RESOLUTION OENO 7/2000

ESTIMATION OF THE DETECTION AND QUANTIFICATION LIMITS OF A METHOD OF ANALYSIS

THE GENERAL ASSEMBLY,

IN CONSIDERATION of Article 5, Paragraph 4 of the International Standardization Convention on Methods of Wine Analysis and Rating of October 13, 1954,

ACTING ON THE PROPOSAL of the Sub-Committee on Methods of Wine Analysis and Rating,

HEREBY DECIDES to add the following "**Estimation of the Detection and Quantification Limits of a Method of Analysis**" to Annex A of the Compendium of International Methods of Wine Analysis.

1. PURPOSE: to establish the detection and quantification limits of a method

N.B. : The proposed calculation procedure sets « detection and quantification limiting » values with respect to the instrumental response. For a given method, the final calculation of these values must take cognizance of factors arising from the preparation of the sample.

2. DEFINITIONS

- Detection limit: the smallest concentration or proportion of the analyzed substance that can be detected with an acceptable level of uncertainty, but that is not quantified under the experimental conditions described in the method
- Quantification limit: the smallest concentration or proportion of the analyzed substance that can be quantified with an acceptable level of uncertainty, under the experimental conditions described in the method.

3. Logic Diagram for Decision-Making

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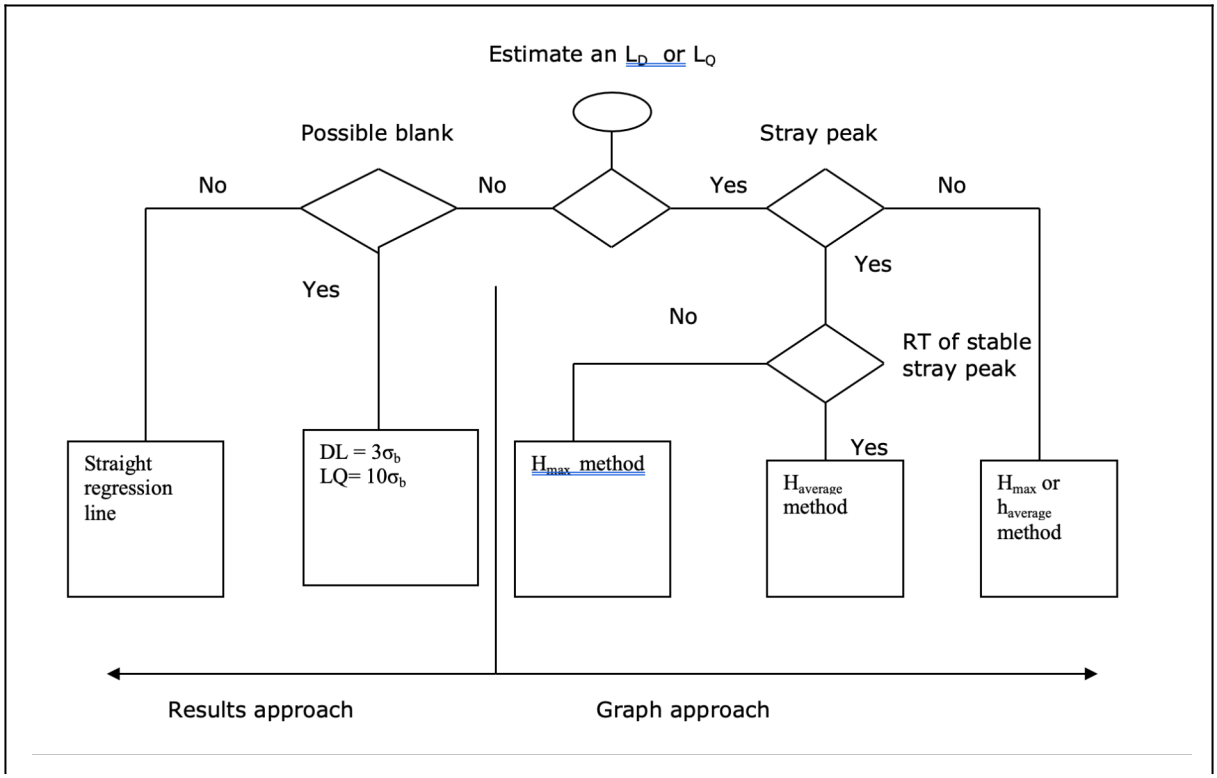

4. METHODOLOGY

4.1. "Results" approach

When the analytical method produces no recorded graph, but only numerical values (i.e., colorimetry), the detection limit (L_D) and the quantification limit (L_Q) are estimated using one of the two following methods.

4.1.1. Method 1:

Directly read n measurements (analyte quantity or response) of separate analytic « blank » samples that contain all of the constituents, with the exception of the substance to be tested for.

- LD = mblank + 3Sblank and
- LQ = mblank + 10Sblank

where m_{blank} and S_{blank} are the mean and standard deviation for n measurements.

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Note: A multiplication factor of 3 corresponds to a 0.13% chance of concluding that the substance sought is present, when, in fact, it is lacking. 10 corresponds to a 0.5% chance.

4.1.2. Method 2:

Using the straight calibration line: $Y = a + bX$

The detection limit is the smallest concentration of a substance that can be distinguished from the blank, with a 0.13% risk of retaining samples containing nothing ; in other words, the value beginning at which a statistical test comparing the response to 0 becomes significant with an error level □ of 0.13%. Hence:

- $Y_{DL} = a + 3S_a$
- $X_{DL} = (a + 3S_a)/b$

Where Sa is the standard deviation on the ordinate at the origin of the straight regression line. The logic is the same for $L_{Q,,}$ where the multiplication factor is 10 (risk of 0.5%).

4.2. "Graph" Approach

For analytical methods which generate graphs (i.e., chromatography), the detection limit is estimated based on the ground noise of the analytic blank recording for a given sample.

- $L_D = 3 \times h \times R$ (associated risk is below 0.13%) and
- $L_Q = 10 \times h \times R$ (associated risk is below 0.5%), where
  - h is the average or maximum amplitude of the signal window corresponding to 10 width s of the mid-height peak on either side of the retention time, as a function of stability.
  - R is the quantity/signal response factor expressed as a function of the quantity of substance/height.

On each occasion, three series of three injections each are performed on test blanks at an interval of several days.

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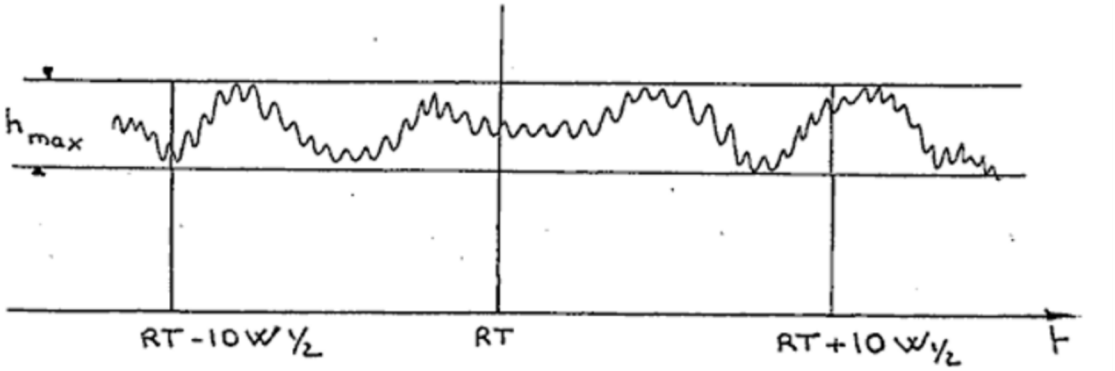
4.2.1. h_{max} method



- Increase ground noise to the maximum (Fig. 1 above)
- center around the retention time (RT) of the product
- draw a window of 10 widths of the mid-height peak (W1/2) on either side of the RT ;
- draw two parallel lines, one running through the highest point of the highest peak, the other through the base of the deepest trough ;
- evaluate height -> h_{max} ;
- calculate the response factor (R factor) ;
- $L_{Dmax} = 3 \times h_{max} \times R$
- $L_{Qmax} = 10 \times h_{max} \times R$

4.2.2. $h_{average}$ Method

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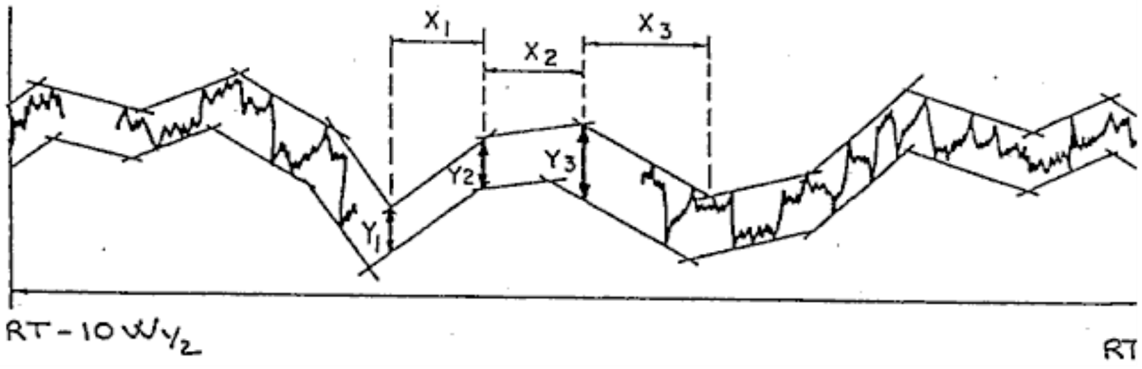

- increase the ground noise to the maximum (Fig. 2 above) ;
- center around the retention time (RT) of the product;
- draw a window of 10 widths of the mid-height peack (W1/2) on either side of the RT
- divide into 20 equal sections (x) ;
- draw two parallel lines in each block, one running through the highest point of the highest peak, the other through the base of the deepst trough ;
- measure the heights, y ;
- calculate the average ($y = h_{average}$);
- calculate the response factor (R factor);
- $L_{Daverage} = 3 \times h_{average} \times R$;
- $L_{Qaverage} = 10 \times h_{average} \times R$

These estimates can themselves be validated by injecting quantities of solute that are close to the calculated limits (Figures 3 and 4).

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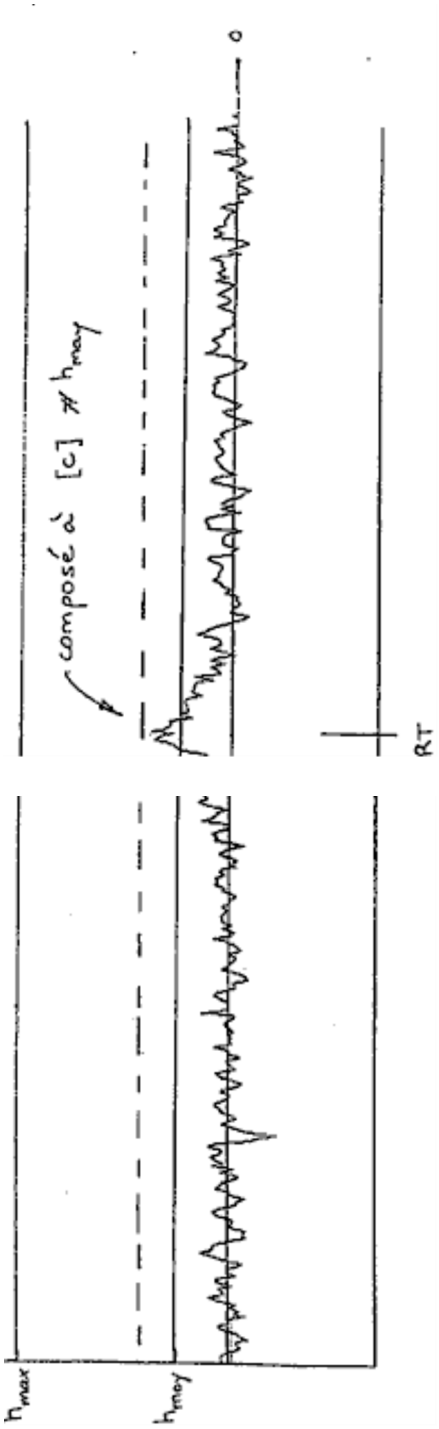

Compound at [c] # h_{max}

Figure No. 3: Validating calculations of limits.

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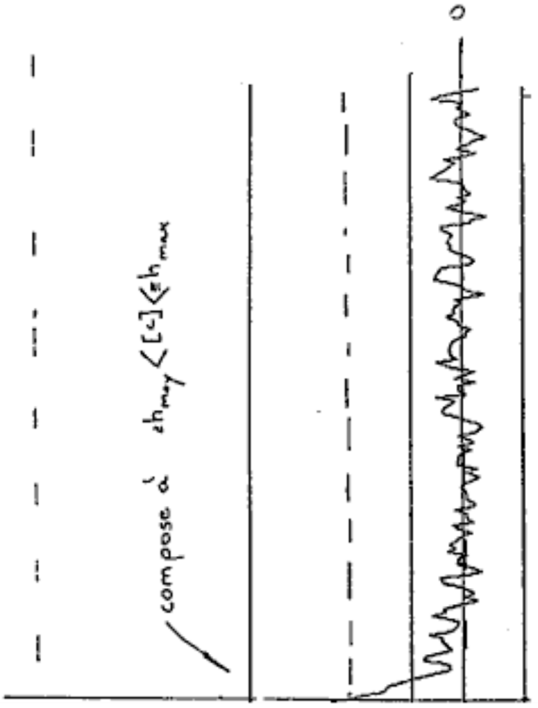
Concentration of the compound approaches $H_{average}$

N.B. : The dotted line corresponds to the real injected value however, since this figure is provided as an example, it may be deleted from the final text.



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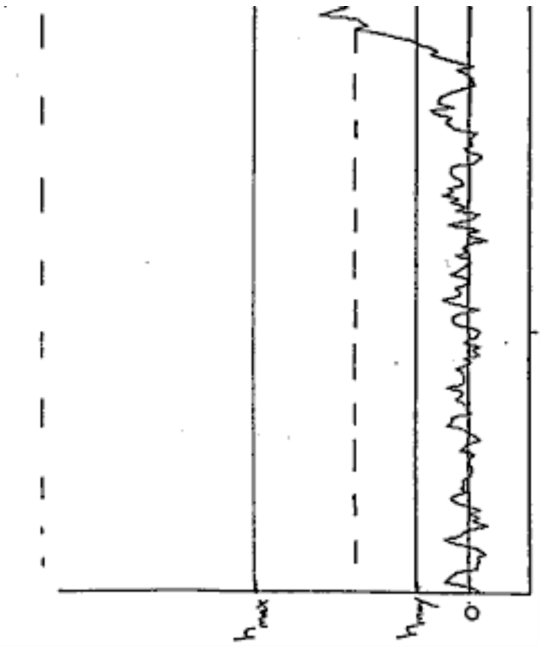

Compound at $h_{average} < [c] < \approx h_{max}$

Figure No. 4: Validating calculations of limits.

Concentration of compound between $H_{average}$ and H_{max}

N.B. : The dotted line corresponds to the real injected value; however, since this figure is provided as an example, it may be deleted from the final text.

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