

Title:**SNIF-NMR and Chemometrics Methods Applied to ^1H NMR in the Study of Brazilian Brandy Authenticity****Authors & affiliations:***Elisangela Fabiana Boffo¹, Márcia Miguel Castro Ferreira², Antonio Gilberto Ferreira¹*

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Abstract:

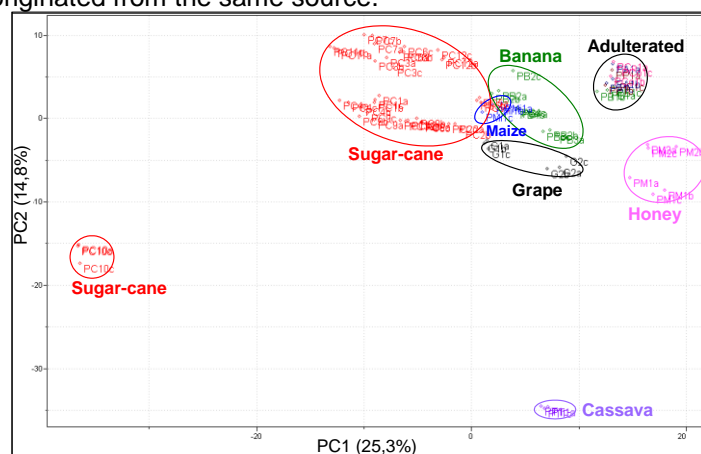
The terminology *aguardente* used for Brazilian brandy designate the alcoholic beverage obtained by fermentation of sugars from diverse sources as grape, honey, banana, sugar-cane, etc. The sugar source will characterise the produced beverage type. SNIF-NMR technique correlates the *aguardentes* biosynthetic origin with plants sugar, through C_3 , C_4 and CAM mechanisms. ^2H and ^1H NMR spectra were recorded on a Bruker DRX400 – 9.4T spectrometer, in triplicate, in 5 mm direct and inverse probes, at 298K.

For the standard samples the $(^2\text{H}/^1\text{H})_i$ values allowed to distinguish unequivocally between C_3 , C_4 and CAM plants (table 1). Honey *aguardentes*, probably, were made from nectars collected from C_3 plants. For banana, peach, coconut, pineapple and maize commercial samples values were similar to them observed to sugar-cane *aguardentes*, suggesting the predominance of C_4 plant in the sugars used in the fermentation.

Table 1. $^2\text{H}/^1\text{H}$ isotopic ratio for methyl (I) site for *aguardentes*

| | $(^2\text{H}/^1\text{H})_i$ | | Pathway |
|------------|-----------------------------|---------------|--------------|
| | standard | commercial | |
| Grape | 101.3 – 102.8 | 101.3 – 106.6 | C_3 |
| Honey | 99.7 – 101.3 | 102.1 – 103.6 | -- |
| Banana | 101.9 – 102.3 | 111.4 – 113.9 | C_3 |
| Cassava | -- | 99.7 | C_3 |
| Peach | -- | 113.0 | C_3 |
| Coconut | -- | 112.2 | C_3 |
| Pineapple | 107.1 – 107.9 | 111.7 – 113.3 | CAM |
| Sugar-cane | 111.7 – 112.3 | 111.7 – 113.4 | C_4 |
| Maize | -- | 113.9 | C_4 |

PCA applied to ^1H NMR spectra showed that it is possible to discriminate samples (Figure 1). Sugar-cane *aguardentes* were discriminated to negative values of PC1. Maize, banana and grape samples were grouped near to the sugar-cane group. Distinct groups were obtained for honey and cassava *aguardentes*. For adulterated group, banana, peach, coconut and pineapple commercial samples, the ^1H NMR spectra are equals, suggesting that they were originated from the same source.

Figure 1. PC1 x PC2 score plot of the ^1H NMR data

In conclusion, SNIF-NMR method and chemometrics analyses applied to ^1H NMR spectra can distinguish *aguardentes* produced from plants with different biosynthetic origin.