

IDENTIFICATION AND QUANTIFICATION OF PLANT VOLATILES BY LOW-COST ELECTRONIC NOSE

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Abstract – The paper explores the possibilities of low-cost prototype of electronic nose based on widely available parts for identification and quantification of plant volatiles. The identification was based on chemometric processing of signals from the set CMOS sensors. The average success rate of the identification was 93.33%. Among the sensors used, Figaro TSG 2611 was most suitable for quantification of compounds with the $R^2 = 0.931$.

Keywords: essential oils, e-nose, sensors

1. BASIC INFORMATION

Plant volatiles, mainly components of essential oils, are valuable natural chemicals, which finds its use in cosmetics, food and agriculture, as well as pharmaceutical industry [1]. Nowadays, the most often used methods for their identification and quantification are different combinations of gas chromatography and mass spectrometry with extraction techniques like distillation, SPME, or thermal desorption. Recently, there are even some systems based on sensors or their combinations, but the main advantage, lower cost, is not significantly achieved by commercial systems when compared to traditional systems. With the wide use of consumer electronics, the availability of components is increasing while their cost is decreasing. The perfect example is programmable platform Arduino, which can be used for controlling of several components and recording of signals and metal-oxide semiconductor gas sensors that are used in commercial applications for measuring of concentrations of different gases. The systems, often called e-noses, are also used in food industry for applications like quality control, monitoring process, aging, geographical origin, adulteration, contamination and spoilage [2]. More specifically in the field of plant volatiles, there are several studies aimed at genuineness [3], characterisation of

developmental stage of aromatic plants [4], or monitoring of the protective effect of plant volatiles for shelf life extension [5]. In these studies, usually commercial e-noses are used, but there are also attempts to use prototypes [6], [7].

The aim of this study was to construct and low-cost prototype of electronic nose with the purpose of evaluating its possibilities of identification and quantification of plant volatiles.

2. MATERIALS AND METHODS

2.1. Construction of electronic nose

The main part of the e-nose was Arduino Mega 2560 board with 53 digital input-output ports. The interface parts were: keyboard, an SD card reader, LCD display, relays and chemical sensors. Sensors were selected according to their high sensitivity to organic compounds. Therefore six sensors, namely Figaro TGS813 (sensitive to propane, butane, methane, alcohols and hydrogen), Figaro TGS822 (carbon monoxide, ammonia, sulphur dioxide, alcohol, gasoline), Parallax MQ-4 (propane, butane, methane), Figaro TGS2600 (various gases, air pollution), Figaro TGS2602 (air contaminants, alcohol, ammonia, butane, carbon monoxide, halocarbons, hydrogen, methane, oxygen, propane, solvent vapours) and Figaro TGS2611 (methane) were used.

Sensors were placed in measurement chamber - a sealed glass container, to which the headspace sample is supplied. The chamber contained the gas sensors and one thermal sensor for measuring of the temperature.

Sampling chamber was also a glass container with two ports. Inlet was equipped with carbon filter to avoid sample contamination from the ambient air. Output was connected to the measurement chamber. The sampling was performed by evacuating the measuring chamber by vacuum pump

and the headspace from the sampling chamber was then sucked into the measuring chamber. All the tubing was airtight, and there were two solenoid valves for controlling of the sampling and evacuation steps. The measurement was done for 5 minutes. Cleaning step was done by sequential evacuation of the measurement chamber three times for 15 seconds.

2.2. Plant volatile compounds

Commercial standards were used: anisole, carvone, carvacrol, β -pinene and β -citronellol (Sigma Aldrich, purity $\geq 99\%$).

2.3. Measurement procedure

At the beginning of each series of measurements first measurement of the blank (blank sample), and then the control sample (anisole) was carried out. Anisole was randomly selected as a control sample for the purpose of fast functional verification of the device. The sample was pipetted onto the filter paper 2x2 cm and was inserted into the sampling chamber, which was placed on the magnetic stirrer. The sample is stirred for 5 minutes to achieve homogenous concentration in the headspace. The measurement was recorded in a 10 Hz frequency – 10 points per second. All samples were measured in triplicate, standards for qualitative analysis were measured 5 times.

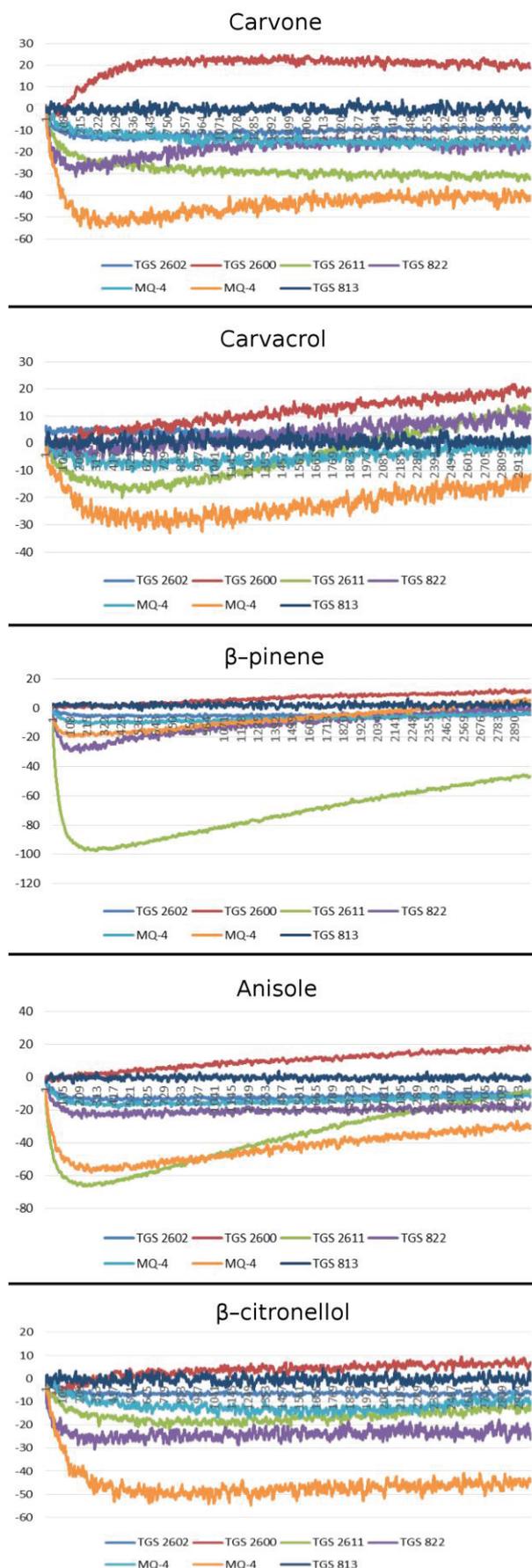
2.4. Data processing

Data were processed in Microsoft excel by simplifying the data points and then the data matrix was created. The comparison of the matrix of the sample was compared with the previously measured library of the standards. The similarity in percent was recorded. For quantification, standards were measured in concentrations 0.3, 1, 3, 10 a 30 μ l and calibration curve was created. Values were then selected at times 1, 10, 20, 40, 60, 120, 180, 240, and 299 seconds from the beginning of measurement. Furthermore, coefficients of determination (R^2) between sample concentrations and the calibration for each sensor was calculated.

3. RESULTS AND DISCUSSION

In Fig. 1 the comparison of the obtained signals for the compounds is shown. In the Tab. 1 similarity of the compounds with the standards is shown.

Fig. 1. Graphs obtained from different standards



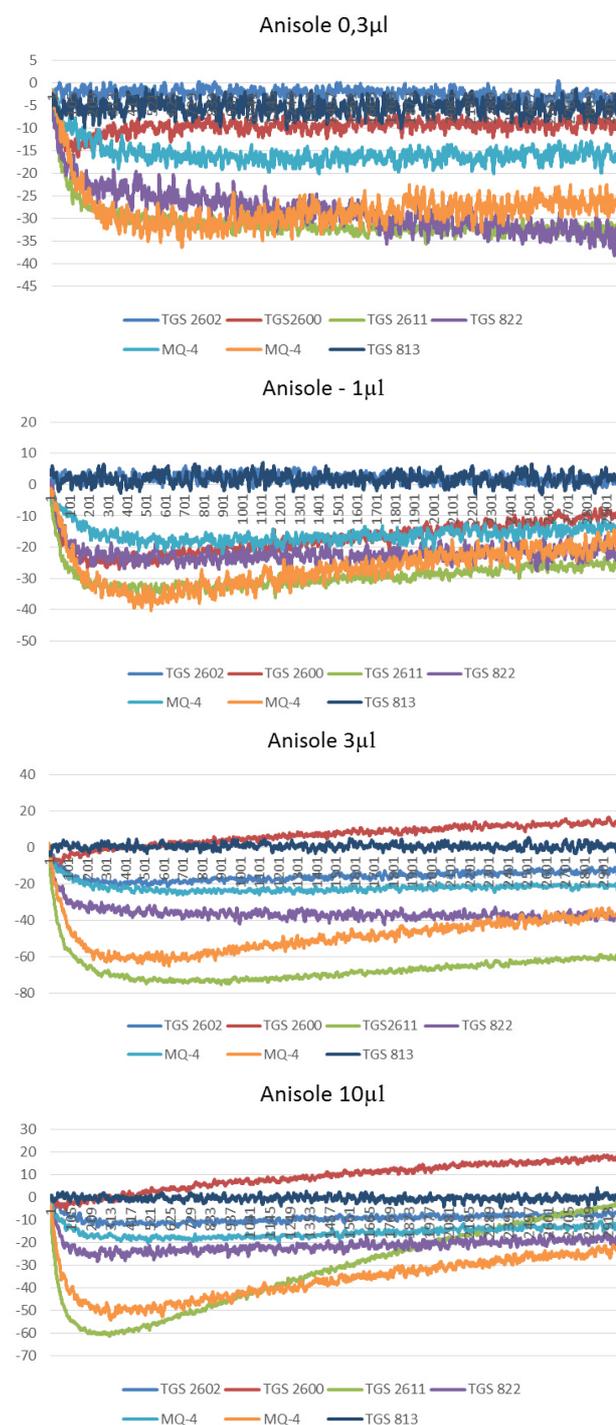
All of the compounds had the highest similarity with the corresponding standard, with exception of carvacrol, which had higher similarity with the standard of anisole, but with only small difference. The best similarity, 99.06%, was achieved for β -pinene, while the lowest for the abovementioned carvacrol, 90.43%.

Tab. 1. Comparison of the similarity values between plant volatiles

Samples	Standards measured				
	anisole	β -pinene	β -citronellol	carvone	carvacrol
anisole	98.08%	94.95%	75.67%	81.45%	86.47%
β -pinene	94.57%	99.06%	73.20%	80.50%	83.52%
β -citronellol	81.11%	78.80%	91.95%	88.21%	86.61%
carvone	81.19%	81.13%	78.58%	94.02%	79.62%
carvacrol	90.80%	87.68%	80.16%	82.65%	90.43%

In Fig. 2 comparison of the curves obtained with different concentrations of anisole is displayed. When the R^2 were compared for different sensors in different times of measurement, significant variances can be seen (Tab. 2). The best results were obtained for two sensors TGS 2611 and MQ-4. These were the only sensors that achieved higher than 0.99 R^2 value, both of them in two similar times and one different. The two similar times of the highest correlation were 40 and 60 seconds. A prototype of the electronic nose used for this study used six chemical sensors, five of which were Figaro TGS and one Parallax, which is important in order to increase the efficiency of the sensors as stated in the work Tang et al [6]. In their work a prototype of electronic nose has been used with very similar design to ours, with eight sensors Figaro, two of which, TGS 2602 and TGS 822, were included in our prototype. The work of Miao, Luo, Wang & Li [7] utilized electronic nose prototype containing all Figaro TGS sensors used in our prototype, with eight additional sensors. In contrast in the work by Sanaeifar, Mohtasebi, Ghasemi-Varnamkhasti, & Ahmadi [8] six different Parallax MQ sensors were used. Detailed study utilizing the possibility of e-nose in discrimination of natural and synthetic bergamot essential oils [3] was performed with commercial e-nose ISE Nose 2000 (ISE, Pisa, Italia), which is equipped with twelve Figaro TGS sensors. Discrimination between natural and processed or synthetic oil was very effective, the data describing different locations of bergamot production were no so significant, but with satisfactory results.

Fig. 2. Graphs obtained from different doses of anisole measurement



Professional electronic noses available on the market, such as Fox 4000, use multiple sensors, in this case 18 [9]. The more sensors, the more detailed spectrum is obtained. Our prototype with only six chemical sensors therefore cannot give as good results as a professional electronic noses, especially because the overall quality of the system is at a

higher level. On the other hand, costs of the system used in professional electronic noses are much higher and the results of our prototype is not significantly worse.

Tab. 2. R² for sensors in different times of measurement of anisole

Time (s)	R ² for different sensors					
	TGS 2602	TGS 2600	TGS 2611	TGS 822	MQ-4	TGS 813
1	0.6542	0.3349	0.7202	0.2447	0.9980	0.0012
10	0.8998	0.3366	0.9764	0.1912	0.9618	0.2359
20	0.8939	0.3175	0.9949	0.1166	0.9816	0.1679
40	0.9390	0.3785	0.9995	0.1285	0.9971	0.3964
60	0.9106	0.3662	0.9999	0.0880	0.9998	0.0882
120	0.9139	0.5080	0.9753	0.0778	0.9609	0.1923
180	0.8850	0.7143	0.9700	0.1350	0.8974	0.1638
240	0.9386	0.9375	0.9376	0.0283	0.7161	0.1468
299	0.9677	0.9376	0.8065	0.0573	0.5406	0.1268

Quantitative determination was conducted at doses of 0.3, 1, 3, 10 and 30 µl, and then the measured values were averaged. Lower concentrations was impossible to measure because the limit of detection is reached. It was shown, that the doses 10 and 30 µl are behind the linear range of the system, and therefore only values between 0.3-3 µl were included. A professional electronic nose Fox 4000 was used in the study by Zhu et al [9] for quantitative analysis. As the test material a sample of artificial raspberry flavor in the concentrations of 1, 2, 3, 4 and 5 mg/ml was used. The R² achieved was 0.99535, in comparison to 0.9999 in case of TGS 2611 in our study. Conversely Di Natale et al [10] in his work used electronic nose for the quantitative analysis of the components of red wine a. It was shown, that the analysis is affected by ethanol content. The good quantitative determination was achieved only in combination with electronic tongue.

The other parameters of the experimental systems than sensors could be also source of differences among particular systems. Most of the systems deliver the headspace sample to the measurement chamber in the stream of synthetic air. Our system utilizes the vacuum to suck the headspace. In fact there was seen a slight carryover of the samples between the measurements, especially when completely different samples were measured (data not shown). In this case the stream of air is probably better in washing off the residues of compounds, that are volatile, but still could condensate in a small amount on the inner surface of the tubing, chamber walls and sensors. Despite some drawbacks that our first prototype shows, the results are satisfactory. Our aim was to construct low-cost prototype, and that was achieved. The

overall material costs were below 200 USD (Tab 3.). The personal costs are hard to evaluate, but it should be noted, that all manufacturing procedures were performed by only semi-skilled persons.

Tab 3. Costs of the components

Component	Price (USD)
Power supply	8.5
3 solenoids	77.37
3 optocouplers	4.77
humidity sensor	6.25
display	9.5
Arduino ATMEga	13.58
4 channel relay module	4.21
5A power converter	3.79
SD card module	1
40 wires dupont	1.5
air flow connections	6.33
boxing	5
Printed circuit board	10
tubing	1
Sensors	
TGS 2600	3.5
TGS-813	7.21
TGS-822	7.58
TGS 2602	12.99
TGS2611	12.99
MQ4	4.5
Total	193.07

4. CONCLUSIONS

It was proven, that low-cost components could be used for the construction of electronic nose, and that the construction itself is possible by semi-skilled persons and the results are still comparable to the professional systems.

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