Determination of the authenticity of commercial coffees using ^{1}H NMR, FT-IR spectra and chemometrics

Leila A. Tavares[1], Elisangela F. Boffo[1], Antonio G. Ferreira[1], Márcia M. C. Ferreira[2]

1. Departamento de Química, Universidade Federal de São Carlos, São Carlos- SP - Brazil
2. Instituto de Química, Universidade Estadual de Campinas, Campinas - SP -Brazil

UFSCar SÃO CARLOS BRAZIL
Lab. RMN

Introduction

Coffee is one of the most widely consumed beverages in the world and Brazil is the first producer. Its quality control is difficult because depends of the weather, harvest conditions, species used, soil nutrients, etc. and it can also be adulterated with cheaper substitutes like barley, chicory, cereals, malt, maltodextrins, caramelised sugar, etc [1,2].

Many techniques have been investigated to tackle the problem of coffee adulteration. Spectroscopic methods such as NMR and FT-IR, that can monitoring a wide range of chemicals in a single spectrum have been a great success. However, the richness of this information makes the spectra too complex and require chemometric analysis to extract the useful information[3].

In order to propose a methodology to determine barley addition into the coffees, chemometric methods were applied to ^{1}H NMR and FT-IR spectra.

Materials and Methods

The samples were prepared from ground coffee and barley in proportions according to the table 1.

TABLE 1: Samples composition

	Sample	Sample cod.	Coffee content (%) NMR	Coffee content (%) FT-IR
Training samples	1	Ca100	100	100
Test samples	2	Ca90	90	84.9
Prediction samples	.	.	.	.
	.	.	.	.
	10	Ca10	10	14.4
	11	Ce100	0	0
	12	Ce70	30	33.7
	13	Ce10	90	90.2
	14	CaCBDc	80	79.4
	15	Ca9832	100	100
	16	CaB129	100	100
	17	CaB056	100	100
	18	Ca2049	100	100
	19	Ca6693	100	100
	20	CaSeGr	-	-
	21	CaArl	-	-
	22	CaRen	-	-
	23	CaCBD	-	-

NMR data: The powder coffee samples were extracted with an espresso coffee maker with 72.0 mL of boiling water and 10.0 g of coffee/barley. All ^{1}H NMR spectra were obtained, in triplicate using a Bruker DRX-400 spectrometer equipped with a 5 mm inverse probe and the acquire/processing data were done with the same parameters. In 0.6mL of extract was added three drops of D_2O. Water suppression was achieved using the zgcppr pulse sequence.

FT-IR data: The spectra of coffee/barley samples was obtained from KBr disks in triplicate using a BOMEM Hartmann & Braun spectrometer. The region 4000 - 400 cm^{-1} were registered.

Chemometric analysis: The Pirouette® software, v. 2.02, was used and the following methods were applied to the spectra data: Principal Components Analysis (PCA) and Hierarchical Clusters Analysis (HCA) for an exploratory data analysis, k-Nearest Neighbour (KNN) and Soft Independent Modelling of Class Analogies (SIMCA) for classification and Principal Component Regression (PCR) and Partial Least Squares (PLS) for quantification analysis. For classify and calibration methods were used samples to build the models (training) to test them and for prediction.

Results and Discussion

The figures 1 and 2 show ^{1}H NMR and FT-IR spectra respectively, of coffee and barley pure samples. Both spectra data presents evident differences between coffee and barley samples and that were used in statistic analysis (unmarked regions).

The PCA analysis of ^{1}H NMR spectra discriminated the samples in two groups. One has higher percentage of coffee in its composition, on the right side (in blue), and the other more barley, on the left (in red), figure 3. Nevertheless, the analysis from the FT-IR spectra is not possible the distinction between coffee and barley samples and three groups were discriminated. One for samples that have higher content of coffee, other of barley and the last with a median content, figure 4.

The KNN classification model presented efficiency for both techniques, and attributed the class correctly for 100% of the test samples. After this, the model were applied in commercial samples and all of them were predicted in the class 2, that have more content of coffee, table 2 and 3.

The coffee content for the test and commercial samples were determined using PLS and PCR, which showed similar predictions, table 2 and 3. When these methods were applied in the NMR data the results were better, with relative errors 5.3 and 5.6% for PLS and PCR, respectively. For the FT-IR spectra data we found 16.8 and 17.5% for the same samples used in the NMR.

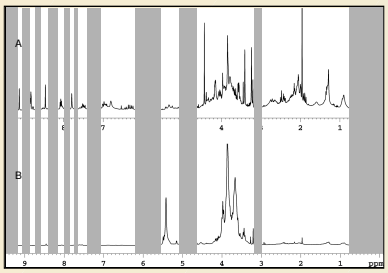

FIGURE 1. ^{1}H NMR Spectra of (A) coffee and (B) barley, showing the regions that was excluded from chemometric analysis

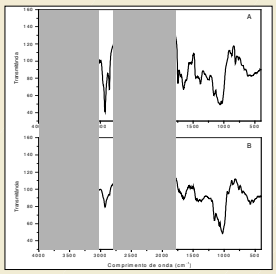

FIGURE 2. FT-IR Spectra of (A) coffee and (B) barley, showing the regions that was excluded from chemometric analysis

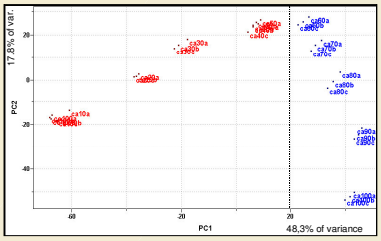

FIGURE 3. PC1 x PC2 score plot of the ^{1}H NMR data of coffee/barley blends

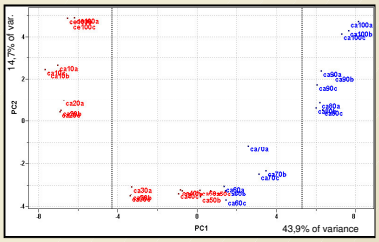

FIGURE 4. PC1 x PC2 score plot of the FT-IR data of coffee/barley blends

TABLE 2. Class prediction for coffee content into coffee/barley blends by chemometric methods applied to ^{1}H NMR data

Sample	Real (%)	PLS	PCR	KNN	Class
ce10	90.0	84.6 ± 1.8	84.1 ± 2.2	2	2
ce70	30.0	30.8 ± 0.3	30.6 ± 0.3	1	1
ca2049	100.0	97.4 ± 0.3	96.8 ± 0.4	2	2
ca6693	100.0	88.6 ± 0.4	88.0 ± 0.3	2	2
ca9832	100.0	94.0 ± 0.7	93.3 ± 0.6	2	2
ca056	100.0	96.7 ± 0.2	96.5 ± 0.1	2	2
ca129	100.0	91.2 ± 0.5	90.7 ± 0.5	2	2
caCBDC	80.0	78.7 ± 0.4	78.8 ± 0.6	2	2
caArl	---	95.9 ± 1.2	96.0 ± 1.2	2	-
caCBD	---	98.3 ± 0.5	98.1 ± 0.4	2	-
caRen	---	94.2 ± 1.1	94.8 ± 1.1	2	-
caSeGr	---	94.9 ± 0.6	95.0 ± 0.5	2	-

Mean error of PLS: 5.3%
Mean error of PCR: 5.6%

TABLE 3. Class prediction for coffee content into coffee/barley blends by chemometric methods applied to FT-IR data

Sample	Real (%)	PLS	PCR	KNN	Class
ce10	90.2	73.9 ± 2.0	73.8 ± 1.9	2	2
ce70	33.7	37.1 ± 3.9	36.7 ± 3.8	1	1
ca2049	100.0	79.6 ± 1.2	77.8 ± 1.1	2	2
ca6693	100.0	82.7 ± 2.3	81.5 ± 2.5	2	2
ca9832	100.0	80.7 ± 0.7	80.0 ± 0.4	2	2
ca056	100.0	79.2 ± 1.6	78.0 ± 1.9	2	2
ca129	100.0	84.3 ± 0.8	83.3 ± 1.0	2	2
caCBDC	79.4	69.4 ± 0.7	68.6 ± 0.8	2	2
caArl	---	74.4 ± 1.0	73.2 ± 0.9	2	-
caCBD	---	72.6 ± 0.4	70.8 ± 0.1	2	-
caRen	---	56.8 ± 0.6	56.2 ± 0.7	2	-
caSeGr	---	74.2 ± 1.6	73.0 ± 1.3	2	-

Mean error of PLS: 16.8%
Mean error of PCR: 17.5%

Conclusions

The results presented showed that ^{1}H NMR spectroscopy together with chemometric methods was a better tool than FT-IR to identify and quantify the presence of barley in coffee. The methods more efficient to classify samples were KNN and PLS to determinate the content of barley added.

References

1. Prodolliet, J. *et al. Z. Lebensn Unters Forsch A*, **1998**, *207*, 1.
2. Charlton, A. J. *et al. J. Agric. Food Chem.* **2002,** *50,* 3098.
3. Suchánek, M. *et al. Fresenius J. Anal. Chem.* **1996**, *354*, 327.

Acknowledgement

CAPES CNPq FAPESP FINEP