introduction

The surface photo-charge effect (SPCE) is observed when any solid surface is being illuminated with an intensity-modulated electromagnetic field. Then an alternating current (AC) between the solid and common ground across the light direction is generated [1, 2, 3] with a frequency equal to that of the modulation [4, 5]. The amplitude of the signal created by SPCE depends on the specific characteristics of the irradiated surface. The SPCE is a universal property of any kind of solid, and has been observed in a very wide range of the electromagnetic spectrum [6]. Possible explanation of the SPCE in the case of conductors [2] and in the case of dielectrics [3] was proposed implying redistribution of the charges in the

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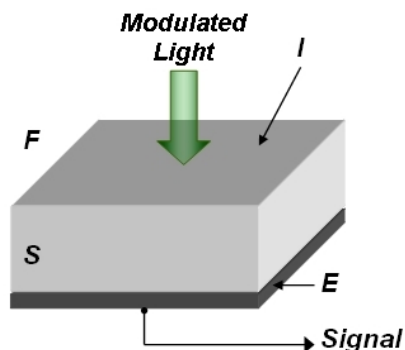
conductor under the force generated perpendicular to the illuminated surface. This takes place when incident light attenuates in depth of the solid and changes in the charge of surface energy states at the irradiated dielectric surface.

In the present review, our experimental setups and results on application of SPCE for studying of fluids are described on some examples including: liquid recognition [7], control of the octane factor of gasoline [8], detection of impurities [8], control of material deposition from solution [8], level meter [9], quality control of milk and food [10].

2. SPCE performance at the liquid-solid interface

The SPCE in liquids is not an inherent property of the liquid itself but is rather generated at the solid-liquid interface. The presence of a liquid most probably changes the capacity of the measuring structure at the illuminated solid-liquid interface, this way increasing the SPCE signal [8]. A scheme of the measuring structure for SPCE in liquid-solid interface is shown in Fig. 1.

When an irradiated solid surface (S) is in contact with a fluid being investigated (F) at the interface (I), any kind of changes in the fluid properties causes a change of the SPCE signal which is measured on the electrode (E), coupled to suitable equipment. The amplitude of the detected signal could be increased by using monochromatic light and a semiconductor substrate sensitive to SPCE.



**Fig. 1. Measuring structure for SPCE in liquid-solid interface:
S-solid; I-solid-liquid interface; F-fluid; E – electrode**

Since the method is capacitive, signals have been obtained not only from conducting electrodes directly contacting the liquid, but from electrodes placed out of the liquid as well.

3. Practical applications

Since the effect is very sensitive to the state of the irradiated interface, i.e. to any changes in the composition and the properties of the studied fluid, this effect is very attractive for practical applications together with the already existing methods for liquid control. In addition, the SPCE-based method is universal and could be used for any fluid under various conditions. It is contactless, rapid and the results are measured in real time.

3.1. Liquid recognition

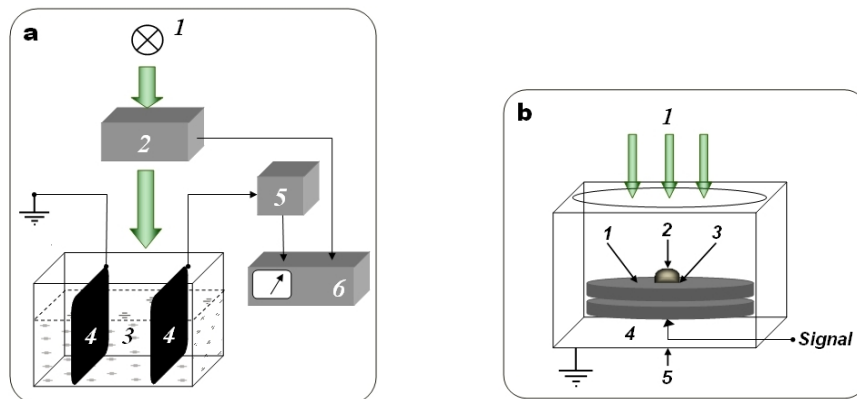


Fig. 2. SPCE detection with electrodes immersed into the liquid

- (a): 1 – light source; 2 – modulator; 3 – vessel with liquid; 4 – electrodes; 5 – pre-amplifier; 6 – lock-in nanovoltmeter; SPCE measurement with a drop of liquid
 (b): 1 – teflon or semiconductor substrate; 2 – liquid drop; 3 – liquid–solid interface; 4 – electrode; 5 – metal grounded box

A setup for SPCE detection is shown in Fig. 2. The light source (1) was a Ne-Ne laser (at $\lambda=633$ nm, and 50 mW) or an Ar-ion laser (at $\lambda=488$ nm, and 250 mW). In Fig. 2a the studied liquid is in a vessel and the SPCE signal comes from the electrodes (4) placed in or out of the liquid. The parameters which determine the signal magnitude are: form, material and the size of the electrodes and the vessel and their configuration as well as the light spot location. In each experiment, 15 ml of liquid were used with the same spot location. If a drop of liquid is measured, the SPCE signal comes from an electrode (4) and a grounded metal box (5) used for avoiding electrical noises.

The potential difference created by this effect has a specific value for each liquid with substantial difference between them. The SPCE signal for several, randomly selected liquids, was: tap water – 190 μV ; filtered water – 209 μV ; distilled water – 175 μV ; alcohol – 115 μV ; ammonia solution – 65 μV ; acetone – 50 μV ; coffee (used as an opaque liquid) – 15 μV .

The data for three types of water (filtered, distilled and from the tap) show that even insignificant treatment of the liquid causes easily detectable signal variations. Thus, analysis and control of drinking water can be carried out [11].

3.2. Control of the octane factor of gasoline

Gasoline samples (30 ml each) having different octane grades and supplied by the Bulgarian Center for Standardization were measured as an example of the fact that various modifications of a given liquid could be detected by changes in the SPCE signal. The SPCE signals were remarkably different as the octane factor changed: A-86 – 29 μV ; A-91 /unleaded/ – 59 μV ; A-93 – 54 μV ; A- 93/unleaded/ – 63 μV ; A-95 /unleaded/ – 64 μV ; A-96 – 46 μV . The amplitudes of the SPCE signal for a series of fuels, purchased from regular gas stations were: diesel – 48 μV ; A-86 – 31 μV ; A-93 – 52 μV ; A-95 /unleaded/ – 68 μV .

The results show that a quality control device could be developed for gasoline quality control after proper calibration.

3.3. Detection of impurities

Significant variations of the SPCE signal were also observed upon mixing two liquids [8]. The liquids were examined in a glass vessel and an Ar-laser was used as an illuminating source. The results showed that only a drop of ammonia solution added to 200 ml of drinking water causes a 15% decrease in the amplitude of the signal, whereas a drop of acetone increases the signal amplitude by 10%.

Thus, any contamination which changes the chemical composition can be detected by the corresponding variation in the SPCE signal. This way, various types of absorbing filters for gases and liquids can be monitored in order to determine when they have to be replaced.

It is clear that the SPCE can be used to monitor environmental pollution as well. Such non-destructive, continuous and real-time test would be useful in the fields of ecology, industry, car production, military equipment, etc.

3.4. Control of material deposition from a solution

The precipitation of a substance from a solution on the volume surface could also be monitored by the SPCE-method. Since the deposition affects the surface, it changes the SPCE signal. For example such a change was observed during CaCO₃ deposition from water solution on a metal surface [8], the signal amplitude being dependent on the intensity of the illuminating light.

3.5. Level meter

Experiments were performed showing that the SPCE signal may become dependent on the level of the liquid. A laboratory model of a level meter for liquid fuel (unleaded A 95H for example) was developed. Its basic scheme is shown in Fig. 3: the measuring structure is deposited on a solid, shaped as a stick (1) whose length is larger or at least equal to the height of the container where the liquid (3) is stored. The measuring electrode (2) is also placed along the length of the stick. Any change of the liquid level causes a change in the area of solid/liquid interface and this way, a change in the SPCE signal. Instead of illuminating with light, the stick was irradiated with modulated electromagnetic field of ultra-high frequency (UHF).

One of the most widespread applications of level meters is the measurement of liquid fuel levels. A small laboratory model was built for testing unleaded petrol A 95H. About 100% change of the electric signal was observed when the change of the liquid level was from 0 to 10 cm. The measurement accuracy was 0.4 mm and it can be increased simply by technical improvement. With a level meter properly built and optimized, the signal could be very sensitive to small changes (of the order of 0.1 mm) in the level of the liquid, and proportionality between the SPCE signal and the level of the liquid in the tank was observed (Fig. 4). The device measures both the level of the water usually being present at the bottom of the tank and the fuel level.

For any sensor based on the SPCE, the choice of material of the solid, accuracy, depth of the tank (size of the solid surface) and working conditions are of great importance for each particular case of the liquid being measured.

In general, the investigations performed so far did not reveal any principal difficulties for the implementation of such device, but there are some problems affecting the measurement accuracy which have to be solved before the device leaves its laboratory-prototype stage. For example, the condensation of vapors on the measuring structure could decrease the accuracy of measurement. Improving the measuring structure in order to minimize the

influence of the condensation or to put the condensation under control is a possible way to avoid such problems. Some preliminary tests were carried out with supplying hot water vapor to a closed chamber, in which the level meter had been placed, until saturation was achieved. At these extreme conditions, the experimental error was about 1 mm.

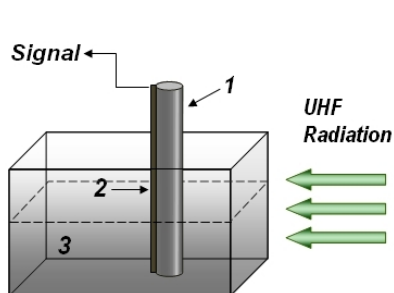


Fig. 3. Scheme of a level meter
 1 – solid stick with deposited measuring structure on it; 2 – electrode; 3 – liquid

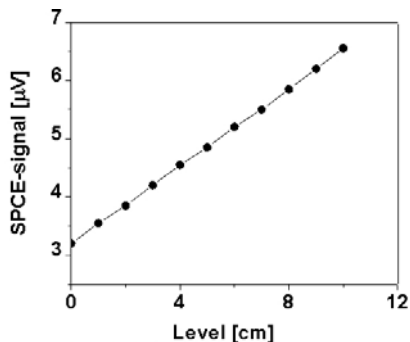


Fig. 4. SPCE response of the laboratory level meter versus the petrol level

An important advantage of the described level meter is that the measuring technique does not pose risk of sparks since the generated potential differences are very small - of the order of nanovolts and microvolts. Another option is the possibility of designing the device with electrical wiring separated from the liquid fuel. Additional advantages are the simple design, small investments for production, sensitivity to very small variations in the liquid level, measuring in real time and no moving parts involved.

The SPCE could be used also for monitoring the flowing velocity since, at certain conditions, the generated voltage depends on this factor as well.

3.6. Quality control of milk

Most analytical methods for milk analysis, including biochemical, microbiological, serological methods, etc. have the disadvantages of being slow, creating problems with consumables, requiring laboratory conditions and needing expensive, extremely unstable, toxic or carcinogenic reagents.

The experiments showed that it is possible to use the SPCE for rapid detection of some specific changes and processes taking place in milk [10].

The scheme of the experimental setup is similar to the one shown in Fig. 2. A continuous wave diode laser (1) was used as a light source generating 25 mW at $\lambda=655$ nm. The laser beam was being chopped by a modulator (2) into periodic pulses with a modulation frequency of 800 Hz (far from the one of the electric network - 50 Hz – to avoid possible parasitic signals). Instead of a mechanical modulator, a pulsed laser or a pulsed LED could also be used. The milk sample (10 ml) was placed in a small vessel in which two electrodes were placed. A setup for testing of only a drop of liquid is also possible. A high-impedance pre-amplifier (5) with a gain of 20 dB at an input resistance of $10^8\Omega$ and a lock-in nanovoltmeter (6) were used for detecting the SPCE-signals, the reference signal to the lock-in being supplied by the modulator.

The SPCE signal is formed at the milk–solid interface and is very sensitive to any minor changes in the milk (concentration, contaminations, pre-treatment, etc.). The milk quality control can be performed either by direct observation of the signal amplitude or by using appropriate liquid reagents to modify the signal. The milk samples were studied by measuring the amplitude of the signal generated by pure milk and its variation after a droplet (0.04 ml) of testing liquid was added to the milk. The testing liquid was introduced in both the incident spot of the laser beam and at a certain distance (1–3 cm) away from it. The signal strongly depends on the nature of the testing liquid (an inhibitor – antibiotic, a preservative or water) added to the milk sample. At the same time, the dependence of the signal on the laser beam spot location was established, which underlines the importance of varying only the liquid properties while keeping all other experimental conditions constant.

An illustration of the opportunity to detect changes in milk composition when inhibitors are added is shown in Fig. 5. In the experiment performed, hydrogen peroxide was used as a testing liquid and the effect of adding 0.04 ml of 25% solution of kanamycin to 200 ml milk sample was monitored. The SPCE response when H₂O₂ was added to the pure milk sample was 753 μ V (Fig. 5a) while the response of the milk sample containing kanamycin was 162 μ V (Fig. 5b).

The moment when the testing liquid was dropped in the milk sample is shown by arrows in the figure. It is seen that the SPCE response was fast and the first droplet caused the strongest change of the measured signal. After that, some saturation effect reflecting in weak and delayed signal was observed due to the increased acidity of the milk sample causing a decrease in the response to the testing liquid.

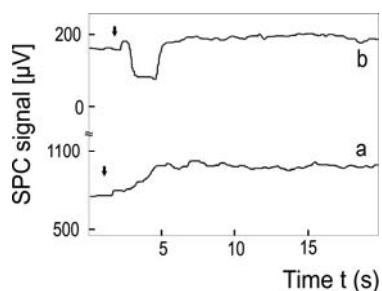


Fig. 5. Influence of the testing liquid (10 drops of 30% solution of H₂O₂) dropped in the incident spot of the laser beam on the signal amplitude for 20 s

a) signal of milk sample (200 ml) containing kanamycin; b) signal of pure milk

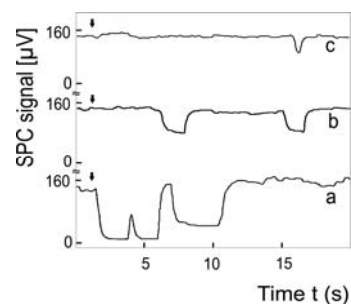


Fig. 6. Signal variation for 20s after dropping concentrated acetic acid in the incident spot of the laser beam

a) after the first drop; b) after the second drop; c) after the third drop

It has to be mentioned that, although the shape of the curves in Fig. 5 depended on the time during which the testing liquid was present in the milk, they always remained different, as did the amplitude of the SPCE signal: that of the pure milk was more than 4 times lower than the one of the sample containing the inhibitor (kanamycin). This allows a method for rapid instantaneous detection of inhibitors to be developed based only on qualitative comparison of signal amplitudes of tested and reference samples. Since the shapes of the curves in Fig. 5 show some time dependence, this suggests also an opportunity for studying the processes taking place in milk when a testing liquid is added to it.

The strong sensitivity of the SPCE signal to any minor change of the milk (concentration, contamination, pre-treatment, etc.) is illustrated in Fig. 6 for the case of adding droplets of acetic acid to the milk one by one.

The method described above could be used also for detection of milk samples produced by different animal species (assuming some differences in composition) since these samples generated SPCE signals with different amplitudes. For example, the comparison of milk from cow, sheep, and buffalo showed that the signal generated by cow milk was 15 % higher than the one generated by sheep milk and 50 % higher than the one detected for buffalo milk [10].

By now, the measurements cannot identify the type of admixtures, nor their quantity in the milk. To make possible quantitative estimations, a considerable additional development is necessary. Nevertheless, the results described show that a qualitative evaluation of milk could be performed in a fast way in real working environment and with minimal expenses for consumables, which could be very attractive for practical applications. A device based on the SPCE could be made portable, fast working and inexpensive.

5. Conclusions

The SPCE provides alternative opportunities to the already known and used methods for control of fluids. Due to the SPCE universality, the methods based on it could be used for characterization of any type of fluid, providing at the same time an opportunity to monitor even small quantities (a drop) with a suitable measurement setup.

The SPCE-based methods have the advantages of a high accuracy and a low cost, of giving instantaneous results and possibilities for rapid measurements in real time with no need to deposit a metal contact on the sample. The measurements do not require complex equipment, qualified personnel or laboratory conditions. The measurement technique is safe and does not pose any health risk or risk of fire, damage, etc. For most cases, the practical solutions do not include large components, which allows small-sized devices to be developed. The SPCE-based sensors can be used for on-line and/or in situ control as well.

The great opportunities provided by that analytical method are due to the combination of optical probing of the sample with detection of an electrical signal. Since the signal is very sensitive to any changes in the studied fluid, sensors could be built for various parameters of interest. The method can easily be implemented in commercial environments, which allows various practical applications to be developed.

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ПОВЪРХНОСТЕН ФОТО-ЗАРЯДЕН ЕФЕКТ: ПРИЛОЖЕНИЯ ЗА ФЛУИДИ

М. Кънева¹, J. Pérez-Díaz²

Ключови думи: датчици, качествен контрол, флуиди, повърхностен фото-заряден ефект

Научна област: взаимодействия поле-материя

РЕЗЮМЕ

Разгледани са методите за изследване на флуиди, основаващи се на повърхностния фото-заряден ефект (ПФЗЕ) за някои практически приложения като идентификация на течност, контрол на октановото число, измерване на нивото на течност, качествен контрол на мляко и вода и др. Описани са експерименталните схеми и резултати, както и основните предимства и възможности на датчици на основата на ПФЗЕ за контрол на място и/или в реално време. Изследването отговаря на приоритета при съвременните научни изследвания – подобряване на качеството на живот.

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