Application of statistical tools for laboratory quality management aiming the ethyl carbamate (EC) monitoring in unsweetened cachaça

PAMELA APARECIDA GRIZOTTO 1, *IGOR RENATO BERTONI OLIVARES 2

1 University of São Paulo, Chemistry Institute of São Carlos (IQSC-USP), pamela.grzt@gmail.com

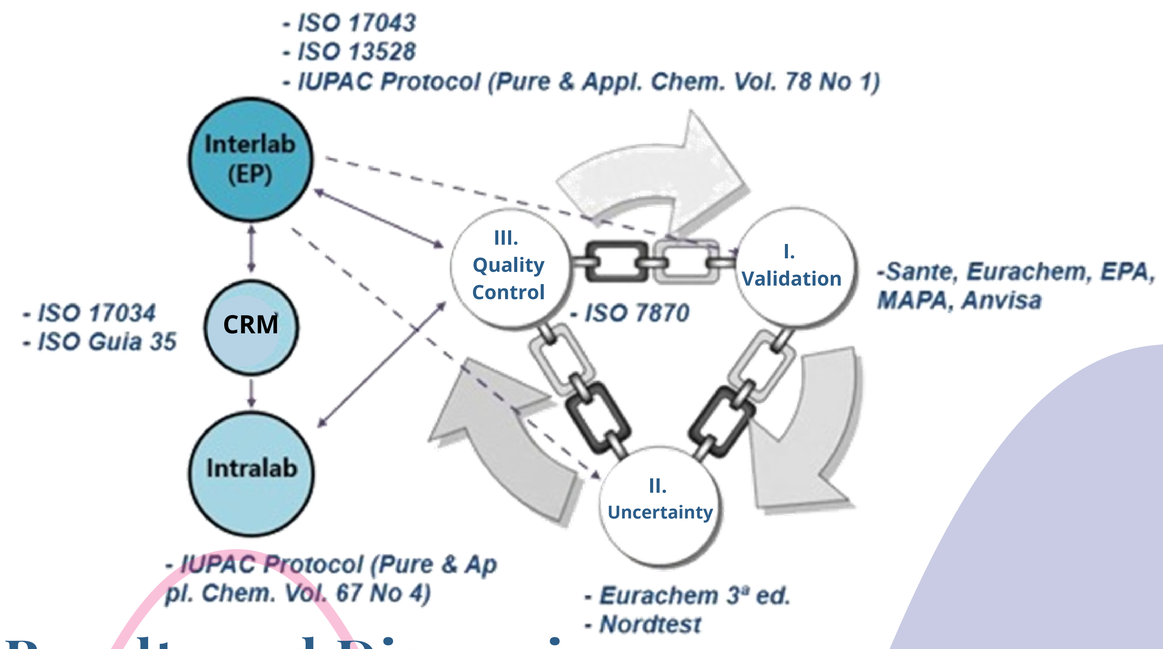
2 University of São Paulo, Chemistry Institute of São Carlos (IQSC-USP), igorolivares@iqsc.usp.br (corresponding author)

Introduction

In distilled beverages, the formation of ethyl carbamate (EC), a potentially carcinogenic organic compound, is common. For this reason, the Ministry of Agriculture, Livestock and Supply (MAPA) is interested in ethyl carbamate monitoring in distilled beverages produced and commercialized in Brazil, following a maximum residue limit (LMR) of 210 µg/L established by the Normative Instruction N. 28, of August 8th, 2014 [1]. Because of this need, this work aimed to develop and validate a method for monitoring EC. Perform the calculations of the uncertainty estimate and produce reference material according to Guide 80 for the internal control of the federal laboratory.

Materials and Methods

The method validated for MAPA used a gas chromatograph Shimadzu model GC 2010, equipped with an automatic sampler model AOC-5000, coupled to a mass spectrometer model GCMS-QP2010 Plus; developed with a stationary phase column of polyethylene glycol in dimensions 30m x 0.25mm x 0.25µm. The MAPA notified that in the analysis, there were many doubts about the identification of the EC only by ion 62. The methods developed were performed with ions 44, 62, and 74 to ensure the identification and quantification continuing with ion 62, which is the most used for the determination of EC [2,3]. For the diagnosis of ethyl carbamate contents, MAPA provided 18 samples from the inspection program. In addition, a proficiency test (PT) of a few participants was carried out with the reference material produced. All statistical calculations of the validation and uncertainty estimates were performed using the ConfLab software.



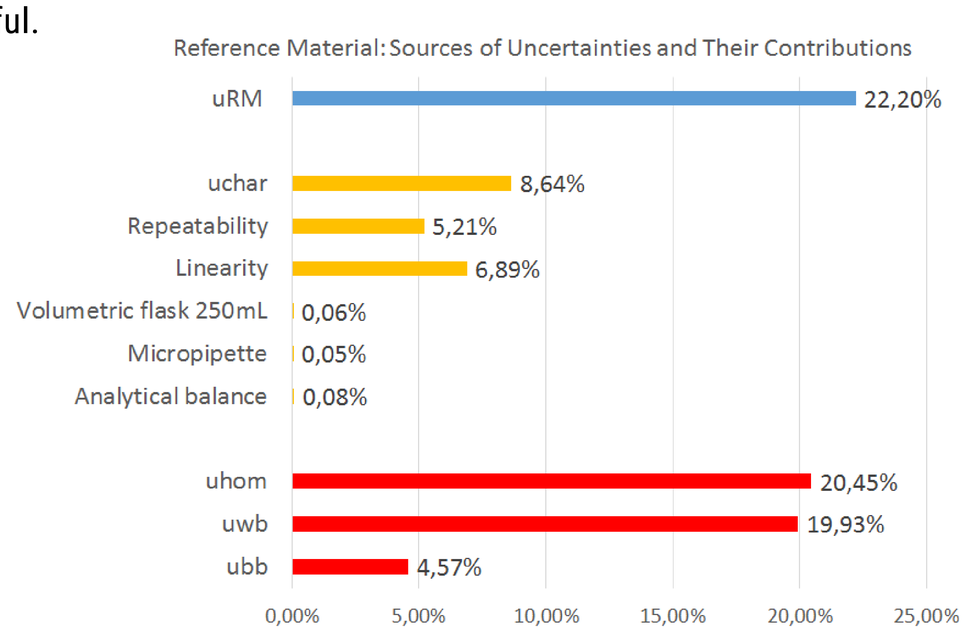
Results and Discussion

A RM for ethyl carbamate was developed in an unsweetened sugar spirit matrix, presenting a reference value of (236,500 ± 105,006) µg/L (k=2, normal) with adequate homogeneity and stability. This RM uncertainty is close compared to the uncertainty of other contaminants in whisky RM developed by Fapas.

The PT was carried out with a small group of participants, making it necessary to study a new way of evaluating the laboratories. ISO 13528: 2015 [4] recommends using the z score as a performance parameter using the Horwitz model adapted by Thompson to calculate the standard deviation from the concentration of the designated value. However, Horwitz's mathematical model for calculating the standard deviation of analytical methods is an empirical model carried out in the 1980s. In 40 years, instrumental analysis has evolved a lot. The analytical power we currently have available compared to when the Horwitz model was developed is unmatched. Thus, the PT evaluation compared the results of the z score (using Horwitz) with the zeta score and normalized error that considers the uncertainties of the RM and the results of the laboratory. It was observed that the performance evaluation considering the uncertainties was more careful.

Performance parameters of the laboratories participating in the proficiency test.

	RQAe097p		RQAe901p		RQAe843p		RQAe965p	
x (µg/L) U (Conflab)	304,00 3,85%	Performance	247,00 1,33%	Performance	247,91 0,69%	Performance	257,00 10,02%	Performance
z (σ Horwitz)	1,44	satisfactory	0,22	satisfactory	0,24	satisfactory	0,44	satisfactory
D%	28,54%	_	4,44%	_	4,82%	_	8,67%	_
zeta (ζ)	3,04	alert	0,47	satisfactory	0,51	satisfactory	0,92	satisfactory
E_n	1,52	unsatisfactory	0,24	satisfactory	0,26	satisfactory	0,46	satisfactory



Through this work, quality tools were provided for the monitoring of the EC that will be important for the accreditation of the scope of laboratory analyzes: a validated method with an estimated uncertainty and 100 vials of 2mL of RM for monitoring the quality of the analyzes, with homogeneity and stability proven and also calculated uncertainty. It was found that there are many beverages being marketed with high levels of EC: of the eighteen samples analyzed, only five were in compliance with the legislation's LMR.

References

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[2] CLEGG, B. S.; FRANK, R. Detection and quantitation of trace levels of ethyl carbamate in alcoholic beverages by selected ion monitoring. Journal of Agricultural and Food Chemistry, Washington, v. 36, p. 502-505, 1988.

[3] DE ANDRADE-SOBRINHO, L. G.; BOSCOLO, M.; LIMA-NETO, B. S.; FRANCO, D. W. Carbamato de etila em bebidas alcoólicas (cachaça, tiquira, uísque e grapa). Química Nova, São Paulo, v. 25, n. 6B, p. 1074-1077, 2002.

[4] INTERNATIONAL ORGANIZATION FOR STANDARDIZATION. ISO 13528:2015. statistical methods for use in proficiency testing by interlaboratory comparison. Geneva: ISO, 2015. 90 p.

Acknowledgments

CAPES FAPESP CNPq MINISTÉRIO DA AGRICULTURA, PECUÁRIA E ABASTECIMENTO PÁTRIA AMADA BRASIL GOVERNO FEDERAL Companhia Müller de Bebidas