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Application of Harmonic Analysis and Principal Component Analysis for Discrimination of Adsorbates in Gas-Sensitive ITO/Nanostructured TiO_2 Heterojunction

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Fast Fourier transform (FFT) and principal component analysis (PCA) were successfully applied to realize a selective technique of adsorbate discrimination by spectral analysis of the waveforms of current through a gas-sensitive ITO/nanostructured TiO_2 heterojunction when a sinusoidal alternating voltage is applied to it. The novel technique shows good differentiation of sensor responses for adsorption of water, ammonia, ethanol and isopropanol molecules with sequential injection of analytes and fair differentiation of methanol, ethanol and isopropanol adsorption even for random injection of analytes. Comparison of the score plots and current epures obtained at various frequencies of the probing signal and various sets of harmonics used as source data for PCA allowed to find the optimal measurement conditions in terms of selectivity and reveal the basic factor, which predetermines substance-dependent variations in the harmonic spectrum of current waveforms. It is considered that substance-dependent changes in the shape of current waveforms are due to the processes of recharging of electron and/or hole traps caused by the interaction of adsorbed molecules with the surface of the structure and their diffusion deep into the porous TiO_2 layer.

Keywords: Harmonic analysis, Fast Fourier transform (FFT), Principal component analysis (PCA), Selectivity, Gas sensor, Heterojunction, Titanium dioxide, Electronic traps.

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1. INTRODUCTION

Quantitative and qualitative analysis of gaseous media is currently becoming more and more relevant due to the urgent need to solve various problems of the petrochemical industry, agriculture, building automation, environmental control, medical diagnostics, automotive applications, etc. At present, the high sensitivity, reliability and low cost of semiconductor metal-oxide gas sensors make them the most popular and widespread devices among a large family of modern gas detection equipment [1, 2]. However, insufficient selectivity remains a great drawback, which prevents further introduction of single semiconductor metal-oxide sensors into systems for highly selective discrimination of chemical analytes.

There are three modern approaches to enhance the selectivity of systems built on the basis of semiconductor metal-oxide gas sensors: 1) to combine several cells with different relative sensitivity to the same analyte into an array and to analyze and compare electrical signals from each cell of the array [3-8]; 2) to analyze multiple responses of different physical origin from the same sensor cell (resistance, capacitance, optical properties, etc.) [9] and 3) to analyze the dynamics of chemical reactions on the surface of a single sensor cell at various temperatures [10, 11].

Unfortunately, the first two approaches require an expensive and difficult procedure of fabrication, complex mathematical algorithms of signal processing [12] and, sometimes, complex matching circuits for different types of electrical signals. The third approach can be realized only in the presence of a heater in the sensor design, but frequent heating/cooling cycles lead to rapid degradation of the sensor characteristics due to long-term irreversible effects of oxide grain coalescence [13, 14] and makes it almost unsuitable in portable electronic devices with accumulator power supply due to high levels of energy consumption [15].

We propose a novel technique of using a single sensor cell with a non-linear current-voltage characteristic (CVC) for highly selective discrimination of chemical compounds based on the harmonic analysis of waveforms of electric current through a gas-sensitive sample with sinusoidal bias of the applied voltage in conditions of analyte adsorption.

The interaction of adsorbate molecules with the semiconductor surface leads to complete or partial alternation of the CVC of the sample, which has an effect on the redistribution of harmonic amplitudes in the spectrum of the transjunctional current attributed to a certain chemical. Therefore, the correlation between harmonic amplitudes can be used for discrimination of analytes by means of PCA visualization.

2. EXPERIMENTAL

Gas-sensitive samples were fabricated on glass substrates (25×20×3 mm) with a 10-20 Ω·cm film of ITO (In_2O_3 + SnO_2) on the upper surface. The most part of ITO was covered with a layer of nanostructured TiO_2 ~ 50 μm thick using a method of screen printing of pure TiO_2 powder from PlasmaChem GmbH with a mean grain size of 21±10 nm. Then, a series of round (1 mm in diameter) metal contacts were formed on the top of the TiO_2 layer and on the uncovered part of the ITO

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film by magnetron sputter deposition from a Ni target in an Ar atmosphere.

Harmonic spectra of current waveforms in the atmosphere of various analytes were obtained using a G3-53 LF generator in an experimental cell containing clamping contacts and a measuring resistor (2.2 kΩ). A PC soundcard and special software were used for data acquisition, fast Fourier transform (FFT) and spectra visualization (Fig. 1). The frequency of the sinusoidal probing signal, applied to the experimental sample, was selected in the range of 2-200 Hz. The attenuator was used to keep the voltage across the measuring resistor within the dynamic range of the soundcard. Vapors of methyl (CH_3OH), ethyl (C_2H_5OH), isopropyl (C_3H_7OH) alcohols and water (H_2O) were pumped into the cell by a membrane air compressor connected to a retort filled with the respective analyte, ammonia (NH_3) was injected into the cell in a gaseous form using the same compressor.

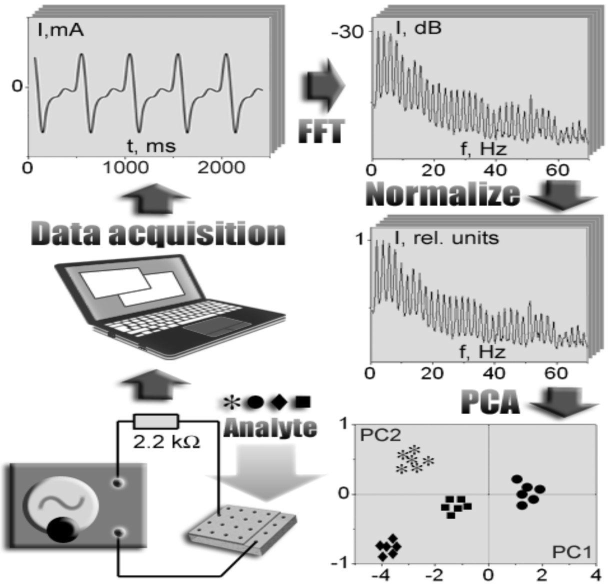

Fig. 1 – Scheme of the experimental procedure

3. RESULTS AND DISCUSSION

Analysis of the behavior of the transjunctional current under the influence of adsorption from vapors of water, ethanol, isopropanol and ammonia shows that not only the entire growth (for water and ammonia) or decrease (for alcohols) in the current are typical of the ITO/TiO_2 sensor reaction to these analytes, but also a significant redistribution of harmonic amplitudes takes place at certain frequencies of the applied probing signal. Fig. 2 shows the typical harmonic spectra of current waveforms for the experimental sample at the input and output of saturated vapor of isopropyl alcohol.

In our previous work [16], it was shown that this redistribution is attributed to a certain chemical and could be obtained as a result of multiple experimental attempts with fairly good repeatability. Moreover, the magnitudes of the harmonic amplitudes are convenient input data for principal component analysis (PCA) that can be used for further visualization of sensor responses and discrimination of chemical analytes.

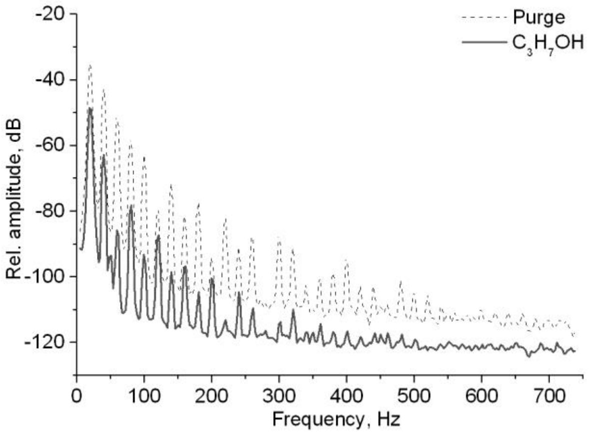

Fig. 2 – Typical harmonic spectra of the transjunctional current waveforms of the ITO/TiO_2 experimental sample in the laboratory atmosphere and under the influence of isopropanol vapor, measured at 20 Hz probing signal

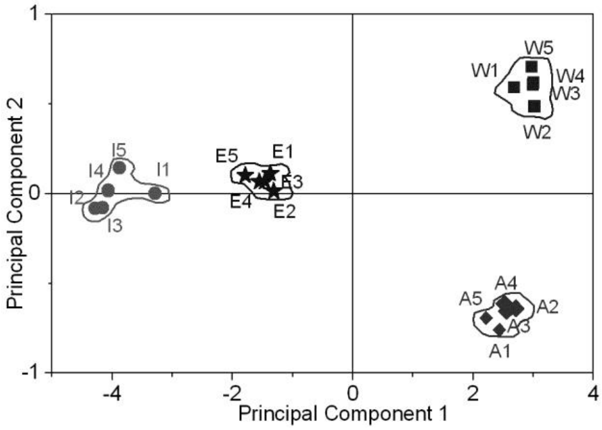

Fig. 3 – Score plots of the amplitudes of the harmonic spectra of the transjunctional current waveforms upon adsorption of water (W), ethanol (E), isopropanol (I) and ammonia (A) in the case of 5-fold sequential injection of analytes, measured at 20 Hz probing signal

The results of applying PCA to harmonic amplitudes with numbers from 2nd to 8th, measured for water, ethanol, isopropanol and ammonia, are illustrated in Fig. 3. Normalization by the amplitude of the first harmonic was fulfilled in this and all other cases for the purpose of neglecting all concentration-dependent and focusing on substance-dependent changes in the harmonic spectra.

As one can see, the scores for each analyte form dense clusters that allows to discriminate responses to each chemical with confidence. Even ethanol and isopropanol, which belong to the same group of organic compounds, are discriminated well.

However, it is important to note that the results presented above were obtained with sequential injection of analytes in the following sequence: 5 measurements for ethanol, 5 measurements for isopropanol, then 5 measurements for water and 5 measurements for ammonia. Alternation of the analytes in a random order significantly worsens selectivity of the technique (Fig. 4). In this case, not only the score clusters become less dense and separation worsens, but also the group of scores for ammonia overlaps ethanol and water clusters.

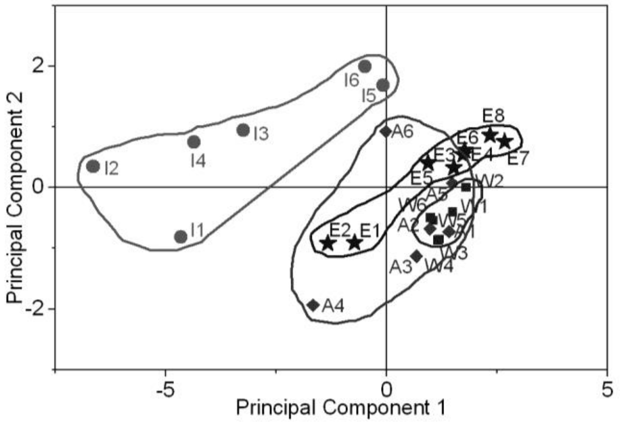

Fig. 4 – Score plots of the amplitudes of the harmonic spectra of the transjunctional current waveforms upon adsorption of water (W), ethanol (E), isopropanol (I) and ammonia (A) in the case of random injection of analytes, measured at 20 Hz probing signal

The deterioration in selectivity can probably be explained by irreversible and/or long-term processes of recharging trap levels in bulk TiO_2 or at the ITO/TiO_2 interface, caused by adsorption of NH_3 and H_2O molecules on the surface of the experimental sample and their migration deep into the porous oxide layer [17, 18]. Since we did not carry out forced desorption by heating or UV irradiation of the heterojunction, the sample did not restore its electrophysical characteristics before each next injection of the analyte, and its reaction to the gaseous medium was rather cumulative.

Satisfactory discrimination in the case of random injection of analytes was achieved only for those chemicals, which belong to the same group of organic compounds: methanol, ethanol and isopropanol. Their score plots form relatively dense and non-overlapping clusters (Fig. 5) as a result of the absence of ammonia and water among the injected analytes at the 2nd stage of the research.

The first important question in terms of selectivity of the proposed technique is the question of the optimal frequency of the probing signal. This parameter was estimated by comparing the score plots of methyl, ethyl and isopropyl alcohols obtained for various frequencies of the probing signal: 2, 10, 40 and 200 Hz, other things being equal (Fig. 6). Amplitudes of 7 harmonics (from 6th to 12th) as the most informative were used as input data for PCA. The criterion for selecting the harmonic numbers will be discussed below.

The main conclusion is that a decrease in the probing signal frequency leads to compaction of the score clusters for each analyte and improvement of recognition.

From a physical point of view, the frequency of the sinusoidal probing signal must be chosen on the basis of consideration that all possible factors, affected by adsorption and influencing the sensor CVC, should be involved in the process of changing current waveforms. Given that, the frequency must be low enough to ensure recharge of trap levels in the TiO_2 layer.

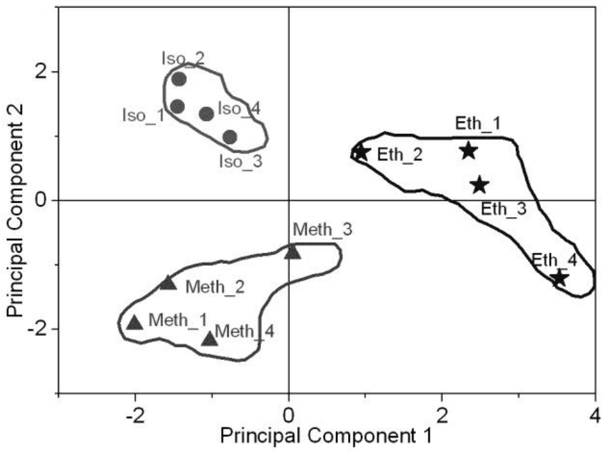

Fig. 5 – Score plots of the amplitudes of the harmonic spectra of the transjunctional current waveforms upon adsorption of methanol (Meth), ethanol (Eth) and isopropanol (Iso) in the case of random injection of analytes, measured at 2 Hz probing signal and built by 6th…12th harmonics

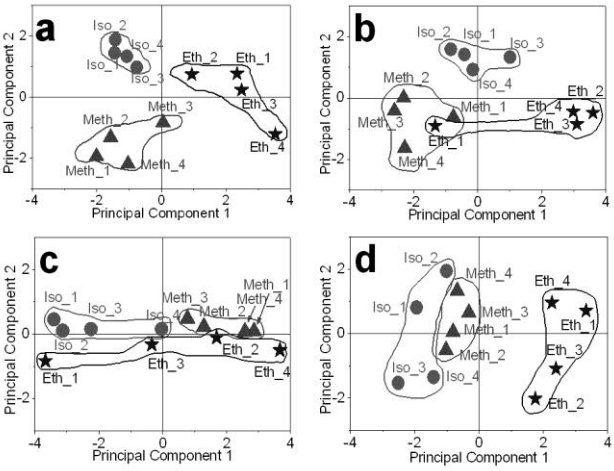

Fig. 6 – Variation in the score plots of the amplitudes of the harmonic spectra of the transjunctional current waveforms upon adsorption of methanol (Meth), ethanol (Eth) and isopropanol (Iso) in the case of random injection of analytes, measured at a) 2, b) 10, c) 40 and d) 200 Hz probing signal

In our case, the optimal conditions for discriminating chemical analytes are those, which allow to focus only on substance-dependent and neglect concentration-dependent factors. In particular, these conditions can be provided by normalizing the harmonic amplitudes to the amplitude of the first harmonic; however, the correct choice of the set of harmonic components is also an important task in terms of repeatability and selectivity. Each of the components can contain more or less information about the change in the CVC. Also, informative contribution and stability of each of them can vary depending on the probing signal frequency.

The informative role of harmonic components can be estimated by loading plots; however, it is difficult to take into account stability and repeatability of the redistribution of harmonic amplitudes in this case, thus comparison of score plots obtained for different sets of harmonics at a constant frequency of the probing signal was used for this purpose (Fig. 7).

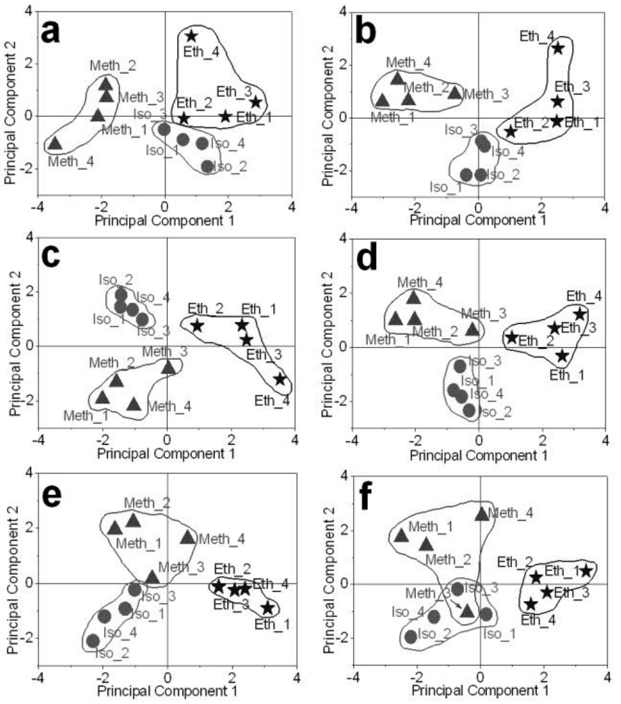

Fig. 7 – Variation in the score plots of the amplitudes of the harmonic spectra of the transjunctional current waveforms upon adsorption of methanol (Meth), ethanol (Eth) and isopropanol (Iso) in the case of random injection of analytes, measured at 2 Hz probing signal and built by a) 3th…9th, b) 5th…11th, c) 6th…12th, d) 7th…13th, e) 9th…15th, f) 11th…17th harmonics

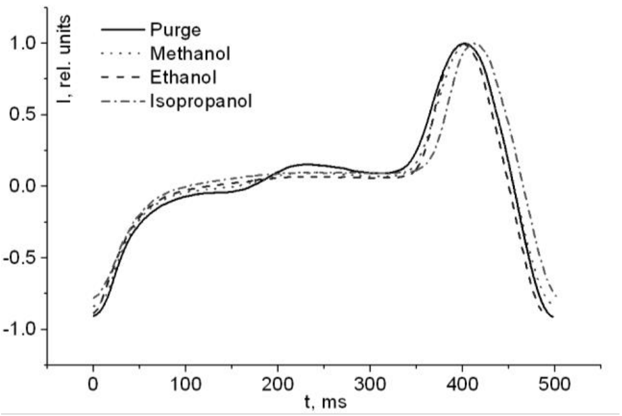

Fig. 8 – Normalized epures of the transjunctional current through the ITO/TiO$_2$ sample in the laboratory atmosphere and upon adsorption of methanol, ethanol and isopropanol, measured at 2 Hz probing signal

Obviously, the best separation and formation of the densest score clusters were achieved for current harmonics with numbers from 5th to 13th approximately. Less compact clusters and even overlapping (Fig. 7f) are typical for sets composed of lower and higher components. Similar rules were also observed for 200 Hz probing signal.

A detailed analysis of the normalized epures of the transjunctional current reveals a distinct non-monotonicity of the first two-thirds of the waveforms measured at 2 Hz, which corresponds to the reverse branch of the CVC (Fig. 8). Adsorption of alcohol molecules on the surface of a semiconductor structure causes its partial or complete smoothing.

Increasing the frequency of the probing signal also leads to a smoothing of the mentioned non-monotonicity for all tested alcohols and for the sample in the laboratory atmosphere, making the difference between the current waveforms for various analytes less pronounced (Fig. 9). Therefore, this circumstance affects the similarity of the current spectra after FFT and, as a consequence, a decrease in the cluster density and causes an overlap of the score clusters after PCA. Thus, lower frequencies of the probing signal are more optimal in terms of selectivity.

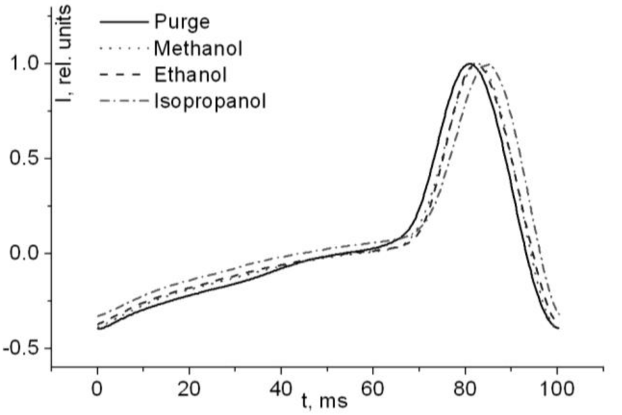

Fig. 9 – Normalized epures of the transjunctional current through the ITO/TiO$_2$ sample in the laboratory atmosphere and upon adsorption of methanol, ethanol and isopropanol, measured at 10 Hz probing signal

4. CONCLUSIONS

The proposed technique of spectral analysis and PCA visualization of sorption-induced changes in the current through a gas-sensitive structure with a nonlinear CVC in some cases could be a promising alternative to the traditional “E-nose” multi-sensor concept, as it suggests highly selective discrimination of chemical analytes using a single gas-sensitive cell instead of array of sensors. This could considerably simplify the fabrication procedure and calibration routines and reduce cost of gas-sensitive equipment built on the basis of this technique.

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Застосування гармонічного аналізу та методу головних компонент до розрізнення адсорбатів за допомогою газочутливої гетероструктури ITO/наноструктурований TiO_2

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Швидке перетворення Фур'є та метод головних компонент були успішно застосовані для реалізації селективного методу розрізнення адсорбатів за допомогою спектрального аналізу імпульсів струму крізь газочутливу гетероструктуру ITO/наноструктурований TiO_2 при прикладанні до неї синусоїдальної змінної напруги. Новий метод продемонстрував добре розділення сенсорних відгуків для адсорбції молекул води, аміаку, етанолу та ізопропанолу при послідовному уведенні аналітів, а також задовільне розділення у випадку введення метанолу, етанолу та ізопропанолу навіть у довільному порядку. Порівняння графіків рахунків та епюр імпульсів струму, отриманих за різних частот тестового сигналу та побудованих за різними наборами гармонічних складових, що використовувалися як вхідні дані для методу головних компонент, дозволило знайти оптимальні умови реалізації методики з точки зору селективності та виявило базовий фактор, що зумовлює речовинно-залежні зміни у гармонічному спектрі імпульсів струму. Ми вважаємо, що речовинно-залежні зміни форми імпульсів струму є наслідком процесів перезарядження електронних та/або діркових пасток, спричинених взаємодією молекул адсорбату із поверхнею структури та їх дифузією углиб поруватого шару TiO_2.

Ключові слова: Гармонічний аналіз, Швидке перетворення Фур'є, Метод головних компонент, Селективність, Газовий сенсор, Гетероструктура, Діоксид титану, Електронні пастки.