

PACS 82.75.-z

## **Effect of molecular sieves on discrimination efficiency of a multisensor gas-analysis system**

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**Abstract.** We investigated the effect of zeolite at the sample input of a gas-analysis system (Electronic Nose) on recognition of volatile molecular mixtures. It is shown that the NaX molecular sieves can remove ketone-type molecules from a gas sample more efficiently than the NaA molecular sieves. A comparison of recognition of four different perfumes, both with and without NaA zeolite at the inlet of a multisensor system, showed that introduction of zeolite reduces responses of all sensors and does not improve recognition.

**Keywords:** Electronic Nose, molecular sieve, zeolite.

Manuscript received 17.12.07; accepted for publication 15.05.08; published online 30.06.08.

### **1. Introduction**

Successful solution of the biosphere protection problem, reduction of the negative effect of industrialization on the natural environment, and many other global problems are related immediately to the development of efficient analysis techniques. There exists a lasting need in simple highly sensitive and precise procedures, which could enable one to determine components in composite mixtures [1, 2].

The standard chromatographic techniques are applied usually to recognize multicomponent chemical media. In recent years, however, the non-chromatographic techniques are receiving wide acceptance. They are based on application of sensor arrays known as "Electronic Nose" (EN) [3]. It was precisely the need in low-cost compact high-speed and completely automated measuring and control facilities to be used in industry, power engineering, medicine and environment control that stimulated search for radically novel approaches for solving such problems.

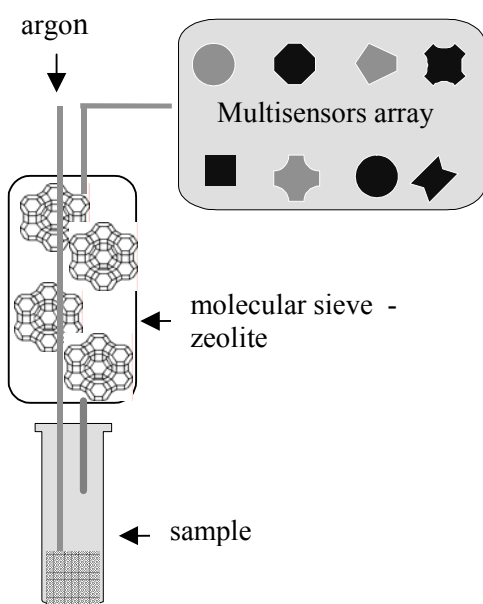
The EN-type multisensor systems [4, 5] involve low-sensitivity sensors that form chemical images of multicomponent chemical systems followed with discrimination (identification) using the image recognition procedures. Chemical functionality of the sensor array as a whole is the governing factor for successful identification of composite mixtures [6]. The sensitive elements may be organic compounds that are affine receptors with molecular cavities from 3–5 nm up

to 10–15 nm. This is just the size range of ligands typical for the molecular elements of odors.

Multicomponent chemical systems involve a big number of various compounds (from tens up to thousands of different chemical components). In addition, the process of analysis is complicated considerably by presence of a predominant component (water, ethanol, etc.). That is why the development of science-based approaches that could make recognition of multicomponent chemical systems with EN quicker and easier seems timely. At the same time, there are practically no works in literature dealing with comprehensive investigation of the effect of sorbents at the gas system inlet on the form of the resulting response of multisensor array [7].

Another problem that is of importance for development of reliable gas-analysis systems is obtaining of pure gas for the system comparison channel without argon cylinders. The traditional opinion is that presence of a sorbent (say, activated carbon) can ensure removal of sorbed molecules from the gas-sensitive elements. However, there are no quantitative data in literature concerning sorptive capacity of the elements used, as well as the degree of their purity, as function of the volume and time of operation.

In this work, we attempted to carry out comprehensive investigations of the effect of zeolite filter at the sample input of an EN-type multisensor system on the response of eight quartz sensors coated with different sensitive layers. Our aim was to compare



**Fig. 1.** A schematic of experiment with nanostructured materials of the NaA-type zeolite.

the responses of a sensor system, both with and without a filter (filled with NaA or NaX zeolite) at the sample input [8, 9].

## 2. Experimental procedure

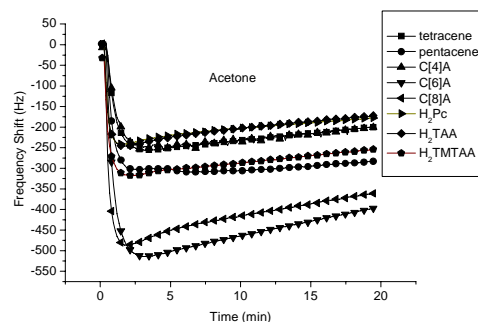
A schematic of experiment is shown in Fig. 1. Before column filling, the zeolite was heated for 5 h in a furnace at a temperature of 450 °C. The temperature in the thermostat with a bubbler, filter and measuring cell was maintained constant in the course of the experiment.

The popular NaA and NaX zeolites (with inside pore sizes of 1.14 and 1.3 nm, respectively) were chosen as sorbents. The pore opening sizes were of 0.42 and 0.74 nm, respectively [10-12]. Therefore the adsorption efficiencies for molecules varying in size and polarity, e.g., ethanol (0.47–0.51 nm) and water (0.28–0.31 nm), may differ by several orders of magnitude.

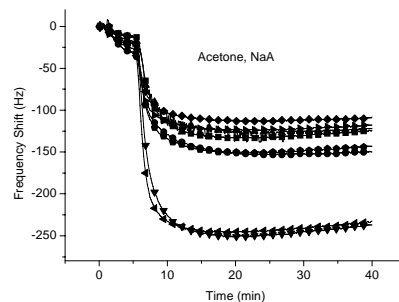
The objects of our investigations were single saturated vapors – ethanol and acetone, as well as several commercial perfumes: Buket, Landysh, Troinoi, and Shipr (GOST 17237-93) (from here on B, L, T, and S, respectively) produced by PKK "Roso" (Zhovkva, Ukraine). The samples (volume of 2 ml) were blown off (bubbled) with a gas-carrier (argon); the vapors of samples to be studied were supplied to the multisensor array through the zeolite column.

## 3. Results and discussion

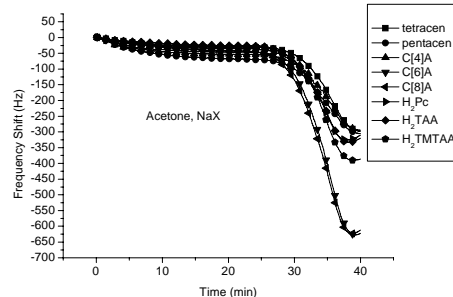
**3.1. Acetone.** Figure 2 shows kinetics of the sensor array responses to leak-in of saturated acetone vapor. Figure 2a corresponds to the case when there is no zeolite at the sample input, while Fig. 2b (2c)



a



b



c

**Fig. 1.** Experimentally taken frequency shifts vs time dependencies: a - for acetone, b (c) - in the NaA (NaX) zeolite–EN system.

corresponds to the case when there is a NaA (NaX) zeolite filter. One should note a pronounced delay of signal (quartz resonator frequency shift) build-up after zeolite introduction into gas flow. When NaA zeolite is present, then the delay time is 300 s, while the signal peak decreases from 550 Hz (Fig. 3a) down to 140–260 Hz (Fig. 3b). When NaX zeolite is introduced, then the delay time increases up to more than 1680 s (Fig. 2c); at the same time, the maximal signal amplitude after delay (550–600 Hz) is approximately equal to that in the case when there is no zeolite.

The signal amplitude for each sensor is proportional to the concentration of molecules in the gas phase, and variation kinetics is close to the Langmuir one. From Fig. 2a one can see that the signal from all sensors flattens out even 150 s after vapor leak-in. (Subsequent drop is related to insufficient rate of molecules evaporation in the bubbler due to small liquid area.) Therefore, one can consider all the sensor readings in Fig. 2b and 2c proportional to the concentration of acetone molecules in argon. It follows from Fig. 2c that NaX zeolite absorbs saturated acetone vapor completely

during  $t_d \sim 1680$  s. The behavior of NaX zeolite in the flow of saturated acetone vapor at the EN input is described adequately within the framework of the known concepts of physical chemistry of zeolites [13]. We conclude that acetone sorption occurs in the sorbent nanocavities.

The behavior of NaA zeolite is less unambiguously. One can see from Fig. 2b that the signal delay time is reduced by a factor over five. This corresponds to substantial decrease of the number of nanocavities easily accessible for acetone molecules. In this case, even after 1000 s, the concentration of molecules at the output (the corresponding signal is no more than 260 Hz) does not reach that at the input (the signal is about 500–550 Hz, see Fig. 3a). This means that only about one-fifth fraction of nanopores still remains easily accessible for acetone molecules. A considerable (about half) portion of sorbent nanopores is difficult of access for acetone molecules. This seems to be related to geometric limitations of acetone molecules diffusion in NaA-type zeolites.

Thus, the NaX molecular sieves can serve for removal of ketone-type molecules from a gas sample more efficiently than the NaA ones. The NaX sorptive capacity is 0.5 g/g, and the effective delay time is 1680 s.

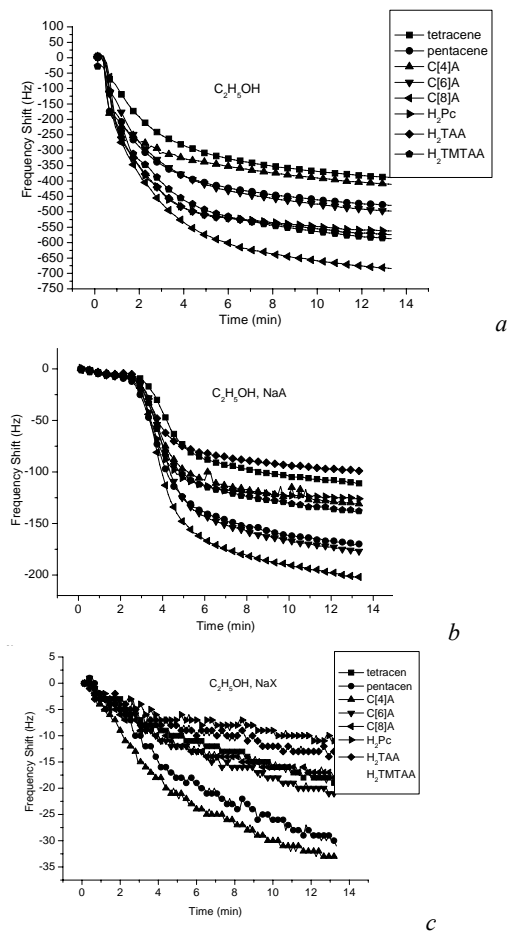


Fig. 3. As in Fig. 2 but for ethanol.

3.2. *Ethanol.* The authors of [14] used a chromatographic column to separate ethanol from water before supplying sample to sensor array in the EN-type system. In our work, we used a column filled with zeolites of two different types rather than a chromatographic column.

The responses of a quartz sensor array to introduction of saturated ethanol vapor in argon are presented in Fig. 3 for three cases: without sorbent at the input (Fig. 3a) and with NaA and NaX molecular sieves (Figs. 3b and 3c, respectively). As it was before, introduction of NaA-type zeolite (Fig. 3b) results in a small (about 172 s) delay of response. After this, the signal from all sensors begins to grow abruptly, with a trend towards saturation at about 780 s. In this case, the signal maximal amplitude is reduced by more than three times – 200 Hz instead of 700 Hz. This means that the ethanol concentration at the zeolite output is reduced by more than three times, i.e., the great bulk of ethanol remains in zeolite even after 780 s.

Introduction of NaX zeolite (Fig. 2c) leads to amplitude decrease by a factor of twenty. This corresponds approximately to the signal level at a stage of the so-called delay (Fig. 2b) and means that NaX zeolite practically does not let ethanol molecules through it for 800 s.

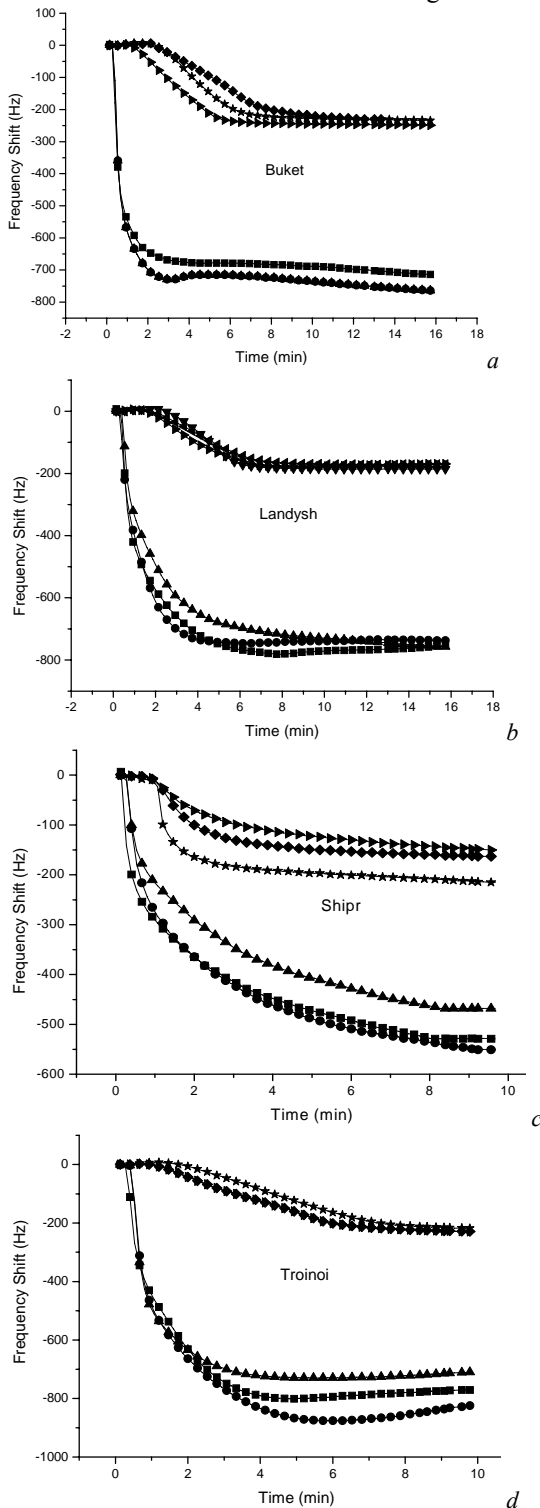
#### 4. Effect of zeolite on discrimination of perfume compositions

When studying the effect of small moisture contents (about 2 mmole of water per 1 g of zeolite) on adsorption of hydrocarbons, the authors of [15] assumed that the following three effects are responsible for reduction of separation efficiency: (i) the water molecules serve as shield between the cations and adsorbate molecules (the shielding effect); (ii) complexes are formed by the water molecules and cations that make the openings between the zeolite cavities smaller (the blocking effect); (iii) adsorbed water decreases the zeolite adsorption volume (the steric effect).

The delay time for ethanol and acetone molecules in the case of NaA zeolite is smaller than in the case of NaX zeolite. Therefore, it seems quite natural to apply just NaA zeolite to control molecular composition of samples. Indeed, at the initial stage when the ethanol and acetone molecules are sorbed completely in the molecular sieve, the molecules of bigger size (those of essences, heavy ketones, etc.) can pass, in principle, through the sieve with no delay. After considerable number of nanopores is blocked with the ethanol and water molecules, the molecules of the essences, heavy ketones, etc. will come to the sensor cell again, thus varying the all sensor readings. Hence, it is possible to obtain an additional facility for discrimination control by varying the complex composition of the mixture studied.

The results obtained in the course of an analysis of vapors of some perfumes, both with and without a zeolite filter (the upper and lower curves, respectively), are

summed in Fig. 4. For the sake of convenience we present the data given by the only sensor 5, (C[8]A). Those obtained from the other sensors are of the similar form, differing in the amplitudes only. To demonstrate reproducibility of the results, those two (three) curves are shown that differ from each other to the greatest extent.



**Fig. 4.** Effect of zeolite on the form of C[8]A sensor response at injection of the B, L, S, and T compositions (lower curves - response without zeolite, upper curves - response with NaX zeolite).

As it was before, the response to inflow of samples into the system without zeolite leads to immediate increase of amplitude of signal from all the sensors for all the perfumes under investigation. In this case, response of the sensor 5 to B, L, and T is somewhat bigger than that to the ethanol vapor. This is related seemingly to presence of water whose partial pressure makes additional contribution to concentration of predominant molecules (cf. Figs. 3a and 4a). In the case of perfume S, the amplitude is somewhat lower (about 600 Hz). This fact indicates lower fraction of ethanol and water in that composition.

Introduction of NaA zeolite changes the situation dramatically. The response is delayed (as in the case of acetone and ethanol), and the amplitude drops by a factor of 3-4 for all the perfumes studied. A spread of the values of response amplitude, as well as delay time, appears (Fig. 3a, 3c). It seems that the sorbent detains not only the interfering molecules of ethanol and water but those of the substances to be discriminated as well.

It seems expedient to apply the standard discrimination techniques (with further comparison of results) for quantitative analysis of the EN discrimination ability, both with and without zeolite. The following two approaches were used: (i) estimation of distance between the position vectors in eight-dimensional (8D) Euclidean hyperspace, and (ii) the software package S-PLUS 2000 (MathSoft Inc.) [16, 17]. In the first approach, the sensor data array (eight values at every moment) is presented as a vector in the 8D Euclidean hyperspace  $x_1, x_2, \dots, x_8$  (here 1...8 number the sensors). It is evident that to each set of  $x$ -s corresponds a point or position vector  $\mathbf{r}$ . It is also evident that, in the course of sensors exposition to a sample, the vector  $\mathbf{r}$  circumscribes a curve. To each perfume under investigation, its own position vector corresponds. In what follows, we shall use the notations  $\mathbf{r}_1 \dots \mathbf{r}_4$  (1 - B, 2 - L, 3 - S, 4 - T). We shall consider that our sensor system discriminates the samples if all the four vectors differ substantially, i.e., the distances between the vectors are much bigger than the dispersion (distance between the vectors for the same sample obtained at different measurements).

The 8D vectors  $\mathbf{r}_1 \dots \mathbf{r}_4$  cannot be presented in the real 3D space. Usually they are described within the framework of the so-called principal components or other similar approaches where a multidimensional system is folded into a 2D one [18].

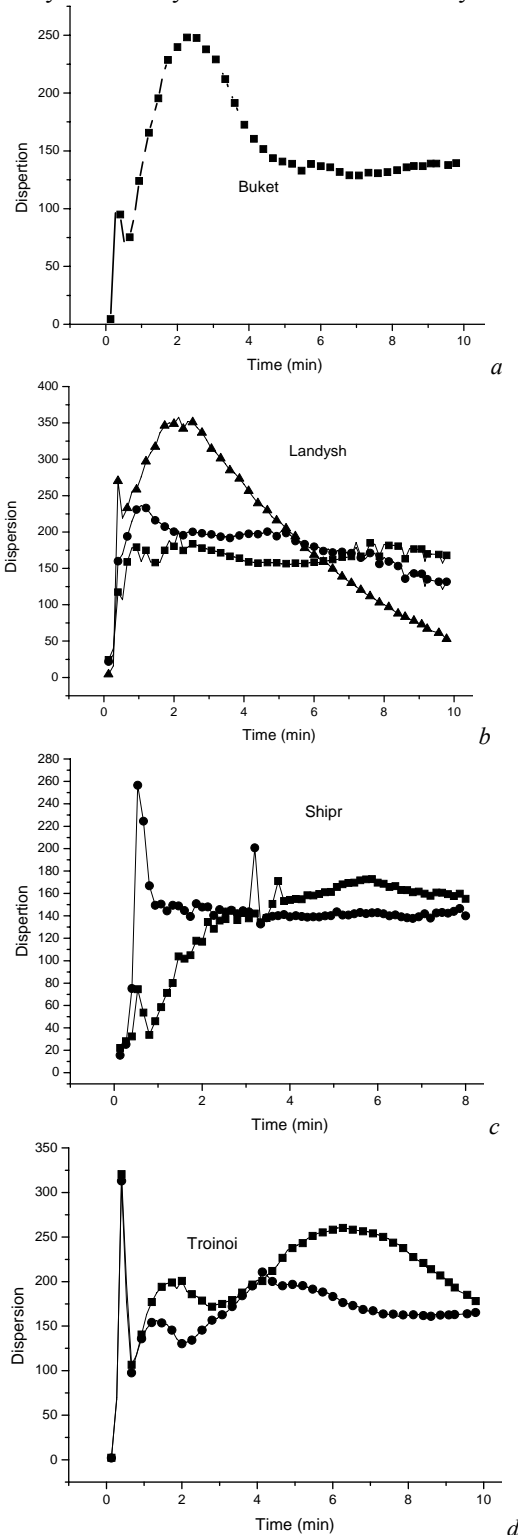
Let us calculate the difference of two vectors,  $\mathbf{r}_{ij}$ , as

$$d_{ij} = \sqrt{\sum (x_{ik} - x_{jk})^2},$$

$k = 1 \dots 8$ . It is evident that, when  $i = j$ , the  $\mathbf{r}_{ij}$  value corresponds to dispersion, i.e., spread of vectors within a certain sampling (measurement of the same perfume).

Shown in Fig. 5 is the difference between vectors,  $\mathbf{r}_{ii}$  ( $i = 1 \dots 4$ ), for different pairs of measurements made for the same sample. It is obvious that the  $\mathbf{r}_{ii}$  value characterizes the spread (dispersion) of experimental

data obtained at different moments. For B, L, and S, dispersion reaches a peak and then stabilizes at a level of 150 Hz (at  $t > 408$  s). The dispersion for T is somewhat bigger; it reaches 150–200 Hz after 640 s only. Starting from this, one should choose time after 640 s for analysis of the system discrimination ability.

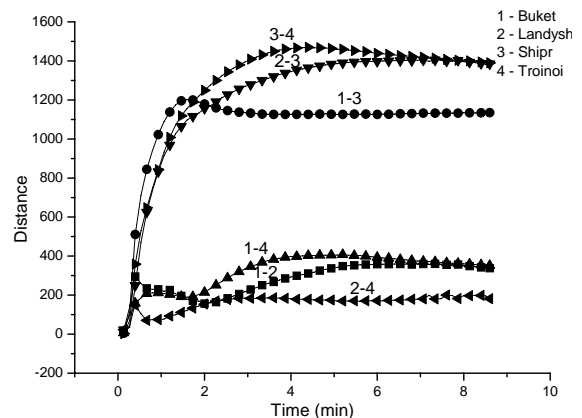


**Fig. 5.** Temporal dependence of dispersion (distance between the vectors for the same sample obtained at different measurements).

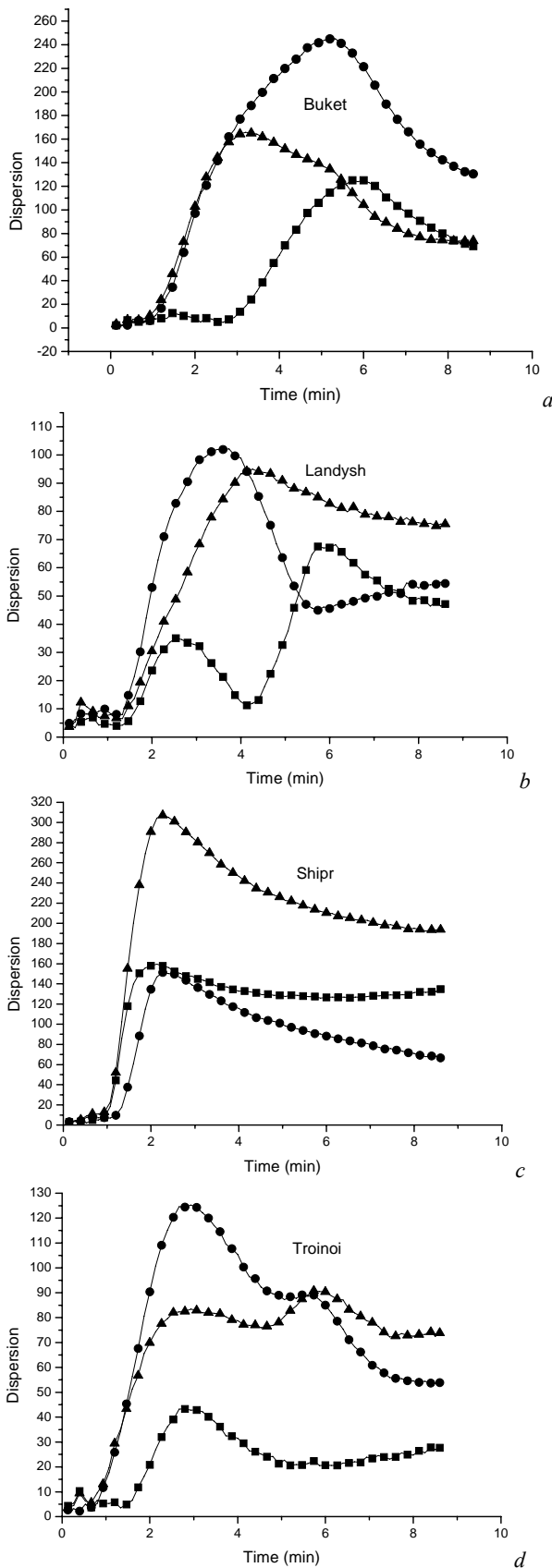
Figure 6 presents temporal dependences of the differences  $r_{ij}$  for all pairs of perfumes, thus making it possible to judge the discrimination ability. The bigger is the difference  $r_{ij}$  between a certain perfume and other samples the better is discrimination. One can see that most of curves have a peak at  $t < 408$  s. This means that the best discrimination ability of the sensor array is realized just at those moments. In this case, however, a considerable dispersion growth (especially for T, see Fig. 5) is observed. Therefore, it seems unreasonable to perform discrimination at that time.

One can see also that the signal from perfume B differs from all others (12, 13, 14) by no less than 300 Hz (at  $t = 380$  s). The perfume L differs distinctly from S (24); however, its distinction from T (24) is weakly pronounced (about 200 Hz at  $t = 380$  s), the dispersion being close to 200 Hz (Fig. 5). At the same time, the perfume S differs strongly from all other perfumes (13, 23, 43): the signal difference is over 1000 Hz at dispersion of 150 Hz. Thus, in the absence of zeolite, for most of perfumes the vector difference  $r_{ij}$  is at least 50% over dispersion. This indicates good discrimination. The only exception is perfume T that may be confused with L because  $r_{24}$  (200 Hz) exceeds the dispersion of both L and T (150 Hz) but slightly, see Fig. 5.

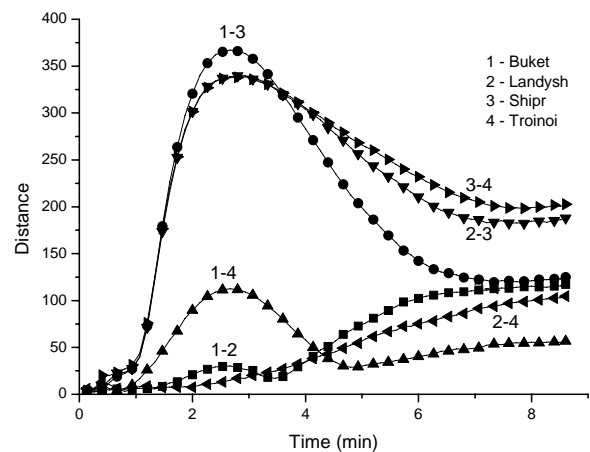
Let us analyze the discrimination ability in the case of the same perfumes but in the presence of NaA zeolite. Figure 7 shows the spread (dispersion) of  $r_{ij}$  values for three measurements of the same sample. (Recall that 1, 2, 3, and 4 correspond to B, L, S, and T, respectively.) The curves in Fig. 7 are nonmonotonic (as without zeolite) and demonstrate a peak in the 160–400 s time range. However, contrary to Fig. 5, the dispersion dropped considerably for B, L, and T. At  $t = 480$  s, it is 50–130 Hz for B, 40–70 Hz for L, and 30–70 Hz for T, while for S it is 50–200 Hz. Most probably, such decrease of dispersion is related to the general signal decrease after zeolite introduction, while the spread between dispersion values for different samples of the tube after high-temperature calcining.



**Fig. 6.** The distance between the vectors  $r_{ij}$  in the 8D Euclidean hyperspace for different perfume pairs without zeolite (1 - B, 2 - L, 3 - S, 4 - T).



**Fig. 7.** Temporal dependence of dispersion (spread of data) for different perfumes, with zeolite at the measuring chamber input.



**Fig. 8.** As in Fig. 6 but with zeolite.

Figure 8 presents the temporal dependence of  $r_{ij}$  when zeolite is present. Unfortunately, introduction of zeolite decreased not only the spread (dispersion) within the set of measurements for each sample; it also decreased appreciably the difference between the vectors corresponding to the pairs of different perfumes (discrimination ability). Due to appearance of a new parameter (delay time), we note an increase of the distance between the vector of L and those of other perfumes (31, 32, 34) during an intermediate period of 80–340 s. However, the spread within the set of measurements for S lies in the same range (Fig. 7c). This fact does not enable one to identify S for sure because the dispersion (100–250 Hz) is comparable with the value of vectors 31, 32, 34 (300 Hz). The same conclusion is true for the rest of the samples as well.

Thus, a mere introduction of zeolite at the input of an EN-type analytical system does not improve recognition of chemical images (at least those of perfumes). This result is somewhat unexpected because the size of pores in zeolite prevents adsorption of big molecules that form chemical images of perfumes. It is probably that in this case adsorption occurs at the outer surface of zeolite grains (where nonspecific adsorption forces act) rather than in the nanopore volume.

## 5. Conclusion

We performed a systematic investigation of the effect of zeolite (placed at the input of the EN-type gas-analysis system) on recognition of elementary (acetone, ethanol) and complex volatile molecular mixtures (four different perfumes). It is shown that the saturated acetone vapor is sorbed efficiently in the pores of the NaX sorbent during 1680 s; after this they pass through the sorbent without hindrance. The adsorptive capacity of NaX zeolite was determined from the delay time and gas-carrier flow; it coincides with the literature data. Contrary to this, acetone adsorption on NaA zeolite is nonuniform. This manifests itself in reduction of retention time during which the acetone vapor is sorbed efficiently in the NaX

sorbent nanopores and slow restoration of molecular concentration after this efficient sorption is ended. The ethanol molecules demonstrate nonuniform adsorption on NaX zeolite as well as NaA. The smallest retention time was that obtained for ethanol molecules on NaA zeolite. A comparison between the degrees of recognition of four perfumes by an eight-sensor array, both with and without NaA zeolite at the input, showed that introduction of zeolite reduces responses from all the sensors and does not improve recognition.

#### Acknowledgments

We would like to thank B. Snopok, J. Burlachenko for helpful discussions and V.G. Lyapin for useful comments and assistance in article preparation.

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