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UNCERTAINTY OF ANALYTICAL RESULTS IN OENOLOGY LABORATORIES

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ABSTRACT – The analytical results (measurements/determinations) concerning the parameters of wine chemical composition and must and wine-based products have shown some uncertainty or doubt. The oenology laboratories must determine the uncertainty of analytical results for each measured parameter, according to the used analysis method, for checking trueness and certainty of the method. In this scientific paper, the authors have shown the uncertainty calculation methodology and the interpretation of uncertainty values according to the analytical results.

Key words: uncertainty, accuracy, trueness, analytical results, oenology

Rezumat – Incertitudinea rezultatelor analitice în laboratoarele de oenologie. Rezultatele analitice (măsurătorile/ determinările) privind parametrii de compoziție chimică a vinurilor şi produselor pe bază de must şi vin sunt însoțite de o anumită incertitudine, îndoială sau nesiguranță. Laboratoarele de oenologie trebuie să-şi stabilească incertitudinea rezultatelor analitice pentru fiecare parametru măsurat, în funcție de metoda de analiză utilizată, pentru verificarea justeței şi fidelității metodei. În lucrare, autorii prezintă metodologia de calcul a incertitudinii şi interpretarea valorilor incertitudinii în funcție de rezultatele analitice.

Cuvinte cheie: incertitudine, exactitate, siguranță, rezultate analitice, enologie

INTRODUCTION

The measurements/determinations carried out in oenology laboratories show some uncertainty/doubt that should be determined according to the norms of the International Organization for Standardization (ISO 5725 norms). This determination is done for checking the trueness and accuracy of obtained analytical values (BIPM, CEI, FICC, ISO, OIML, UICPA, 1995; NF ISO 5725, 1981; Snakkers and Cantagrel, 2004).

The uncertainty/doubt expresses the possible error on the obtained analytical value and characterizes the

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interval/length field where the real value is found. The trueness / accuracy of the values of measurements expresses the tight correlation between the obtained results and the accepted reference value. The accepted reference value is the real conventional value, estimated on the basis of analytical results, obtained in more laboratories by the official method of analysis. The accuracy of measurements/ determinations expresses the tight connection between the independent analytical results, obtained in many laboratories, under working conditions established by ISO 5725 norms.

NECESSARY CALCULATION

Trueness /accuracy of analysis. They calculate the mean value (*M*) of the chemical composition parameter, which was studied on more samples (Bouvier, 2004; EURACHEM, 2003; United Kingdom Accreditation Service, 2000):

$$M = \frac{\sum \frac{(x - ref)}{tol}}{n}$$

where,
x = Obtained analytical values;
n = Number of samples;
ref = Analytical reference value;
tol = Tolerance value compared to reference value.

The mean value (*M*) is subunitary and is expressed in tolerance. If it has the value of 0.5, it means that, on the average, the results are greater by 0.5 tolerance, compared with the reference value.

It is likely to establish the trust/confidence interval, in order to know if the hypothesis M=0 is true. The trust interval is calculated by means of the following relationship:

$$M - \frac{t_{1-\alpha/2}(\gamma)S}{\sqrt{n}} \leq mean \leq M + \frac{t_{1-\alpha/2}(\gamma)S}{\sqrt{n}}$$

where,
M = Mean calculated value;
S = Calculated type-interval;
n = Number of calculated analytical values;
$1-\alpha$ = Trust level (if we consider 95%, α=0.05);
γ = Number degrees of freedom =n-1;
t= Values of the Student factor, for γ freedom degrees, trust level $1-\alpha$ (*Table 1*).

Table 1 – Values of $t_{1-\alpha/2}$

Number degrees of freedom	Trust/ confidence level	
	95%	99%
4	2.776	4.604
5	2.571	4.032
6	2.447	3.707
7	2.365	3.499
8	2.306	3.355
9	2.262	3.250
14	2.145	2.977

The formula of trust interval is for a mean in which the variance of population (determinations) is unknown.

Calculation of fidelity (dispersion), that is of the type-interval (*S*) that measures the dispersion of analytical values around the *M* mean.

The relationship:

$$S = \sqrt{\frac{\sum (Y - M)^2}{n-1}} = \sqrt{\frac{\sum \left(\frac{(x - ref)}{tol} - M \right)}{n-1}}$$

For the mean, *S* type-interval is subunitary, being expressed in tolerance. The *S* fidelity interval may be compared to 0.5, if it is expressed in subunitary value or with ½ tolerance, if it multiplies with the tolerance value.

The fidelity/confidence interval is given by the following relationship:

$$\sqrt{\frac{(n-1)S^2}{\chi^2_{1-\alpha/2}(\gamma)}} \le S \le \sqrt{\frac{(n-1)S^2}{\chi^2_{\alpha/2}(\gamma)}}$$

Where:
S = Estimated type-interval;
n = Number of calculated analytical values;
1-α = Trust level (if we consider 95%, α=0.05);
γ = Number degrees of freedom =n-1;
χ^2= Values of Hi-square of the Pearson Law at γ degrees of freedom and trust level 1-α (*Table 2*).

Table 2 – Values of χ^2

Number degrees of freedom	Trust/confidence level			
	95%		99%	
	$\chi^2_{\alpha/2}$	$\chi^2_{1-\alpha/2}$	$\chi^2_{\alpha/2}$	$\chi^2_{1-\alpha/2}$
4	0.484	11.1	0.207	14.9
5	0.831	12.8	0.412	16.7
6	1.24	14.4	0.676	18.5
7	1.69	16	0.989	20.3
8	2.18	17.5	1.34	22
9	2.7	19	1.73	23.6
14	5.63	26.1	4.07	31.3

Calculation of type uncertainty (accuracy/reference = trueness + fidelity) is done by summing up the mean values (*M*), that is the trueness of analysis and dispersion of analytical values around *M*, therefore the fidelity of analysis (*S*).

The *u* type uncertainty is:

$$u = \sqrt{M^2 + S^2}$$

Because for mean (*M*) and interval (*S*), the value of uncertainty is subunitary, it is expressed in tolerance. The type incertitude may be compared to 0.5, if expressed subunitary or to ½ tolerance, if it multiplies with the tolerance value. The trust interval for the type uncertainty is calculated with the following relationship:

$$\sqrt{\frac{(n-1)u^2}{\chi^2_{1-\alpha/2}(\gamma)}} \le \text{type uncertainty} \le \sqrt{\frac{(n-1)u^2}{\chi^2_{\alpha/2}(\gamma)}}$$

where:
u = Estimated type interval;
n = Number of analysis values for calculation of type interval;
1-α = Trust level (if we consider 95%, α=0.05);
γ = Number degrees of freedom =n-1;
χ^2 = Values of Hi-square of the Pearson Law at γ degrees of freedom and trust level 1-α (*Table 2*).

The wide uncertainty is calculated according to the relationship $U = 2u = 2\sqrt{M^2 + S^2}$.

The value of the *U* uncertainty shows the quality of the analytical results, obtained in the oenology laboratories.

INTERPRETATION OF UNCERTAINTY

According to ISO / IEC 25, laboratories will put at clients' disposal the necessary documentation through which were established the results of standardizing measurements, results - related uncertainties and estimate of conformity to specification.

The value of measurements may be found over or below the specification limit with a trust level < 95%. Therefore, the result of measurements is reported, together with the uncertainty value for the trust level of 95% (P = 95%): measurement value ± measurement uncertainty.

There might be some cases (ILAC, 1996; Snakkers and Cantagrel, 2004):

- The result of measurement is on the specification limit: product conformity or non-conformity cannot be declared. However, where there is a good trust level < 95% and the specification limit is defined as being ≤, the product conformity may be not declared. When the specification limit is lower, the product non-conformity may be declared.
- The result of measurement is below the lower limit of specification, with a smaller difference than half of the uncertainty interval, therefore, the product non-conformity cannot be declared. However, where there is an allowable trust level < 95%, the product non-conformity is possible.
- The result of measurement is over the lower limit of specification, even when it is diminished by half of the uncertainty interval. In this case, the product is in accordance with specification.
- The result of measurement is above the lower limit of specification, with a smaller difference than half of the uncertainty interval. In this case, the product conformity cannot be declared.
- The result of measurement is over the lower limit of specification, when it is higher by half of the uncertainty interval. In this case, the product is not in accordance with specification.
- The result of measurement is below the upper limit of specification, even when it is higher by half of the uncertainty interval. In this case, the product is in accordance with specification.
- The result of measurement is below the upper limit of specification,

with a smaller difference than half of the uncertainty interval. In this case, the product conformity to specification cannot be declared. However, where there is an allowable trust level < 95%, the product non-conformity is possible.

- The result of measurement is over the upper limit of specification, with a smaller difference than half of the uncertainty interval. In this case, the product conformity to specification can be declared. However, where there is an allowable trust level < 95%, the product non-conformity is possible.
- The result of measurement is over the upper limit of specification, even when it is diminished with half of the uncertainty interval. In this case, the product conformity to specification cannot be declared. The simplest case is when the specification expresses clearly that the result of measurement/determination, which is increased by uncertainty at a given trust level, must not exceed the specification limit.

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