New methodology for the analysis of volatile organic compounds (VOCs) in bioethanol by gas chromatography coupled to mass spectrometry

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New methodology for the analysis of volatile organic compounds (VOCs) in bioethanol by gas chromatography coupled to mass spectrometry

M S G Campos[1], **J E S Sarkis**[1]

[1]Institute of energy and nuclear research-National (IPEN/CNEN-SP), Av. Professor Lineu Prestes 2242 05508-000 São Paulo, SP, Brazil

E-mail: mauricio_campos@usp.br

Abstract. The present study presents a new analytical methodology for the determination of 11 compounds present in ethanol samples through the gas chromatography coupled to mass spectrometry (GC-MS) technique using a medium polarity chromatography column composed of 6% cyanopropyl-phenyl and 94% dimethyl polysiloxane. The validation parameters were determined according to NBR ISO 17025:2005. The recovery rates of the studied compounds were 100.4% to 114.7%. The limits of quantification are between 2.4 $mg.kg^{-1}$ and 5.8 $mg.kg^{-1}$. The uncertainty of the measurement was estimate in circa of 8%.

1. Introduction

Ethanol is a product of molecular formula CH_3CH_2OH, obtained by fermentation of simple sugar present in biomass [1,2]. It is colorless, volatile, flammable, water-soluble, with characteristic flavor and odor [4]. Ethanol is widely used in automotive industry various other industrial processes for the production cleaning products, paints, perfumes, cosmetics, varnishes, solvents among other products.

In Brazil, ethanol is used as biofuel produced from sugarcane, however, it can also be obtained by other renewable sources as the beetroot (Germany), corn (USA), sorghum saccharine (Africa) and wheat (Europe) can be used [1,2].

However, to be marketed in its various forms, it must comply several specifications regulated by regulatory agencies, laws in force in each country or even by companies that are purchasing the product. Consequently, daily, thousands analysis are performed to guarantee the quality of the product and its safe use. For this reason, it is necessary a continuous improvement of the used analytical, as well as the development of new ones which can improve all analytical process. Based on this premise, this work presents a new methodology for the simultaneous determinations of 11 VOCs in ethanol samples, based on gas chromatography coupled to mass spectrometry (GC-MS) technique.

2. Experimental

2.1. Reagents and standard

All analytical reagents used in this study have purity greater than 99.0%. In the validation of the methodology, were used the reference materials: INMETRO – Cachaça Proficiency Testing – 4th round and NSI Lab Solutions – Lot 052316 – Expiration date: 05/31/2018.

2.2. Instrumentation

A chromatographic Shimadzu system composed of a gas chromatograph, model GC-17A, coupled to a single quadrupole type mass spectrometer, model QP-5050 were used for the measurements. The sample introduction into the chromatograph was performed through an autosampler, model AOC-5000 Shimadzu.

The chromatography column used was a fused silica capillary DB-624 (6% cyanopropyl-phenyl 94% dimethyl polysiloxane), with dimensions of 60 m length x 0.25 mm inner diameter x 1.4 µm of film thickness, J Brand & W Scientific. Helium with 99.999% purity was used as carrier gas. The injection of sample was performed with a 10 µL Hamilton microsyringe. The analytical solutions were prepared gravimetrically, with automatic pipettes 10 µL, 100 µL, 1000 µL, 10 mL volumetric flasks and analytical balance (accuracy of 0.0001 g). The samples were injected, without need for preparation, filtration or dilution.

2.3. Chromatographic conditions and validation parameters

The chromatographic conditions defined for the study were as follows: initial temperature of 35°C held for 10 minutes, followed by an increase of 10°C per minute until 80°C, remaining at this temperature for 5 minutes. Second heating ramp 5°C per minute until it reaches 120°C, remaining at this temperature for 7.5 minutes. Third heating ramp 15°C per minute until 150°C staying at this temperature for 3 minutes. With this temperature program the total chromatographic analysis will be of 40 minutes. The injection temperature was 230°C, and 2µL volume was injected in split mode with a split ratio of 1:25. Carrier gas was helium with 2.0 mL/min flow. The mass spectrometer was operated in electron impact (EI) mode, ion source temperature 230ºC, MS transfer line 230ºC, SIM mode; solvent delay 6.0 min

The validation parameters followed the requirements by NBR ISO 17025:2005: selectivity, linearity, limit of detection, limit of quantification, repeability, precision, accuracy, recovery and uncertainty measurement. In this last parameter, a cause and effect diagram (Ishikawa) was elaborated to identify the sources of uncertainty [8].

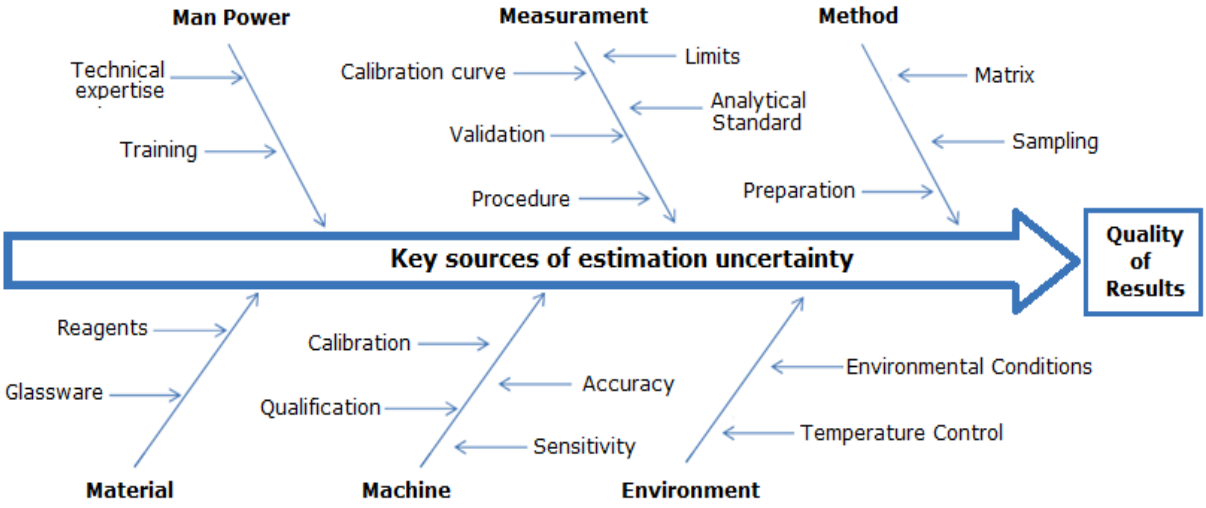

Figure 1: Ishikawa Diagram.

3. Results and discussion

In order to demonstrate capability of the methodology, 6 constituents were selected, 5 of them polar: methanol, 1-propanol, Isobutanol, 1-butanol, 2-butanol and 1 apolar: cyclohexane.

3.1. Limit of detection and quantification

Limit of detection is the lowest concentration of analyte in the sample that can be detected but not necessarily quantified under the conditions established for the assay. Limit of quantification is the

smallest amount of analyte in the sample that can be quantitatively determined with acceptable accuracy and accuracy [3].

Table 1. Limits of detection and limit of quantification in $mg.kg^{-1}$ (ppm).

Limits	Limit of Detection	Limit of Quantification
Methanol	1.8	5.8
1-propanol	0.8	2.4
Isobutanol	1.6	5.6
1-Butanol	1.1	3.9
2-Butanol	1.0	3.3
Cyclohexane	0.03	0.11

In this study, the LOD and LOQ were calculated by the method based on analytical curve parameters, corresponding to 3 times and 10 times standard deviation of the linear coefficient of the equation by the angular coefficient of the analytical curve, respectively.

3.2. Selectivity

Is the degree to which the method can quantify the analyte in the presence of other analytes, matrices or other potentially interfering material [3].

3.3. Linearity

Linearity refers to the ability of the method to generate results linearly proportional to the analyte concentration in the sample [5]. In this study, linearity ($R^2 > 0.9999$) was obtained in the range from 2.0 $mg.kg^{-1}$ to 300 $mg.kg^{-1}$.

3.4. Precision

Precision is the general term for evaluating the dispersion of results between independent assays, repeated in the same sample, similar samples or standards under defined conditions [3].

3.5. Repeatability

It is the measurement condition in a set of conditions, which includes the same measurement procedure, the same operators, the same measuring system, the same operating conditions and the same place, as well as repeated measurements on the same object or similar objects for a short time [3].

Table 2. Comparison of relative standard deviations at different concentration levels.

Compound	Level	Average Intensity	Standard Deviation	%RSD
Methanol	Low	2.9	6980	**9.87**
	Medium	29.4	17126	**2.60**
	High	147.7	31107	**0.96**
1-propanol	Low	3.1	4774	**3.64**
	Medium	31.0	42904	**2.94**
	High	155.6	101018	**1.33**
Isobutanol	Low	3.1	2099	**3.94**
	Medium	31.2	13838	**2.27**
	High	156.7	40063	**1.25**

1-Butanol	Low	3.6	2798	**5.28**
	Medium	36.1	14743	**2.43**
	High	181.1	44661	**1.41**
2-Butanol	Low	3.5	2854	**2.22**
	Medium	14.3	7702	**1.37**
	High	71.2	33091	**1.15**
Cyclohexane	Low	0.09	130	**2.39**
	Medium	1.99	903	**1.41**
	High	10.7	7709	**1.23**

The values shown in Table 02 show that the lower the concentration of the analyte greater the value of the relative default deviation.

3.6. Recovery

Recovery is the proportion of the amount of the substance of interest, present or added in the analytical portion of the analyzed material, which is extracted and quantifiable. It can be estimated as the percentage of the analyte after processing the sample compared to that of a solution containing the analyte in a concentration corresponding to 100%. The reference materials used in recovery, were: INMETRO – Cachaça Proficiency Testing – 4th round and NSI Lab Solutions – Lot 052316 – Expiration date: 05/31/2018. The expected values are shown in table 3.

Table 3. Recovery rate of the studied compounds.

Parameters	**Reference Value**	**Concentration**	**Recovery (%)**
Methanol	82.4	87.9	106.7
1-Propanol	268.0	307.4	114.7
Isobutanol	209.6	210.5	100.4
1-Butanol	35.8	37.9	106.0
2-Butanol	62.1	64.3	103.6
Cyclohexane	3.1	3.2	103.2

3.7. Measurement uncertainty

According to Eurachem/CITAC, the uncertanty is defined as "a parameter associated with the result of a measurement that characterises the dispersion of the values that could reasonably be attributed to the measurand" [7]. So, the uncertainty of an analytical methodology is a parameter characterizing the dispersion of the values attributed to a measured quantity considering all steps of the analytical procedure.

Table 4. Combined and expanded uncertainty in the studied method.

Parâmetros	**u[a]**	**U[b]**	**U(%)**
Methanol	2.7	5.4	10.1
1-Propanol	15.0	29.9	9.8
Isobutanol	10.6	21.2	9.5
1-Butanol	1.6	3.1	8.5
2-Butanol	2.7	5.4	8.4
Cyclohexane	0.1	0.3	8.3

[a] – Combined uncertainty
[b] – Expanded uncertainty, covarage factor K = 2
U(%) – Relative expanded uncertainty

4. Conclusions

As described previously, the method presented good results of selectivity, linearity, repeatability, recovery and the expanded uncertainties and analytical quality similar to the commonly used methods for this same purpose. In addition, once it uses only one chromatography column for the analysis of compounds with different polarity, it allows a cost savings and enhancement in the laboratory throughput.

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