

## Using a Piezosensor-Based “Electronic Nose” for Establishing the Adulteration of Gasoline with Different Octane Numbers

T. A. Kuchmenko<sup>a,\*</sup>, R. P. Lisitskaya<sup>b</sup>, and V. S. Shabel'skii<sup>b</sup>

<sup>a</sup> Voronezh State University of Engineering Technology, Voronezh, 394000 Russia

<sup>b</sup> Military Air Academy, Voronezh, 394064 Russia

\*e-mail: tak1907@mail.ru

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**Abstract**—We substantiate an approach to the creation of a device for establishing gross adulteration of gasoline by replacing their part with fuel with a lower octane number and demonstrate the application of mass-sensitive sensor electrodes using the specific features of the adsorption of volatile compounds from the headspace of gasoline with different octane numbers (AI-92, AI-95) by the sensor modifiers. The results helped select three coatings most sensitive and selective to traces, differently adsorbing compounds of the highly volatile gasoline fraction. Simple recorded and calculated signals of the “electronic nose”  $S_{\Sigma}$ ,  $S_{\tau}$ ,  $A(i/j)$ ,  $A_{\Sigma}(\tau_1/\tau_2)$ , giving information on the composition of a gasoline sample and assessing the change in composition on adding fuel of a different type or brand, are proposed. The algorithm for calculating and making a decision is simple and can be programmed into the microcircuit of a mobile device. Introducing an “electronic nose” gas analyzer based on piezoelectric balances into the fuel quality control system is helpful to reveal the facts of adulteration of high-octane gasoline by adding gasoline with a lower octane number and to estimate the amount of the additive. A method is developed for in situ analysis performed by experts or untrained users; it readily gives an assessment of adulteration with an additive concentration of 6 to 50 vol % with an error of no more than 12%.

**Keywords:** analysis, fuel, gasoline, adulteration, test system, chemical sensors, “electronic nose”

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Modern motor gasoline is a mixture of volatile hydrocarbons obtained, depending on the brand of gasoline, by direct distillation, catalytic cracking, hydrocracking, catalytic reforming, alkylation, and other methods of oil refining [1, 2]. All gasoline components consist of a mixture of individual hydrocarbons of various classes of  $C_4$ – $C_{12}$ . For example, approximately 250 volatile substances (linear and branched alkanes, alkenes, mono- and bicyclic naphthenes, aromatic hydrocarbons) were identified in catalytic cracking gasoline by gas chromatography using high-performance capillary columns [3].

The chemical composition of cracked gasoline determines its properties like chemical stability and octane number (ON). The stability of gasolines depends on the presence of unsaturated hydrocarbons in them. High ONs of catalytic gasolines are due to a significant amount of isoalkanes in light fractions and aromatic hydrocarbons in higher fractions; they characterize the detonation resistance of the fuel [4]. According to *GOST* [5], depending on the ON value, gasoline grades of AI-80, AI-92, AI-95, and AI-98 are distinguished that meet the technical requirements of the European Standard *EN 228:2008* for AI-92-K5-

Euro, AI-95-K5-Euro, and AI-98-K5-Euro brand (*STB 1656-2016*).

The production of motor fuels in Russia is regulated by *GOSTs* [5–8], primarily intended to control the quality of products and optimize technological processes at oil refineries. Large refineries value their reputation, and factory specifications are often even stricter than the requirements of *GOSTs*. However, hydrocarbon fuel is sold not only by large refineries but also by enterprises that are not engaged in oil refining but produce gasoline from purchased oil products. In addition, the composition of high-quality fuel may change during transportation or at a gas station, and the consumer receives a counterfeit product. According to various expert estimates, counterfeit fuel may account for up to 30% in large cities and 70% in the periphery [9].

The simplest and most common way to adulterate motor gasoline is to mix high-ON gasoline with low-octane products or even a surrogate [10]. For example, instead of AI-95 gasoline, gasoline with a ON of 92 or less or their mixtures can be sold.

Adulteration by mixing high-octane gasoline with low-octane gasoline is found by conventional tests for

determining the octane number with the involvement of qualified specialists and specific equipment such as CFR and UIT [11] or by gas chromatography [12–14]. The State Standard of the Republic of Belarus has developed and certified a method for the gas chromatographic determination of the parameters of motor gasoline [12, 15]. A procedure is known for establishing the adulteration of gasoline using micro-column HPLC [16].

Infrared spectroscopy is commonly used to determine the structural and fractional composition of gasoline and study the spectral properties of individual hydrocarbons [14, 17, 18]. Several ASTM methods are known that use IR spectrometry, for example, to determine the concentration of methyl-*tert*-butyl ether, its analogs, and aromatic compounds in gasoline [19, 20].

The identification of the brand and the quality control of gasoline are urgent problems, especially for consumers at the points of sale. An analytical review of the existing methods for identifying petroleum products has shown their undoubted advantages, but such an analysis is laborious, involves complex, expensive equipment, and is unsuitable for in situ analysis.

The development of portable devices and rapid, objective procedures is promising from the viewpoint of organizing the quality control of automobile fuel. These procedures make it possible to judge about the gross adulteration of gasoline by individual results, a combination of results, or criteria calculated on their basis. These devices include chemical sensors.

Individual chemical sensors and their arrays, after preliminary training with a set of test compounds (state markers), are widely used to assess the quality of fuel [21, 22] and for environmental monitoring [23–25].

The operation of a multisensor gas analyzer, “electronic nose,” is based on the principle of piezoelectric quartz microweighing, where the analytical signal is converted into a physical one, that is, a change in the oscillation frequency of the piezoresonator ( $\Delta F$ , Hz) by the interaction of volatile components of the analyte with the absorption coating of the AT-cut quartz electrodes.

In recent years, there has been a trend in routine analysis to compare the general profiles of the sample components rather than the sample composition; that is, a set of compounds, the so-called “image” of a sample, reflecting the concentration and ratio of individual classes of compounds, is detected. An electronic nose gas analyzer based on piezo balances with different selectivity and sensitivity of the sensor array to certain classes of hydrocarbons was proposed for an objective qualitative and quantitative assessment of the highly volatile gasoline fraction.

The purpose of this work was to develop a low-cost method for establishing the fact of gasoline adulteration by mixing fuels with different ONs, based on the

qualitative and quantitative criteria of an electronic nose gas analyzer with a set of piezoresonance sensors. During the study, the following tasks were solved:

- Selection of sensitive coatings for electrodes of piezoelectric quartz resonators (PQR), adsorbing differently the compounds of the highly volatile fraction of gasoline;
- Substantiation of parameters for evaluating the efficiency of the adsorption of vapors of highly volatile components (HVCs) of gasoline;
- Selection of qualitative and quantitative criteria for the response of the sensor array to samples, carriers of information on the composition of gasoline for objective assessment and digitization of the HVC composition of gasoline to ensure the reproducibility of the quality indicators and establish the authenticity of the fuel.

## EXPERIMENTAL

The electronic nose detecting device, based on MAG-8 piezoelectric balances (SNT, Russia), consists of an array of chemical sensors based on six PQRs of bulk acoustic waves with a natural vibration frequency of  $F_0 = 10$  MHz. Specific adsorbents are applied on the electrodes of the sensors: trioctylphosphine oxide (TOPO, synthesized at the Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences, Novosibirsk), dicyclohexane-18-crown-6 (18K6), di- $\beta,\beta'$ -cyanoethoxy diethyl ether (DCEDEE), and chromatographic phases polyethylene glycol adipate (PEGA), polyoxyethylene(21)sorbitan monooleate, Tween-40 (Tween), octylpolyethoxyphenol, and Triton X-100 (TX-100) (Alfa Aesar, United States), weighing 10–13  $\mu\text{g}$ . The selection of modifiers for PQR electrodes is due to the selective affinity of nonpolar and low-polar compounds that make up the highly volatile fraction of gasoline to some standard chromatographic phases and specific adsorbents of different polarity.

The modifiers of the sensor electrodes selected at the preliminary stages are characterized by high film stability without renewal: it is possible to carry out 150–200 adsorption/desorption cycles. The weight loss of the film after 150 adsorption cycles does not exceed 0.5%. The reproducibility of the measurement results was evaluated for the most informative and active modifier films. For example, for 18K6, TOPO, and Tween films, in analyzing the headspace of the gasoline samples, the relative mean standard deviation (RSD) does not exceed 1.5–2.0%, and the relative error is 2–4%. Under the recommended conditions of vapor injection into a closed detection cell, the measurement error on the selected array of sensors does not exceed 5%.

We selected motor gasoline grades AI-92 and AI-95 from different manufacturers as test samples. As standards for simulating adulterated gasoline samples,

mixtures of AI-92 with AI-95 gasoline in volumetric ratios of 1 : 4, 1 : 3, 1 : 1, and 3 : 1 were studied. The test gasoline samples were placed in a hermetically sealed sampler and kept for vapor saturation for 20 min. A 2-cm<sup>3</sup> portion of the headspace was taken and injected into a 60 cm<sup>3</sup> electronic nose detection cell with an array of sensors installed in it. In the MAGSoft software, the responses of all sensors ( $\Delta F$ , Hz) were simultaneously recorded for 60 s with 1-s discreteness as chronofrequency diagrams; the measurement results were statistically processed.

The following characteristics of the array of sensors and their derivatives were selected as the main criteria for assessing the difference in volatile compounds of the test gasoline samples and “reference” samples of fake gasoline:

- Maximum analytical signal of the sensor ( $\Delta F_i^{\max}$ , Hz), characterizing the efficiency of vapor adsorption on the adsorbent thin films and the sensitivity of the adsorption coating of the sensor and using in the calculation of these parameters; sector charts, that is, “visual imprints” of the maximum responses  $\Delta F_i^{\max}$  of the sensors in the headspace of the samples for the selected measurement time, which made it possible to establish the degree of identity of the fuel composition;

- The parameter of the adsorption efficiency of gasoline vapors  $A(i/j)$ , that is, the ratio of the maximum responses of individual sensors  $A(i/j) = \frac{\Delta F_i^{\max}}{\Delta F_j^{\max}}$

(where  $i$  and  $j$  are different adsorbents, modifiers of the electrodes), estimating the concentration ratio of different classes of compounds in the sample and measuring the affinity of two adsorbents to a particular substance or a mixture [26];

- Kinetic visual imprints, that is, sector charts, the dependence of the signals of the selected or all sensors on time,  $\Delta F_i = f(\tau, s)$ ;

- The area of the visual imprint was a quantitative criterion that was determined by the total mass of HVCs adsorbed by the adsorbent thin films within the entire measurement time ( $S_\Sigma$ , Hz s) or for a certain period ( $S_\tau$ , Hz s) and was proportional to their concentration in the headspace of the sample;

- The kinetic criterion  $A_S(\tau_1/\tau_2)$  was the ratio of the area under the chronofrequency diagram at certain moments of the adsorption of the gasoline HVCs,  $A_S(\tau_1/\tau_2) = S(\tau_1)/S(\tau_2)$ , which characterized the qualitative and quantitative constancy of the composition of mixtures and, in fact, the constancy of the rates of vapor accumulation by the adsorbent at different times of measurement.

To assess the sensitivity of sensors to gasoline vapors, we calculated the relative mass sensitivity of

microweighing ( $S_m$ , Hz m<sup>3</sup>/mg) as the ratio of the analytical signal of gasoline vapor adsorption ( $\Delta F_i^{\max}$ , Hz) to its concentration in the near-sensor space ( $c$ , mg/m<sup>3</sup>). The concentration of gasoline vapors in the detection cell at 25°C was calculated using the given Clapeyron–Mendeleev equation [27],

$$c = 1.22 \times 10^4 \frac{p_i M V_1}{P T V_2}, \quad (1)$$

where  $M$  was the molar weight of organic substances, g/mol;  $p_i$  was the saturated vapor pressure of gasoline, kPa;  $P$  atmospheric pressure, kPa;  $T$  was absolute temperature, K;  $V_1$  was the volume of the injected sample containing gasoline vapors, cm<sup>3</sup>; and  $V_2$  was the volume of the detection cell, cm<sup>3</sup>.

The saturated vapor pressure of gasoline ( $p_i$ , kPa) was calculated using the Antoine equation,

$$\log p_i = A - \frac{B}{T + C}, \quad (2)$$

where  $T$  was temperature, °C;  $A$ ,  $B$ , and  $C$  were constants [28].

The static reliability of all applied parameters and analytical signals was assessed according to the Student and Fisher tests ( $n = 4-5$ ,  $P = 0.95$ ).

To smooth out random noise and the effect of external conditions on the sensor signals during the test assessment of the quality of gasoline and the quantitative determination of the volume fraction of possible additions of gasoline of a different brand, we transformed the initial data, that is, performed the relative normalization of the integral analytical signal of the sensor array, the area of visual imprints. We brought the sample of piezoelectric quartz microweighing data ( $S_\Sigma$  values) of vapors of nine different samples of AI-92 gasoline and nine samples of AI-95 gasoline from three manufacturers, selected at filling stations from different batches within 1 month, and the average level of 36 variations of the initial fuel and gasoline mixtures in different volumetric ratios to a form convenient for comparing the analysis results. Linear data transformation in the range of [0 ... 1] was performed using the “minimax” method,

$$\tilde{S} = \frac{S_\Sigma - S_{\min}}{S_{\max} - S_{\min}}, \quad (3)$$

where  $\tilde{S}$  was the normalized area of the visual imprint of the analytical signals of the sensors;  $S_{\min}$  and  $S_{\max}$  were the values of the visual imprint area for samples without signs (samples of AI-95 gasoline in the absence of additives of other gasoline) and with the maximum signs of admixtures of AI-92 gasoline, respectively.

The physical parameters of gasoline and gasoline mixtures were determined according to *GOSTs* [29, 30]: density ( $\rho^{20}$ , g/cm<sup>3</sup>) by the densimetric method

**Table 1.** Physical indicators of density ( $\rho^{20}$ ) and kinematic viscosity ( $\nu$ ) of gasolines and their mixtures ( $n = 3$ ,  $P = 0.95$ )

Gasoline	$\rho^{20}$ , g/cm <sup>3</sup>	$\nu$ , mm <sup>2</sup> /s
AI-92	0.7650 ± 0.0012	0.8620 ± 0.0015
AI-95	0.7495 ± 0.0012	0.7915 ± 0.0015
AI-95 + 25% AI-92	0.7533 ± 0.0013	0.8140 ± 0.0014
AI-95 + 50% AI-92	0.7575 ± 0.0012	0.8255 ± 0.0012

and kinematic viscosity ( $\nu$ , mm<sup>2</sup>/s) with a VPZh-2 capillary viscometer.

## RESULTS AND DISCUSSION

The main physical indicators (density, kinematic viscosity) of gasoline and gasoline mixtures (Table 1) showed that the studied petroleum products complied with the standards [29, 30]. However, such indicators as, for example, the density of gasoline are more dependent on the technical regulations of the refinery, the conditions of catalytic cracking, catalytic reforming, or platforming of gasoline and are not decisive for gasoline with a high ON (according to *GOST 33364-2015*, the density is 0.725–0.780 g/cm<sup>3</sup> for all for high-octane types of gasoline [29]). Physical indicators are low informative and do not enable to recognize the belonging of gasoline to a particular brand; therefore, portable refractometers or densimeters cannot be used to determine the adulteration of gasoline at the point of sale or quality control.

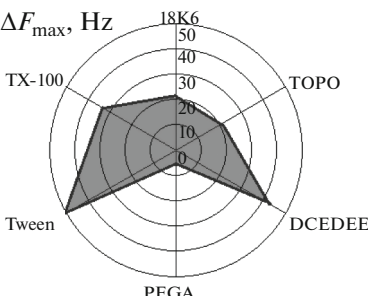
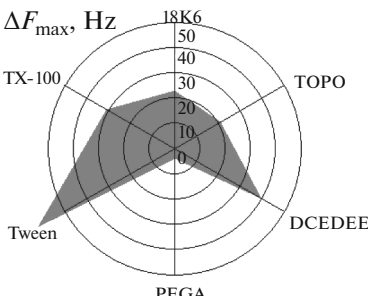
For the analysis of gasoline with an array of chemical sensors, the selection of sensitive layers of transducers (modifiers) is essential, because they should be able to assess the difference in the composition of the HVCs in the headspace of the samples. To determine the qualitative and quantitative features of the interac-

tion of volatile hydrocarbons and their derivatives in the headspace with electrode coatings, their adsorption capacity and sensitivity to HVC vapors were preliminarily estimated, and the optimal adsorbents were selected based on the formed database [31–33].

The kinetics of the adsorption of vapors of AI-92 and AI-95 gasoline on six thin-films modifiers of the PQR electrodes were studied under identical conditions. The analytical signals of the sensor array were obtained during HVC adsorption as output kinetic curves and visual imprints of maximum sensor signals (Table 2).

The investigated motor gasoline samples were close in composition but differed in the quantitative ratio of the components [14] (paraffinic and naphthenic hydrocarbons, aromatic and polyaromatic hydrocarbons, ether, and alcohol additives). In the methodology of integral analysis methods, which include the piezoelectric microweighing of vapor mixtures on arrays of multiselective sensors, the determination of the component composition is not required. Changes in the concentration of individual fuel components are reliably recorded in the values of quality indicators, parameters  $A(i/j)$ . The primary, most easily recorded quantitative criterion of the efficiency of HVC adsorption on the phases of the sensor modifiers, the visual imprint area  $S_{\Sigma}$  of the array signals, can also change. The difference in statistically reliable  $S_{\Sigma}$  values for the two brands of gasoline confirms the more complex composition of the volatile fraction of AI-95 gasoline, containing high-octane additives of aromatic hydrocarbons, alkyl ethers, or alcohols, compared to AI-92 gasoline. In a sample of AI-95 gasoline, a higher concentration of oxygen-containing additives was recorded, confirmed by differences in the signals of the sensors based on Tween, DCEDEE, and TX-100. The dependence of  $S_{\Sigma}$  on the concentration of gasoline vapors in the detection cell was consistent with empirical data for determining the saturated vapor

**Table 2.** Results of microweighing of gasoline vapors by an array of electronic nose sensors ( $n = 4$ ,  $P = 0.95$ )

Parameter	Gasoline	
	AI-92	AI-95
Visual imprint of the maximum responses of the sensor array in gasoline vapors		
$S_{\Sigma}$ , Hz s	1810 ± 20	1906 ± 22
$c$ , mg/m <sup>3</sup>	21.7	24.7

**Table 3.** Efficiency parameters  $A(i/j)$  of adsorption of highly volatile compounds of gasoline on thin films of adsorbents ( $n = 4-5$ ,  $P = 0.95$ )

$A(i/j)$	Gasoline	
	AI-92	AI-95
$A(18K6/TOPO)$	$1.1 \pm 0.1$	$1.0 \pm 0.1$
$A(18K6/DCEDEE)$	$0.55 \pm 0.02$	$0.50 \pm 0.02$
$A(18K6/PEGA)$	$5.5 \pm 0.2$	$4.6 \pm 0.2$
$A(18K6/Tween)$	$0.35 \pm 0.02$	$0.39 \pm 0.02$
$A(18K6/TX-100)$	$0.74 \pm 0.03$	$0.66 \pm 0.05$
$A(TOPO/DCEDEE)$	$0.52 \pm 0.03$	$0.50 \pm 0.03$
$A(TOPO/PEGA)$	$5.3 \pm 0.2$	$4.6 \pm 0.2$
$A(TOPO/Tween)$	$0.33 \pm 0.02$	$0.40 \pm 0.02$
$A(TOPO/TX-100)$	$0.69 \pm 0.03$	$0.67 \pm 0.03$
$A(DCEDEE/PEGA)$	$10.0 \pm 0.3$	$9.1 \pm 0.3$
$A(DCEDEE/Tween)$	$0.64 \pm 0.04$	$0.76 \pm 0.05$
$A(DCEDEE/TX-100)$	$1.3 \pm 0.1$	$1.3 \pm 0.1$
$A(PEGA/Tween)$	$0.06 \pm 0.01$	$0.08 \pm 0.01$
$A(PEGA/TX-100)$	$0.12 \pm 0.01$	$0.15 \pm 0.02$
$A(Tween/TX-100)$	$2.0 \pm 0.2$	$1.7 \pm 0.10$

pressure of motor gasoline of various brands and manufacturers [34], where the lower saturated vapor pressure of AI-92 gasoline than that of AI-95 gasoline was experimentally proved for several manufacturers (Gazprom, Rosneft, Lukoil).

The visual imprint shape is determined by the qualitative composition of the volatile fraction of the gasoline sample and the concentration ratio of different compounds, and a comparison of the absolute signals of the sensors enables the estimation of the proportion of various substances in the sample [35]. However, even for individual gasoline samples, sensor responses

$\Delta F_i^{\max}$  are insufficiently sensitive criteria for identifying gasoline belonging to a particular brand. The degree of identity of the integral signals of the sensor array, which is calculated automatically in the electronic nose software, in comparing gasoline samples of different brands and samples upon mixing, is 62–80%. This parameter reflects falling into the confidence interval of the responses at each time instant of each sensor in the array in recording mixtures of HVCs. The relative difference in the integral parameters of the visual prints of the sensor signals was calculated separately. A stable correlation was observed among all recorded parameters between the  $S_z$  value and the headspace volume of gasoline and gasoline mixtures in the detection cell. Some geometrical features of the visual imprints are also noted, that is, in the concentration ratio of different classes of compounds. New approaches can enhance the differences to processing data from an array of sensors with cross-selectivity.

The information content of the measurement results of the selected array of sensors can be increased using the identification parameter of the vapor adsorption efficiency  $A(i/j)$  to measure the affinity of two adsorbents to a mixture of volatile hydrocarbons. The parameters  $A(i/j)$  calculated for all possible 15 combinations of sensors (Table 3) suggest the determination of only a few parameters as identification ones:  $A(18K6/PEGA)$ ,  $A(18K6/TX-100)$ ,  $A(TOPO/PEGA)$ ,  $A(TOPO/Tween)$ , and  $A(DCEDEE/Tween)$ . We singled out the parameters  $A(i/j)$  that establish differences in the adsorption of individual groups of organic compounds in gasoline vapors: (1) 18K6 is an adsorbent specific for polar compounds, (3) DCEDEE is an electrophilic chromatographic phase, and (5) Tween is a nonionic surface-active adsorbent.

The algorithm for reading signals and forming the visual imprints and the number of sensors in the array are optimized to achieve the maximum difference in the visual imprints for the headspace of different gasoline samples. This decreased the number of measuring elements and made it possible to shrink the size of the detection cell, decrease the number of microcircuits, and make the case of the mobile device more compact.

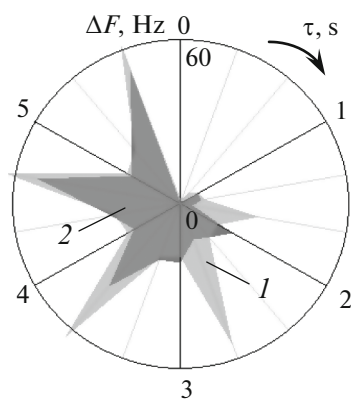
We calculated the relative mass sensitivity of the piezoelectric sensors (Table 4). The studied modifiers differed in their sensitivity to the HVCs of gasoline, with the Tween-based sensor being the most sensitive. At the same time, the sensor with the DCEDEE phase was characterized by the best differentiating properties concerning the HVCs of gasoline.

**Table 4.** Evaluation of mass sensitivity ( $S_m \times 10^2$ , Hz  $m^3/mg$ ) of the sensors based on 18K6, DCEDEE, and Tween

Gasoline	$c$ , $mg/m^3$	Sensor modifiers		
		18K6	DCEDEE	Tween
AI-92	21.7	$97 \pm 3$	$199 \pm 2$	$236 \pm 8$
AI-95	24.7	$85 \pm 2$	$162 \pm 3$	$270 \pm 10$

The differences in sensitivity and selectivity to gasoline components are most fully reflected in the kinetic visual imprints of the sensor signals (time diagrams) in the first moments of adsorption of volatile substances (up to 15 s), when the Langmuir filling of the adsorbent with a substance occurs. Figure 1 shows the kinetic visual imprints of the responses of the three most informative sensors for the first 5 s of adsorption. The degree of identity of the integral signals of the sensors does not exceed 60%; the relative difference in the areas of visual imprints ( $S_\tau$ , Hz s) of the sensor signals is 30.0%, which confirms the correctness of the optimization of the composition of the measuring elements in the array. The geometry of the scanning diagram of the sensor signals changes significantly, reflecting the difference in the qualitative composition of the vapor mixture. Such a presentation of the signals of the selected sensors, compared to the visualization of the maximum signals, makes it possible to distinguish better between samples of both initial gasoline samples with different ONs and their mixtures.

Under identical conditions, we studied the kinetics of adsorption of the headspace of model adulterated gasoline based on AI-95 with the addition of 25, 33, 50, and 75 vol % of AI-92 gasoline. We selected different adsorption times for the HVCs: 5, 30, and 60 s, and compared the nonequilibrium (5 s) and equilibrium (60 s) responses of the sensor array in gasoline vapors. For the total time of adsorption of substances, the sig-



**Fig. 1.** Comparison of kinetic visual imprints of signals of the 18K6, DCEDEE, and Tween sensors in vapors of (1) AI-95 and (2) AI-92 gasoline.

nals of the sensor array and their calculated characteristics are hardly distinguishable. The time diagrams of sensors in AI-95 gasoline vapors and mixtures that simulate counterfeits are given in Fig. 2 for the first 5 s of adsorption.

With a small volume fraction of AI-92 in AI-95 gasoline, the response of sensors to a mixture of HVCs in the headspace differs significantly. The effect of low concentrations is quite common in the practice of gas piezoelectric sensors and, as a rule, is not taken into account to determine differences in real samples [35] because of the significant error in reproducing trace concentrations during calibration. However, direct weighing of vapors on piezosensors combines the highly sensitive detection of molecules and the possibility of separating information on the composition of the mixture due to the peculiarities of adsorption on modifiers with a limited small area and minimal contact time with vapors. When AI-92 gasoline is introduced into high-octane gasoline, a synergistic effect of changing the integral analytical signal (the area of the kinetic visual imprint) is observed at any volume ratio of fuels (Fig. 3). At a more than 60 vol % additive of AI-92 in AI-95, the peculiarities of the composition of trace impurities of both fuels are smoothed out, and the differences are not recorded.

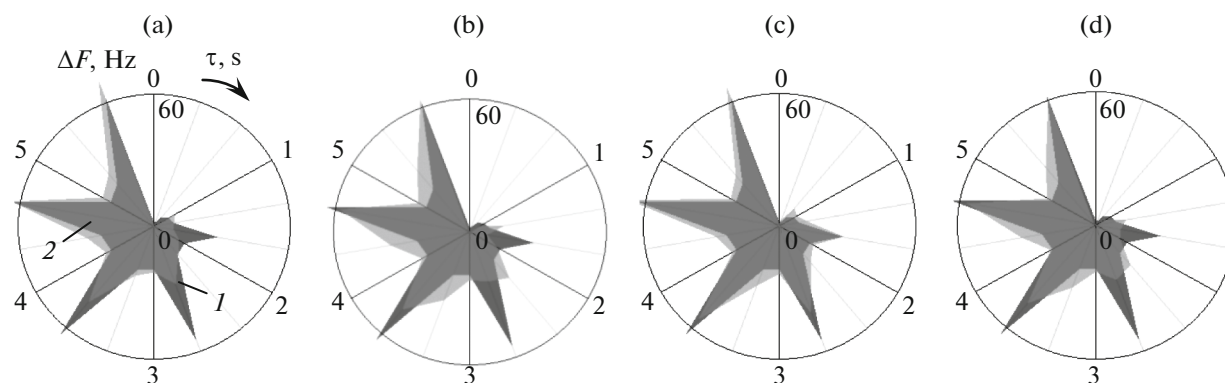
The maximum synergistic effect was achieved when the ratio of gasolines was 1 : 1; this regularity was retained when the integral analytical signal  $S$  is recorded both for 30 s and for the total adsorption time of 60 s (Fig. 3). Identical results were obtained using the change in the area of visual imprints of the maximum signals of all sensors for the total measurement time ( $S_\Sigma$ , Hz s) and kinetic visual imprints of the signals of the three most informative sensors for 30 s of adsorption ( $S_{30}$ , Hz s). This confirms the correct selection of informative fields for forming analytical signals of sensors in time:

$$\tilde{S} = 0.0187\omega + 0.0343 (R^2 = 0.9995), \quad (4)$$

the normalized area of the visual imprint; ( $\omega$ , vol %, is the volume fraction of the AI-92 additive in the AI-95 gasoline sample.

The absolute response of the sensor array and  $S_\Sigma$  may vary for the products of different manufacturers and batches of gasoline, but these differences are smoothed out during normalization. The error in determining the volume fraction of the additive during in situ examination does not change the fundamental fact of fuel adulteration. The equation can be applied for the rapid assessment of gasoline and the detection of samples with obvious adulteration.

To improve the reliability of the classification of samples and to solve the problem of authentication, an additional new calculation criterion was applied that characterized the constancy of the composition of mixtures (qualitative and quantitative), that is, the kinetic criterion  $A_S(\tau_1/\tau_2)$  for an array of three sensors.



**Fig. 2.** Comparison of kinetic visual imprints of electronic nose signals based on the 18K6, DCEDEE, and Tween sensors for 5 s of adsorption of vapors of (1) AI-95 gasoline and (2) gasoline mixtures with a volume fraction of AI-92 of (a) 25, (b) 33, (c) 50, and (d) 75 vol %.

Considering the maximum changes at the initial moment of the interaction of mixtures with adsorbents on piezosensors, we selected three parameters for different time intervals: 5 and 8, 5 and 10, and 5 and 15 s. The dependence of the three calculated kinetic parameters on the volume fraction  $\tilde{S}$  of the AI-92 additive was represented by functions of an identical type (Fig. 4).

The dependences of the criteria  $A_S(\tau_1/\tau_2)$  on the volume fraction of AI-92 additive are described by quadratic equations with close coefficients of determination. However, in a wide range of variations, the composition of the mixture cannot be unambiguously determined from the data obtained during the measurement. If the addition of gasoline with a lower octane number does not exceed 50 vol %, a linear region of the dependence of one of the parameters on the proportion of AI-92 gasoline added can be applied to solve analytical problems:

$$A_S(5/8) = -0.0043\omega + 0.79 \quad (R^2 = 0.9626), \quad (5)$$

$$A_S(5/10) = -0.0049\omega + 0.74 \quad (R^2 = 0.9920), \quad (6)$$

$$A_S(5/15) = -0.0039\omega + 0.65 \quad (R^2 = 0.9775). \quad (7)$$

Taking into account the time step of fixing the vibration frequency of the quartz plate of the PQR under load ( $\Delta\tau \pm 1$  s), we estimated the change in the coefficients in the equation with a decrease in the response time and obtained the equation for parameter  $A_S(4/11)$ ,

$$A_S(4/11) = -0.0050\omega + 0.60 \quad (R^2 = 0.9992). \quad (8)$$

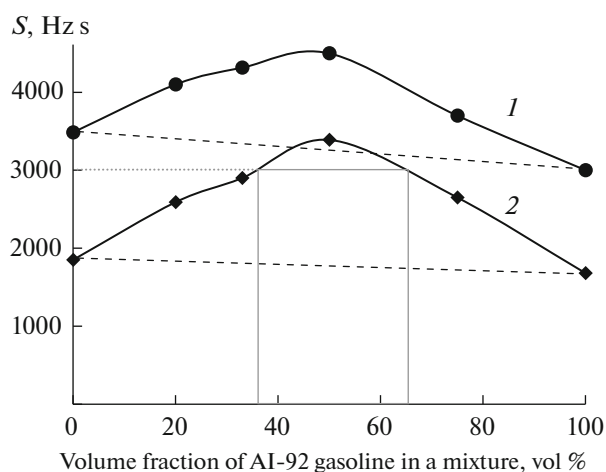
Given the coefficient of reliability of the approximation  $R^2$ ,  $A_S(4/11)$  is a more reliable parameter. However, considering the errors in recording the sensor signals by the microcircuit with a step of  $\pm 1$  s to predict the proportion of possible addition of gasoline with a lower octane number, the average result of Eqs.

(6) and (8) should be used for the indicators  $A_S(5/10)$  and  $A_S(4/11)$ , respectively, which minimizes the measurement time to 15 s > that is,

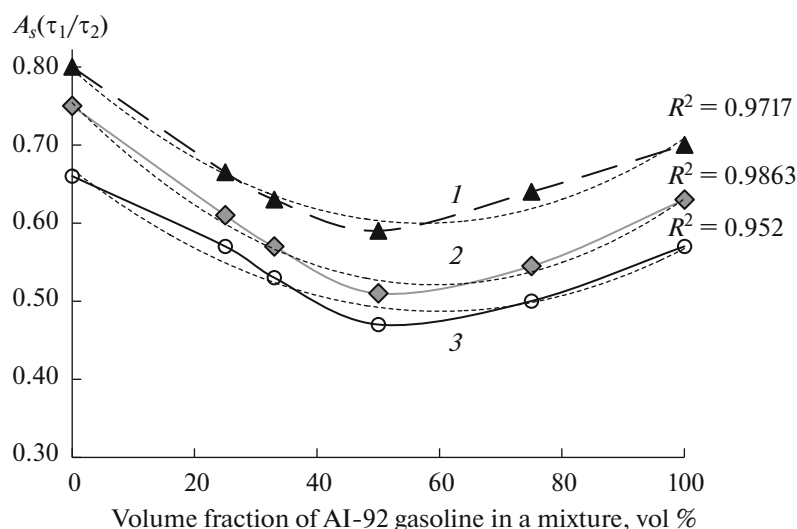
$$\bar{A}_S = -0.0049\omega + 0.67 \quad (R^2 = 0.9990). \quad (9)$$

The results obtained made it possible to develop a method for establishing the adulteration of gasoline by adding gasoline with a lower ON.

The general procedure was as follows (Fig. 5): an average sample of gasoline vapors with a volume of 2 cm<sup>3</sup> was collected directly above the fuel surface from the car's tank (containers, canisters, etc.) and injected into the electronic nose detection cell; the responses of all sensors in the array were simultaneously recorded for at least 15 s (in situ mode) or 30 s in the laboratory. A matrix of data was obtained, which was then processed according to the algorithm



**Fig. 3.** Dependence of the areas of (1) kinetic visual imprints of signals of the sensor array in AI-95 gasoline vapors for 30 s of adsorption ( $S_{30}$ ) and (2) visual imprints of the maximum signals for the total time ( $S_{\Sigma}$ ) on the volume fraction of AI-92 additive.



**Fig. 4.** Dependence of criteria (1)  $A_s(5/8)$ , (2)  $A_s(5/10)$ , and (3)  $A_s(5/15)$  in AI-95 gasoline vapor on the volume fraction of AI-92 addition.

(Fig. 5). At the first stage, general information about the state of the sample was obtained, and the degree of difference between the geometry and areas  $S_\Sigma$  and  $S_\tau$  of the visual imprints of the test sample with the reference gasoline of this brand (for the laboratory) was assessed. If the difference between the visual imprints of the test sample and the reference was significant (more than 20%), the calculated parameters were used at the second stage of data processing. Thus, information about the possible adulteration of gasoline of this category by adding fuel of a different brand was obtained. For this, a quantitative parameter was calculated that depended on the concentration of gasoline vapors, the pressure of saturated gasoline vapors, and temperature, obtaining the area  $S_\Sigma$  of the visual imprint of the maximum responses of the sensor array. The resulting value was normalized by Eq. (3), where  $S_{\min} = 1600 \text{ Hz s}$  and  $S_{\max} = 3400 \text{ Hz s}$ . The volume fraction ( $\omega$ , vol %) of the possible AI-92 addition to AI-95 gasoline was found by the equation

$$\omega = \frac{\bar{S} - 0.0343}{0.0187}. \quad (10)$$

To improve the reliability of the determination of gasoline dilution, the calculated values of the kinetic criterion  $\bar{A}_s$  were used for an array of three sensors, which depended on the nature and constancy of the composition of the hydrocarbon mixture. In the laboratory, uninformative sensors were turned off in the electronic nose software, and then the calculation was carried out. In a mobile device based on only these three sensors, the equation was written into a micro-circuit, and the result was displayed on the screen. The volume fraction of AI-92 additive  $\bar{A}_s$  ( $\omega$ , vol.%) in AI-95 gasoline was calculated by the equation

$$\omega = \frac{0.67 - \bar{A}_s}{0.0049}. \quad (11)$$

Gasoline can be considered adulterated by adding gasoline with a lower ON if  $\omega > 6 \text{ vol } \%$ . According to the developed algorithm, several samples of AI-95 gasoline with additives of AI-92 gasoline in arbitrary ratios were examined. The results of a quantitative assessment of the additive by various parameters are shown in Table 5.

Regarding all the proposed criteria, the adulteration of high-octane gasoline can be established by determining the approximate proportion of the additive with a spread of  $\pm 1.5 \text{ vol } \%$  and a relative error of up to 12%. These characteristics are relatively good for test systems with a minimum cost and a less than 20 min test time. In addition, a smaller number of sensors in the array contributes to developing a pocket mobile device with an autonomous power supply and a programmed calculation algorithm with the output of a clear result on the screen.

## CONCLUSIONS

Studying the kinetics of the adsorption of gasoline vapors on thin film-modifiers of the PQR electrodes resulted in selecting three most sensitive and informative coatings that adsorb compounds of the highly volatile gasoline fraction in different ways. The method reliability can be improved using new modifiers; nanostructured materials, particularly, modified carbon materials, are promising in this field. Simple signals of the electronic nose  $S_\Sigma$ ,  $S_\tau$ ,  $A(i/j)$ ,  $A_s(\tau_1/\tau_2)$ , which can be recorded and calculated in the software, give information on the composition of a gasoline sample and assess the change in composition in add-



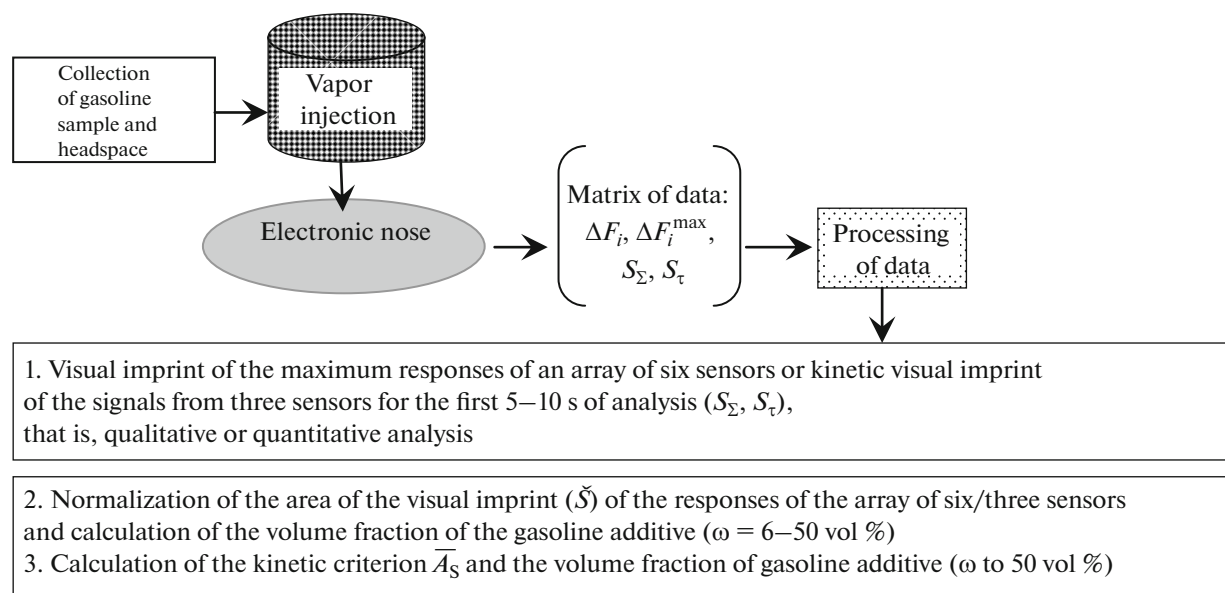


Fig. 5. Schematic diagram of the general procedure for analyzing gasoline.

Table 5. Results of analysis of counterfeit AI-95 gasoline by the electronic nose parameters using the standard addition method ( $n = 4$ ,  $P = 0.95$ )

Added Ai-92, vol %	Found AI-92 additive in AI-95 gasoline, vol %			
	by normalized $S_{\Sigma}$		by $\bar{A}_S$	
	$\omega$ , vol %	RSD, %	$\omega$ , vol %	RSD, %
18.0	$18.6 \pm 1.6$	5.4	$18.8 \pm 3.8$	12.0
26.0	$27.2 \pm 2.0$	4.5	$27.0 \pm 4.0$	9.3
50.0	$51.3 \pm 2.7$	3.3	$50.2 \pm 4.0$	5.0

ing fuel of a different type or brand. Simulation of the dilution of fuels of different quality, brands, and manufacturer creates a catalogue of design equations for routine analysis and in-lab expertise. This makes it possible to integrate the electronic nose” gas analyzer based on piezoelectric balances into the fuel quality control system to establish the adulteration of high-octane gasoline by adding gasoline with a lower octane number and to estimate the amount of the additive.

#### CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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