

GAS CHROMATOGRAPHIC BOUQUET QUALIFICATION OF WINES. PART IV. APPLICATION OF THE PROCESS DEVELOPED FOR THE TESTING OF HUNGARIAN HIGH-QUALITY WINES OF IDENTICAL CHARACTER*

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Introduction

To increase the efficiency of control of the commercial quality of food-stuffs and commercial goods undergoes intensive research all over the world. However, the elaboration of objective qualifying processes, directly utilizable in practice, is made rather difficult by the fact that the primary characteristics of these products are organoleptic, and thus, subjective properties.

To contribute to the solving of the problem, experiments were carried out, selecting as model substance Hungarian wines, and bouquet as the organoleptic property tested. Results of these experiments satisfy first of all the requirements of commercial quality control: an easy and rapid head-space analysis, suitable for routine tests, has been developed [1]. Under consideration of a multidirectional view-point system, the following relationship has been defined between the magnitude of the areas enclosed by the chromatographic peaks obtained in head-space analysis and the quality (richness) of the bouquet [2]:

$$I_j = \frac{3 \cdot \frac{\bar{T}_1}{\bar{T}_{1v}} + 3 \cdot \frac{\bar{T}_2}{\bar{T}_{2v}} + \frac{\bar{T}_3}{\bar{T}_{3v}}}{3 \cdot \frac{\bar{T}_4}{\bar{T}_{4v}} + 3 \cdot \frac{\bar{T}_5}{\bar{T}_{5v}} + \frac{\bar{T}_6}{\bar{T}_{6v}}}$$

where:

I_j is the so-called bouquet qualification index of the j -th wine sample tested;

\bar{T}_i ($i = 1-6$) is the average magnitude [mm^2] of the area enclosed by the gas-chromatographic peak belonging to the i -th aroma component of the j -th wine sample tested;

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\bar{T}_{iv} ($i = 1-6$) is the average magnitude [mm²] of the area enclosed by the gas-chromatographic peak, belonging to the same (i -th) aroma component of the reference wine.

The criterion for qualifying the bouquet as different (or identical) has been deduced as a refinement of our approximation formula [2], starting from Welch's analysis [3]. According to this quadratic discriminance analysis, the bouquets of two wine samples, characterized by the two bouquet qualification indices I_j and I_j , can be considered as different with a probability P_k belonging to the t_{fP} value, if

$$\frac{I_j}{I_j} > \frac{1 + t_{fP} \cdot s_{I_r} \sqrt{\frac{n + m - t_{fP}^2 \cdot s_{I_r}^2}{m \cdot n}}}{1 - \frac{t_{fP}^2 \cdot s_{I_r}^2}{m}} \quad (2)$$

(If $\frac{I_j}{I_j}$ is less than the right side of inequality (2), then the compared bouquets can be considered with a probability $P_a = 1 - P_k$ as identical.)

Relationship (2) comprises the following quantities:

s_{I_r} is the relative standard deviation of the bouquet qualification index, the magnitude of which is determined by the $\frac{sT_i}{\bar{T}_i}$ relative standard deviations, which can be assigned to the areas enclosed by the peaks of aroma components $i = 1-6$:

$$s_{I_r}^2 = \frac{3^2 \left(\frac{\bar{T}_1}{\bar{T}_{1r}} \right)^2 \cdot \left(\frac{sT_1}{\bar{T}_1} \right)^2 + 3^2 \left(\frac{\bar{T}_2}{\bar{T}_{2r}} \right)^2 \cdot \left(\frac{sT_2}{\bar{T}_2} \right)^2 + \left(\frac{\bar{T}_3}{\bar{T}_{3r}} \right)^2 \cdot \left(\frac{sT_3}{\bar{T}_3} \right)^2}{S_z^2} + \frac{3^2 \left(\frac{\bar{T}_4}{\bar{T}_{4r}} \right)^2 \cdot \left(\frac{sT_4}{\bar{T}_4} \right)^2 + 3^2 \left(\frac{\bar{T}_5}{\bar{T}_{5r}} \right)^2 \cdot \left(\frac{sT_5}{\bar{T}_5} \right)^2 + \left(\frac{\bar{T}_6}{\bar{T}_{6r}} \right)^2 \cdot \left(\frac{sT_6}{\bar{T}_6} \right)^2}{N^2} \quad (3)$$

where: S_z is the numerator and N the denominator of relationship (1).

(Using our experimental data published earlier [2], the average value of s_{I_r} was found in the investigation of bottled sample populations to be 0.0544). t_{fP} is the probability limit, which can be looked up in the Student's distribution table in knowledge of the selected confidence P_k and the distribution parameter f . On the basis of several theoretical and practical considerations [3], we recommend the calculation of the f value, starting from Welch's statistics, in the following way:

$$\frac{1}{f} = \frac{1}{(n+m)^2} \left(\frac{m^2}{n-1} + \frac{n^2}{m-1} \right) \quad \text{and} \quad f = 2(n-1) \quad (4)$$

(if $m \neq n$) (if $m = n$)

n and m are the numbers of samples analyzed from the j -th and from the j' -th wine varieties, resp.

The objective bouquet qualifying process briefly outlined above qualifies the bouquet of the samples of a given wine variety of identical vintage and bottling — with the exception of a few flagrant cases — by definition as identical. Thereby, the process is suitable to distinguish between the bouquet quality of the population of different wine varieties or of different vintages and bottlings of a given wine variety. The confidence of qualification and the number of the test samples can be discretionally selected by the user, to suit best the given problem.

Experimental objects

In the elaboration of the process serving for the objective bouquet qualification of wines, the aromagrams of varieties representing a relatively wide quality region (from Tokaji Aszu to Hárslevelű (linden-leaf) from Debrő) were started from, in the interests of safe organoleptic calibration. In the definition of the mathematical form of the bouquet qualification index, samples of sweet Tokaji Szamorodni (vintage of 1967, bottled in Mád) were used as reference. Thereby, in relationship (1) the numerical values

$\bar{T}_{1v} = 181.6$; $\bar{T}_{2v} = 97.7$; $\bar{T}_{3v} = 137.9$; $\bar{T}_{4v} = 33.1$; $\bar{T}_{5v} = 122.2$ and $\bar{T}_{6v} = 279.4$ were substituted [2].

Though good results were obtained with the so-called basic process developed in this way, actual conditions were likely to be still closer approached by suitable modifications. This modification involves that the method developed is not uniformly applied to wines of different character, but, leaving essentially the mathematical form of the index unchanged, always a representant of the given relatively narrow quality interval is used as reference instead of sweet Tokaji Szamorodni. (In this way it can be attained namely that relationship (1) shall contain, besides the general characteristics, also the unique character of the wine to be qualified.)

Investigations in this direction were begun with the study of individual samples of considerably poorer quality than that of the calibrating varieties [4]. It has been proven that the original mode of calculation and the modified mode of calculation, including also the character of the wine tested, are not equivalent. However, the superiority of the latter could not be practically proven without overstepping the requirements of safe organoleptic evaluation.

It should be emphasized here that a process qualifying instrumentally some organoleptic characteristic cannot be infinitely "refined", as for example a law of nature. While the latter must be namely in harmony with cognizable

objective reality, the first must be in keeping with organoleptic evaluation. Therefore, in the precisising of our method elaborated for the qualification of the bouquet of wines, results obtained must be repeatedly compared with the evaluation of oenologists.

Experimental results and their evaluation

The pertinence of the method and the necessity of possible modifications were checked by organoleptic and instrumental comparison of the bouquet of Hárslevelű and Muskotály samples, high-quality Hungarian commercial wines of identical character.

In each case the contents of 5 bottles were analyzed, carrying out 5 parallel tests on samples from each bottle. (In view of the large number of the aromagrams obtained, only one is presented here by way of example, see Fig. 1.)

The results of head space analysis, i.e. the average magnitude (in mm^2) of the areas enclosed by the gas-chromatographic peaks belonging to the single aroma components, are shown in Tables I and IV. The bouquet qualification indices I_j obtained with the basic process, i.e. using the data of sweet Tokaji

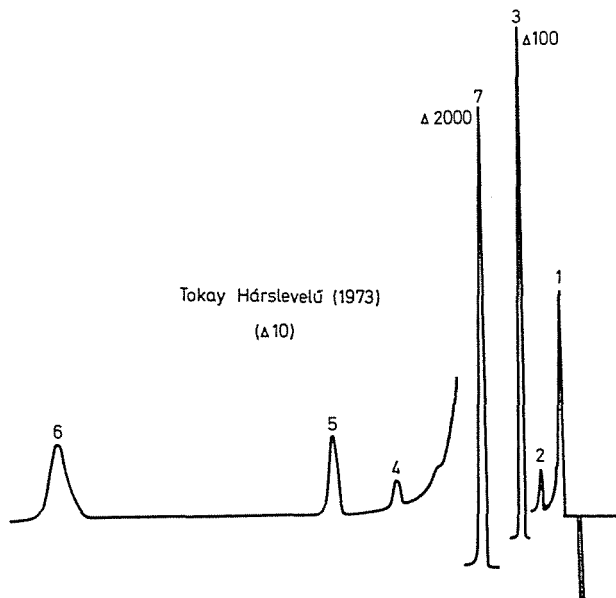


Fig. 1. Aromagram of Tokaji Hárslevelű (1973) obtained by head space analysis
1. Acetaldehyde; 2. Ethyl formate; 3. Ethyl acetate; 4. n-Propanol + butyl acetate;
5. Isobutanol + isoamyl acetate; 6. Isoamyl alcohol; 7. Ethanol

Szamorodni (1967, Mád) as reference wine, and the ratios $\frac{I_j}{I_{j+1}}$ of the bouquet qualification indices of wine varieties following each other in the organoleptic order of bouquet are also given in these tables.

It can be established on the basis of the data that according to the basic process developed, the bouquet quality of the Hárslevelű wine samples listed in Table I improves upwards from below. The confidence of qualifying as "different" is better in all the cases than 99.9% (see values in Table II calculated on the basis of relationships (2)–(4)).

Table I

Results of the instrumental bouquet qualification of Hárslevelű wine varieties obtained by the basic method (reference: sweet Tokaji Szamorodni)

Wine sample	\bar{T}_1	\bar{T}_2	\bar{T}_3	\bar{T}_4	\bar{T}_5	\bar{T}_6	I_j	$\frac{I_j}{I_{j+1}}$
Tolcsvai Szentvéri Hárslevelű (1973)	203.7	30.8	148.2	29.1	136.3	268.9	0.776	1.419
Tokaji Hárslevelű (1973)	81.3	24.5	208.3	30.9	119.7	238.0	0.547	
Tokaji Hárslevelű (1972)	103.1	25.8	98.2	27.5	164.9	252.4	0.431	1.269
Debrői Hárslevelű (1975)	17.5	10.7	63.0	29.6	134.9	159.7	0.164	2.628

Table II

Criteria for distinguishing with a probability P_k between the bouquets of bottled wine samples in the case of a given ($m = n = 5$) number of samples

Differing by bouquet with a probability P_k	if $\frac{I_j}{I_j} >$
99.9%	1.261
99.0%	1.170
95.0%	1.115
90.0%	1.092
80.0%	1.069
75.0%	1.061
60.0%	1.044

Wine experts invited by us established for the samples of the same vintage and bottling (!) the same order as that obtained by instrumental analysis. However, according to their opinion, the bouquet qualities of the 1972 and 1973 vintage samples of Tokaji Hárslevelű can be considered as very close, almost as identical.

This slight "difference in opinion" justified already to contemplate a changing over to a reference wine of identical character.

To evaluate the effect of modification, the Tokaji Hárslevelű of vintage 1973, representing both in the organoleptic and instrumental order of bouquet an intermediate quality, has been considered in the further as reference. Thus, the values $\bar{T}_{1v} = 81.3$; $\bar{T}_{2v} = 24.5$; $\bar{T}_{3v} = 208.3$; $\bar{T}_{4v} = 30.9$; $\bar{T}_{5v} = 119.7$ and $\bar{T}_{6v} = 238.0$ were substituted in relationship (1).

With the aid of this modified process, the bouquet qualification indices $I_{j\text{Hárslevelű}}$ and their ratios have been determined, shown in Table III. On comparing $\frac{I_j}{I_{j+1}}$ data in this table with the respective data in Table I, it can be established that the basic and the modified processes give a fundamentally identical order of bouquet quality, but they are not equivalent in the evaluation of differences.

For drawing further conclusions, it must be investigated first, whether the conditions of the qualification "different (or identical) bouquet" did not change in the latter case.

Among quantities in the inequality (2), furnishing these criteria, modification, that is to say, changing of the \bar{T}_{iv} values, can affect only s_{I_i} , the average

Table III

Results obtained in the instrumental bouquet qualification of Hárslevelű wine varieties by the modified process

(Reference: Tokaji Hárslevelű, 1973)

Wine sample	$I_{j\text{Hárslevelű}}$	$\frac{I_j}{I_{j+1}}$ (Hárslevelű)
Tolcsvai Szentvéri Hárslevelű (1973)	1.628	1.628
Tokaji Hárslevelű (1973)	1.000	
Tokaji Hárslevelű (1972)	0.945	1.058
Debrői Hárslevelű (1975)	0.326	
		2.899

relative error of the bouquet qualification index. The magnitude of this error is given by relationship (3) in a general form, making possible its determination at any $\frac{\bar{T}_i}{\bar{T}_{i_0}}$ ($i = 1-6$) ratio. It can be concluded already from the mathematical form of this relationship that the numerical value of s_I , will be independent of these values within relatively wide limits.

To verify that the changes are actually within the limits of error, the relative errors of the Hárslevelű wine samples from Tokaj and Debrő were compared by F-test. (For the calculations, relative errors published earlier [2] for the aroma components 1-6 of these wine varieties have been used.)

After having established that the criteria for the qualification "different bouquet", determined for the application of the basic process are virtually identical with the conditions to be satisfied in the application of the modified method, the following conclusions could be drawn:

Samples of Tolcsvai Szentvéri Hárslevelű and Tokaji Hárslevelű (vintage 1973), further of Tokaji Hárslevelű (vintage 1972) and Debrői Hárslevelű were qualified by the modified process to differ by more, than were by the basic method. On the other hand, the difference in bouquet of the vintages 1973 and 1972 of Tokaji Hárslevelű proved to be less by changing over to a reference of identical character, in accordance with organoleptic evaluation. (As contrary to the virtually complete confidence of the basic process, the modified method gave preference with a probability of only 75% to the vintage of 1973.)

Since after elimination of the minor insufficiencies of the basic method, the results of the modified process agreed in every respect with the evaluation of the oenologists, it could be established that changing over to an "internal standard" in the investigation of wines of Hárslevelű varieties increased the accuracy of our bouquet qualification method.

On the other hand, in the case of Muskotály samples of a rather similar character to the original reference, to sweet Tokaji Szamorodni, the following results were obtained:

For the wine varieties listed in Table IV, the basic process established — in accordance with the evaluation of the oenologists — a bouquet quality decreasing downwards from the top. The bouquets of Tokaji Muskotályos vintages 1973 and 1975 further the bouquets of the Muskotály varieties from Badaacsony and Boglár, here too in accordance with the results of organoleptic tests, were distinguished with complete confidence (see data in Tables II and IV).

At the same time, the basic method could distinguish between the bouquets of Tokaji Muskotályos (vintage 1975) and Badaacsonyi Muskotály at a probability as low as 80%. The oenologists did not find either a substantial difference between the bouquets of these wine varieties.

Thus, in the investigation of Muskotály samples, the basic process developed for the objective qualification of the bouquet of wines furnished results

Table IV

Results obtained in the instrumental bouquet qualification of Muskotály wine varieties by the basic process

(Reference: sweet Tokaji Szamorodni)

Wine sample	\bar{T}_1	\bar{T}_2	\bar{T}_3	\bar{T}_4	\bar{T}_5	\bar{T}_6	I_j	$\frac{I_j}{I_{j+1}}$
Tokaji Muskotályos (1973)	48.1	32.7	168.4	34.0	109.0	152.8	0.479	} 1.687 } 1.072 } 1.497
Tokaji Muskotályos (1975)	5.1	30.6	125.5	30.9	134.3	195.2	0.284	
Badacsonyi Muskotály (1975)	10.3	24.1	150.2	32.3	150.2	258.1	0.265	
Boglári Muskotály (1976)	11.5	18.5	61.2	33.3	128.7	172.9	0.177	

correct in every respect, which were fully in accord with the evaluation of expert organoleptic qualificators. Therefore, there was no reason to modify the basic process, and sweet Tokaji Szamorodni is recommended also further on as reference. However, the possibility cannot be excluded that in the course of future practical application, the basic process will be modified also in the case of Muskotály samples, under utilization of the test results by oenologists.

Summary

The authors developed earlier a vapour testing method based on gas chromatographic head-space analysis. After the definition of a so-called bouquet qualification index, a relationship has been established between the quality of the bouquet of wines and the magnitude of the areas enclosed by the peaks obtained. As reference, the respective values of sweet Tokaji Szamorodni have been used.

Using high-quality Hungarian wines of identical character, the present report is discussing refinement of the method in several directions. It has been established, on the one hand, that in the comparison of the bouquet of Hárslevelű samples, the changing over to a reference of identical character furnishes data still in better agreement with the evaluation of oenologists, while in the case of Muskotály samples such change-over is unnecessary.

On the other hand, a novel mathematical apparatus is briefly outlined, the application of which in objective quality control is thought to have wide possibilities.

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