

Processing of signals obtained under conditions of modulation of the operating temperature of a conductometric sensor based on thin films PdO

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The results of resistive tests of thin (30 nm) PdO sensor films in air with different ozone concentrations are presented. The mode of harmonic temperature modulation of sensors is used in the work. The specimens show high sensitivity to ozone concentrations in *ppb*-range. Consideration of electrical conductivity σ , mS instead of resistivity R , k Ω revealed good reproducibility of absolute increase signals $\Delta\sigma$. This made it possible to extract the contribution of the analyte to the raw conductometric response by simple subtraction, and to build a multivariate calibration based on the features of such an extracted response and its Fourier image.

Keywords: palladium oxide, ozone, chemical sensor, temperature modulation, extracted signal, Fourier transform, multivariate calibration.

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The problem of detecting microconcentrations of ozone, the threshold limit value (TLV) of which in the air is ~ 0.1 mg/m³ or ~ 50 *ppb*, is relevant in view of safety of facility, where this gas is used: water ozonation stations, sterilization of medical premises, etc. The first experiments using palladium oxide as a sensor base gave encouraging results [1], which require analysis and processing in order to build a selective calibration of the sensor to create on its basis the gas analytical system for ozone detection. For the simple visual difference between signals from O₃ and responses from gas-distractors should be expressed by mathematical means, as a difference from a similar set of certain variates of multivariate calibration [2]. This work is devoted to the analysis and processing of signals from a PdO-based sensor precisely for the purpose of constructing such a calibration.

Thin polycrystalline films of tetragonal structure PdO were obtained by thermal sputtering of metallic Pd onto polycore (Al₂O₃) structures and oxidation in air at the optimal temperature 550°C [3]. The material had a *p*-type of conductivity with a band gap $E_g = 2.3$ eV, determined from presented in Tauc coordinates light absorption data in the range 300–900 nm. The optimal in terms of gas sensitivity thickness of the PdO layer was $d \approx 30$ nm [ibid].

Ozone concentrations in the air (RH = 35–38%, 20°C) $C = 25, 55, 90$ and 250 *ppb* were created by the GS-024-25 generator (JSC „OPTEK“), and nitrogen dioxide $C = 1–10$ *ppm* — by diluting the test gas mixture (200 *ppm* NO₂) with artificial air. The temperature of PdO layer during the modulation process varied from 50 to 350°C according to a sinusoidal law with a period

of 300 seconds when measuring resistance every 5 s (Figure 1, a).

For a proportional relationship between the current response value and the increase in the number of free carriers ΔN , the recorded resistance signals $R(t_i)$, k Ω were converted into electrical conductivity as $\sigma(t_i) = 1/R(t_i)$, mS. Its modulation change (variation) in the air was calculated using the formula

$$\Delta\sigma(t_i) = \frac{1}{R(t_i)} - \frac{1}{R(0)}, \quad i = 1–60,$$

and it served as a measure of the non-analyte related change in the number of free carriers ΔN_{air} . The results from 4 series of measurements spaced apart in time indicated good reproducibility of a rather complex modulation pattern $\Delta\sigma$, mS, due to the entire composition of the air. Thus, there was a maximum at $t_{\text{max}} = 84 \pm 2^\circ\text{C}$ and a minimum at $t_{\text{min}} = 320 \pm 5^\circ\text{C}$. It is characteristic that the signals do not formally have a specific nature — donor or acceptor, and change sign at the inversion temperature $t_{\text{inv}} = 173 \pm 0^\circ\text{C}$.

From the point of view of detecting the analyte Y, only the sorption change in the number of carriers $\Delta N_Y = \Delta N_{\text{total}} - \Delta N_{\text{air}}$ is of interest, which is an analogue of the chemisorption value $N_Y^{\text{surf}}(n_Y^{\text{gas}}, t^\circ\text{C})$, and this, in turn, is analogue of the concentration Y in the gas phase n_Y^{gas} . However, the variation in electrical conductivity does take into account the already existing sorption increase in this number at the beginning of temperature modulation $N_Y^{\text{surf}}(n_Y^{\text{gas}}, t^\circ\text{C} = t_{\text{min}})$. However, good stability and noise-free resistance signals from both pure air and added analytes (O₃, NO₂) allowed a) to operate with signals

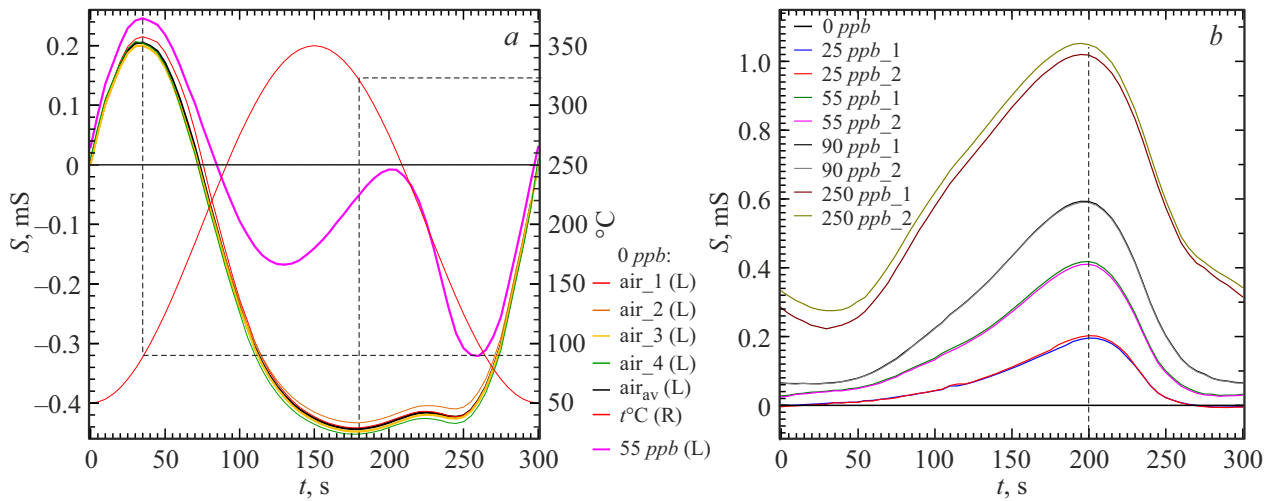


Figure 1. Signals of increase in electrical conductivity $\Delta\sigma, \text{mS}$ of sensor: *a*) initial from the base value at 50°C in air (RH 35–38%): 0 ppb air₁, air₂, air₃, air₄, air_{av}, $t^\circ\text{C}$, 55 ppb ozone; *b*) net signals of increase in conductivity at ozone concentrations $C = 0, 25, 55, 90$ and 250 ppb.

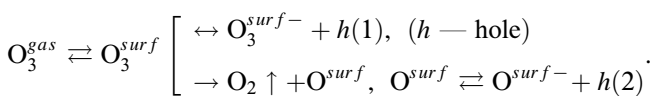
Estimation of the calibration factor Q depending on $A(0) = Q \cdot C$

Model is: $A(0) = Q^* \cdot C$ (Calibration_O ₃)						
Dep. Var. : $A(0)$ Level of confidence: 95.0% (alpha = 0.050) adj-R ² = 0.98367644						
	Estimate	Standard error	<i>t</i> -value df = 8	<i>p</i> -value	Lo. Conf Limit	Up. Conf Limit
$Q, \text{c.u.}$	0.017749	0.000531	33.44922	0.000000	0.016526	0.018973

of absolute rather than relative [3] change, *b*) isolate, extract the useful signal of analyte chemisorption by simple subtraction. Namely, from the initial (raw) or gross signal of electrical conductivity $\sigma(t_i) = 1/R(t_i)$ its response in clean air averaged over $n = 4$ experiments at different times was subtracted

$$\bar{\sigma}_{\text{air}}(t_i) = \frac{1}{4} \left(\frac{1}{R_{\text{air}_1}(t_i)} + \frac{1}{R_{\text{air}_2}(t_i)} + \frac{1}{R_{\text{air}_3}(t_i)} + \frac{1}{R_{\text{air}_4}(t_i)} \right).$$

This periodically updated reference signal had a pronounced asymmetry of the heating and cooling fronts (Figure 1, *a*). After its subtraction, the net signals $\sigma_C^{\text{netto}}(t_i)$, well reproducible from experiment to experiment, and due to Y itself remain. They were acceptor in nature (Figure 1, *b*), and all their levels increased with concentration C_Y increasing. This fully corresponded to the sensitivity according to the reversible (1) and irreversible (2) schemes:



The asymmetry of the fronts of the original signals (curve „55 ppb“, Figure 1, *a*) decreased during extraction. However, significantly higher concentrations of another acceptor gas $\sim 10 \text{ppm}$ NO₂ in artificial air gave absolutely symmetrical initial signals [4]. Therefore, there is reason to

assume that it is associated with the presence in the air of a large number of polar molecules H₂O (1.84D), competing for adsorption centers with less polar ones O₃ (0.53D). It is worth paying attention to the similarity of the shape of all net signals, for which the maximum S_{max} occurred at the same temperature $t^* = 270^\circ\text{C}$ at the stage of its fall.

The net signals were subjected to Fourier transform according to the formulas:

$$A_C(f) = abs \left((2\pi \cdot 300)^{-0.5} \int_0^{300} S_C^{(4)}(t) \exp \left(-\frac{2\pi i f t}{300} \right) dt \right),$$

$$\varphi_C(f) = \arg \left(\int_0^{300} S_C^{(4)}(t) \exp \left(-\frac{2\pi i f t}{300} \right) dt \right),$$

where $S_C^{(4)}(t)$ — 4th order spline by levels $\sigma_C^{\text{netto}}(t_i)$. The obtained dependences (Figure 2) demonstrated at low frequencies $f < 1.6f_0$, $f_0 = 1/300 \text{ s}^{-1}$, almost identical phases $\varphi_C(f)$ and ranked by concentration C decreasing curves $A_C(f)$ for amplitudes.

The quasi-identity of the phases confirms the similarity of the net response curves with the exception of $C = 250 \text{ ppb}$, the phase-frequency response of which, as for the net response, stands out slightly from other dependences $\varphi(f)$ (Figure 2, *b*).

As for the AFR, then up to frequencies $\sim f_0$ there is a visible similarity of the descending curves $A_C(f)$ (Figure 2, *a*). Therefore, to calibrate the sensor it is better to take the largest one, i.e. zero amplitude $A(0) = F_1(C)$. The proportional model $F_1(C) = Q \cdot C$ selection gives an accurate estimate of both the multiplier Q and the model itself (coefficient of determination $\text{adj-R}^2 = 0.983$) (Table, Figure 3, *a*).

Such proportionality is absent if we use the parameters of gross signals [3], which indicates the productivity of subtraction of the background signal from the carrier medium, not only in the case of detecting ozone, but, probably, any analyte.

As a second independent option for calibration, the value of the signal maximum of the net responses

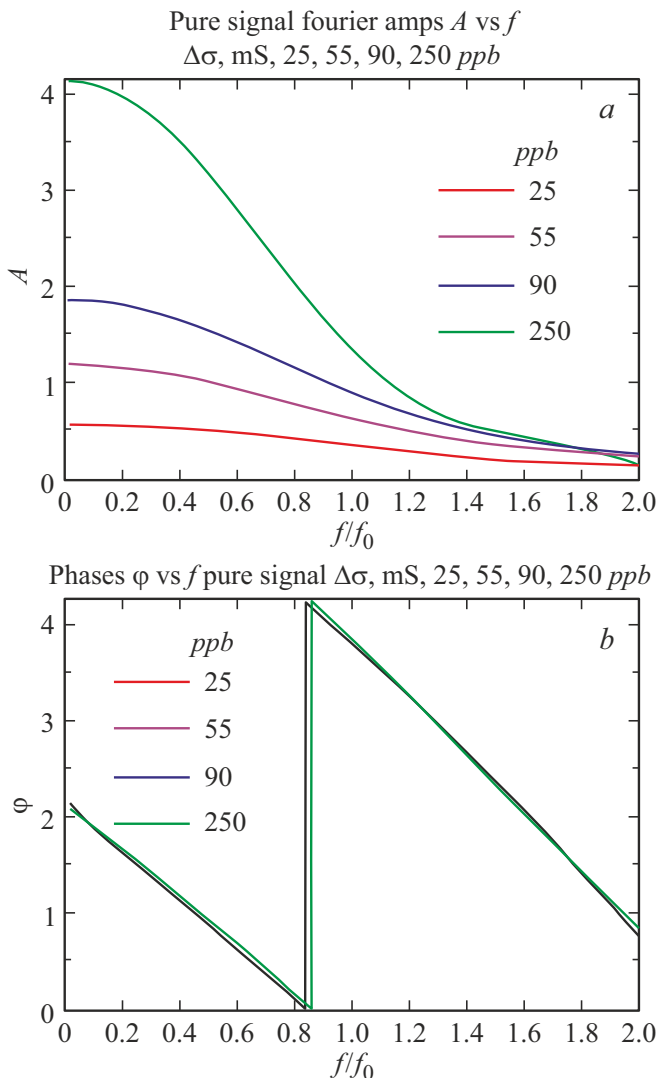


Figure 2. Amplitude-frequency response (AFR) *a*) and phase-frequency response (PFR) *b*) Fourier characteristics of images from net responses for frequencies $f = 0 - 2f_0$, $f_0 = 1/300 \text{ s}^{-1}$ at different ozone concentrations: 25, 55, 90, 250 ppb. (Almost identical phases $\varphi_C(f)$ in the Fourier images of net responses at frequencies $f < 2f_0$).

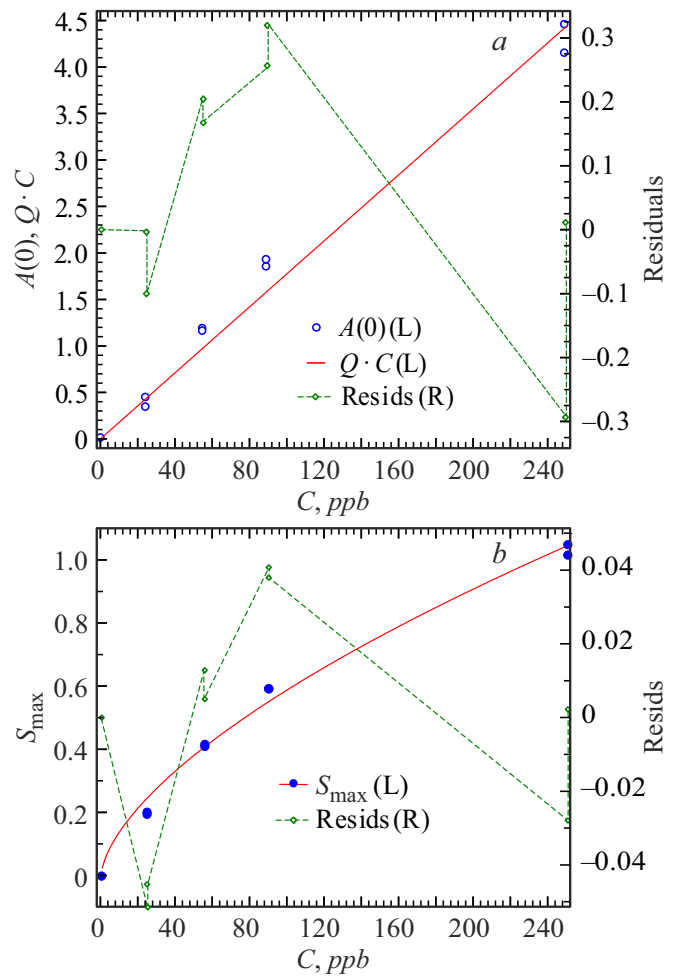


Figure 3. Multivariate calibration of the sensor *a*) by the zero amplitude of the Fourier integral *a*) $A(0)$ and *b*) — by the maximum net response value S_{\max} .

$F_2(C) = S_{\max}(C)$ (Figure 1, *b*) may be taken. Interpolation of its power function $F_2(C) = M \cdot C^n$ (proportional has a low $\text{adj-R}^2 = 0.84 < P = 0.95$) gives $\text{adj-R}^2 = 0.99$, $n = 0.626 \pm 0.070$ (Figure 3, *b*), however, with low precision of the multiplier $M = 0.033 \pm 0.006$.

In principle, these two quantities are sufficient for formal multivariate ($D = 2$) calibration of the sensor according to the calibration type [2] in order to ensure its selectivity for ozone among other few acceptor-distractors (NO_x , Cl_2 , Cl_2O , ClO_2).

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Conflict of interest

The authors have no conflict of interest.

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