CHARACTERIZATION OF ODORANT AREAS IN THREE WINES FROM LOCAL GRAPE VARIETIES FROM REPUBLIC OF MOLDOVA USING GAS CHROMATOGRAPHY – OLFACTOMETRY

CARACTERIZAREA ZONELOR ODORANTE A TREI VINURI DIN SOIURI AUTOHTONE DIN REPUBLICA MOLDOVA UTILIZÂND GAZ CROMATOGRAFIA – OLFACTOMETRIA

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Abstract. *Three wines from local grape varieties from Republic of Moldova were submitted to both sensory and gas chromatography – olfactometry analyses (GC-O). Through descriptive analysis, a set of aroma attributes has been described, but the volatile compounds responsible for the characteristic sensory notes have not been investigated. In order to identify these odor active compounds, the wines were evaluated using qualitative detection frequency analysis (n=7). The panelists generated in total 697 descriptions distributed in 126 odorant areas (OAs), but only 565 (81 %) distributed in 45 OAs were validated as being representative.*
Key words: gas chromatography – olfactometry, detection frequency analysis, odorant area.

Rezumat. *Trei vinuri din soiuri autohtone din Republica Moldova au fost supuse analizei senzoriale şi gaz cromatografiei – olfactometriei (GC-O). Analiza descriptivă a generat un şir de caracteristici aromatice, însă compuşii volatili responsabili de notele aromatice caracteristice nu fuseseră investigaţi. Pentru identificarea acestor compuşi, vinurile au fost evaluate prin metoda frecvenţelor de detecţie (n=7). Evaluatorii au generat în total 697 descriptori distribuiţi în 126 zone odorante, însă numai 565 (81 %) distribuiţi în 45 zone odorante au fost validaţi ca fiind reprezentativi.*
Cuvinte cheie: gaz cromatografie – olfactometrie, metoda frecvenţelor de detecţie, zonă odorantă.

INTRODUCTION

The gas chromatography-olfactometry (GC-O) is an analytical method that combines the gas chromatography and sensory perception, using the human nose as a detector to assess odor components. The human nose has an odor detection limit of about 10^{-19} moles, making GC-O an extremely valuable and sensitive tool for odor detection (Grosch W., 2000).

After injection, the content of the sample (the extract) is separated by the chromatographic column. Before leaving the column, the effluent is divided into

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two parts: the smallest is directed to the instrumental detector, usually a flame ionization detector (FID); the largest part is directed to a smelling device (sniffing port) placed at the evaluator's nose height. Therefore, this method provides simultaneously two signals: the chromatogram of the extract and the recording of odor events perceived by assessors (Le Guen et al., 2000).

In order to perform this analysis, three methods can be used: successive dilution of an aroma extract, direct estimation of the intensity and detection frequency of odorant areas.

The odorant areas frequency is correlated to the concentration logarithm of the compound responsible for stimulus. This relationship is based on the hypothesis that, for a certain compound, the perception thereshold has a Gaussian distribution. Each assessor must perceive the beggining and the end of the flavor and describe it. The individual aromagrams are summed, yelding the global aromagram where frequence of detection is represented in dependence on time or retention index. In both cases, the olfactometric indices can be used for ranking odorant areas in function of their olfactory impact (Pollien et al., 1997).

The odorant areas obtained via GC-O are characterized by three parameters: olfactometric index, average linear retention index (LRI) or LRI interval and flavor descriptors. All this information is used later in the identification of compounds.

Some studies reinforce that ILR and descriptors are not enough for individualization of odorant areas (Le Fur et al., 2003). Authors relied on the morphology of chromatograms by peak numbering and on the LRI interval. In this study were defined five types of odorant areas:

1 – associated with an isolated peak, well separated from other peaks;
2 – associated with a part of the chromatogram without peak;
3 – extended, associated with a wide peak;
4 – located within a very wide peak;
5 – associated with two relatively separated consecutive peaks and which descriptors are used to distinguish two successive zones.

MATERIAL AND METHOD

For analysis were used wines made from local grape varieties: Startovyi, Hibernal and Muscat of Ialoveni (harvest 2010) produced at the Practical Scientific Institute of Horticulture and Food Technology from Chişinău.

In order extract aromatic compounds was used the dichloromethane extraction, based on the method proposed by Moio (Moio et al., 1995).

The olfactometric analysis was performed on 3 extracts by 7 assessors selected in advance and informed that they will analyze three white wines, but no other detail has been specified. The extracts were analyzed by the participants in a different and balanced sequence. Total length of a session was 45 minutes. After injection of the solution into chromatograph column, in order to avoid inhalation of the solvent, the assessor was announced to wait 5 minutes before approaching the nose to the sniffing port (fig. 1).

Fig. 1 – Sniffing-port (with the glass nose mold), button and microphone for recording

Gas chromatograph Hewlett-Packard 5890 was equipped with split/splitless injector and DB-1701 capillary column. Simultaneous processing of both signals was performed using EZchrom Elite (Agilent Technologies) and AcquiSniff ® (© INRA) software. The FID signal was recorded on the computer through channel A and the olfactometric signal through channel B.

Linear retention indices (LRI) of chromatographic peaks and odorant events were calculated using a daily injection of a solution of 13 n-alkanes (from C_7 to C_{19}), analyzed under the same chromatographic conditions as the extracts.

The results of each individual data processing were presented in Excel tables where the LRI peak, the assessor codes, the extract codes and their respective descriptors were indicated. Therefore, 21 tables with olfactometric data were obtained (3 wines x 7 assessors), that subsequently were submitted to mathematical processing. Mathematical processing of olfactometric data was performed using Matlab ® (The Mathwork Inc.), which implements an iterative mathematical function to get a table that contains the number of detections for each tandem wine/odorant area.

RESULTS AND DISCUSSIONS

Initially the wines were submitted to sensory analysis sessions (tab. 1). Though considerable dispersion of responses, it was achieved conclusive data. The intensity of wine aroma was appreciated with values within a range from 62.5 to 75 points out of 100.

Table 1

Descriptors set out by tasters during the sensory evaluation

The wine	Types of aromas			
	Floral	Fruity	Vegetal	Spicy
Startovyi	Honey	Pear, apple, lemon	Freshly cut hay	Pepper, coconut
Hibernal	Basil, thyme	Pomelo, grapefruit	Herbaceous	Laurel leaves, paprika
Muscat of Ialoveni	Muscat intense, acacia flower	Citrus, pineapple	Celery	Nutmeg

The olfactometric study, performed by using frequency detection method, generated 21 individual aromagrams. Global data of olfactometric analysis are cumulated in table 2. The total number of odorant events related to each wine is situated between 228 (Muscat of Ialoveni) and 238 (Hibernal), meaning that for three wines, seven assessors had spotted 697 events. The assessors, with some exceptions, have described each event with only one term, the report terms / events being nearly 1.1.

Table 2

Global data of olfactometric analysis

The wine	Total odorant events	Total descriptors	Events without description	% Events without description
Startovyi	231	259	22	8,5%
Hibernal	238	272	26	9,5%
Muscat of Ialoveni	228	250	31	12,4 %
Total 3 wines	697	781	79	10,1 %

In order to process data obtained by using Matlab® software, it was previously set an eliminatory threshold. This corresponds to the value of first quartile of distribution, i.e., to consider an odorant area as representative it must contain at least 5 odor events. Of the totality of 697 odor events, 565 (81%) were distributed within 45 odorant areas that contain at least 5 events per area. Consequently, the areas with the number of events lower than the eliminatory threshold have been removed (fig. 2).

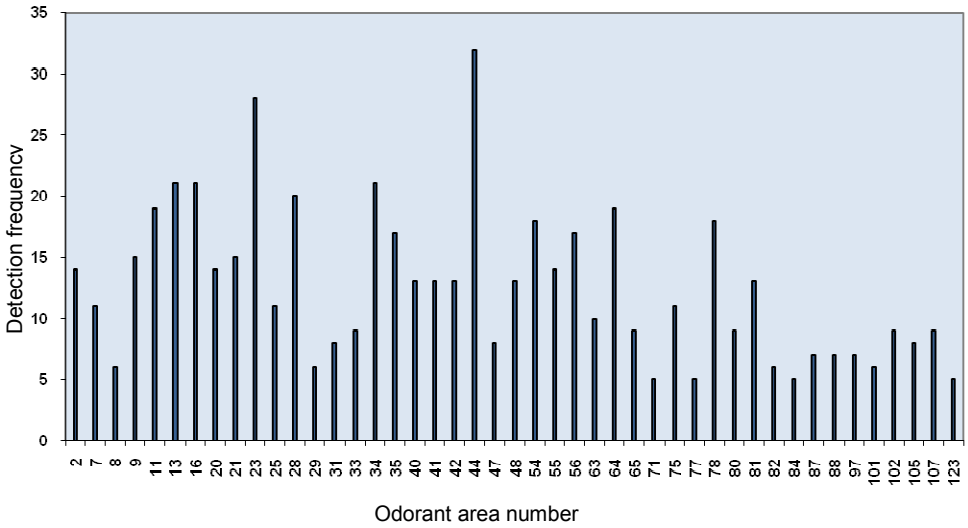

Fig. 2 – Global aromagram of studied wines

The results obtained by GC-O analysis were summarized in table 3. It is provided further identification of odorant compounds responsible for odor events from the described areas.

Table 3

Characteristic of representative odorant areas for studied wines

Area number*	LRI **	Detection frequency	Odorant area description
2	695	14	Yoghurt, cream, butter
7	766	11	Fruity, solvent
8	770	6	Vinegar, pungent
9	778	15	Fruity, brandy
11	816	19	Fruity, strawberries, pineapple
13	845	21	Cocoa, chocolate, yeasty
16	862	21	Tutti frutti, strawberries, raspberries
20	906	14	Fruity, kiwi, pineapple
21	912	15	Fruit candy, linden, verbena
23	938	28	Peanuts, roasted, banana, pear
25	957	11	Cheese
28	1009	20	Cheese, rancid
29	1014	6	Apple, cheese
31	1027	8	Dried herbs
33	1053	9	Cooked potatoes, gnocchi
34	1060	21	Fruit candy, apple, citrus
35	1074	17	Black currant buds
40	1149	13	Flowers
41	1154	13	Sulfurous, plastic
42	1174	13	Fruity, balsamic
44	1194	32	Lily of the valley, lavender, citrus, marshmallows
47	1235	8	Caramel, chocolate
48	1240	13	Cotton candy, caramel
54	1284	18	Honey, rose, lilac
55	1292	14	Flowers
56	1305	17	Caramel, cotton candy
63	1350	10	Cheese, smoky, dusty
64	1357	19	Spicy, curry, fennel
65	1371	9	Bergamot, citrus
71	1432	5	Licorice
75	1473	11	Floral, herbaceous
77	1489	5	Chemical, pharmaceutical
78	1494	18	Balsamic, clove, curry
80	1508	9	Polyfloral honey
81	1512	13	Prune, floral, smoky
82	1518	6	Clove
84	1529	5	Spicy
87	1545	7	Mineral
88	1550	7	Floral, herbaceous

97	1619	7	Fruity, vegetal
101	1644	6	Sulfurous, fermented
102	1662	9	Vanilla
105	1728	8	Mulled wine, balsamic
107	1748	9	Coconut
123	1909	5	Fruity, berries

* Odorant areas that contain at least 5 events per area;
** average LRI in DB-1701 capillary column (30 m x 0,32 mm x 1 μm).

CONCLUSIONS

1. Olfactometry analysis (GC-O) allows the selection of odorant compounds using human analyzer, sequentially combining gas chromatography (instrumental analysis) and sensory perception (subjective analysis), thus being a very precious technique for detection of compounds with higher detection threshold than their concentration in wine, and thereby solving some problems in the aroma analysis.

2. The central method of this research was the olfactometry analysis by using the detection frequency method to generate 21 individual aromagrams, which were later summed into a global aromagram for all three wines.

3 According to mathematical processing of experimental data using Matlab® software, it was established that out of 697 odor events spread in 123 odorant areas, 565 (81%) were distributed within 45 odorant areas that contain at least 5 events per area.

4. By analyzing the global aromagram, it can be concluded that the odorant areas have well separated peaks (odor events), except the odor events of compounds with a perception threshold inferior to the sensorial capacity of assessors, as well as differences between their ability to recognize a flavor.

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