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Mathematical prediction of sensory properties in cocoa liquor using volatile compounds composition

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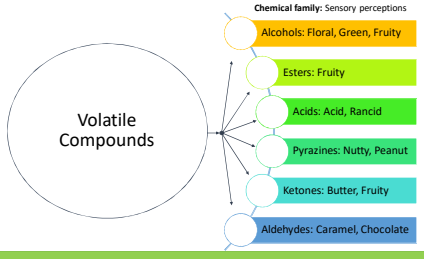
1. Problem Definition

Main challenge

The tasting process is used worldwide for the sensory characterisation of cocoa beans and cocoa mass. However, in many countries there are not enough tasting panels to qualify the quality of cocoa mass. On the other hand, it is well known that the composition of volatile compounds is associated with sensory properties and this knowledge has been used to derive mathematical models to predict the sensory profiles of wine [1],[2] and cheese matrices [3].



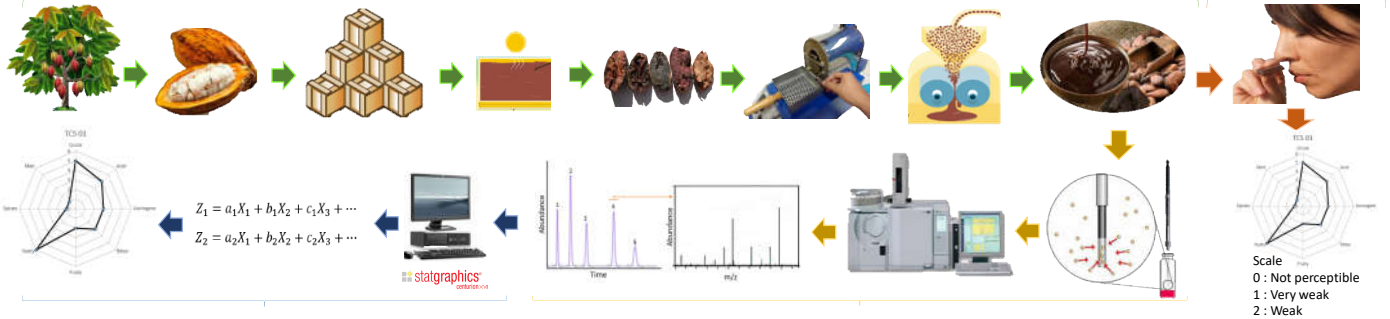
2. Objective

Propose six mathematical models to predict sensory attributes: cocoa, nutty, floral, fruity, acid and sweet.

3. Methods

1. Post-harvest evaluation of cocoa beans on aroma compounds
- Fermentation and drying time
- Roasting time and temperature
- Processing of cocoa liquor

2. Determination of the sensory profile of cocoa beans



Scale
0 : Not perceptible
1 : Very weak
2 : Weak
3 : Significant
4 : Moderate
5 : Strong
6 : Very strong
NTC 3929 : 2006

4. Relationship between aroma characteristics and volatile compound concentrations
- Principal Components Analysis
- Partial Least Squares Regression

3. Determination of the profile of volatile compounds associated with aroma characteristic
- Exposure time and temperature of microfibres
- Identification and quantification of volatile compounds (Selection of internal standard, LOD, LOQ, repeatability, reproducibility)

4. Results

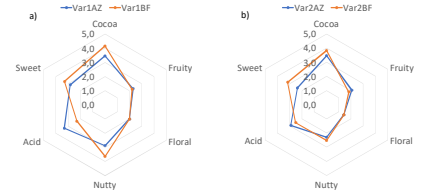
• Volatile compounds in cocoa liquor

Table 1. Volatile compounds identified in the 10 cocoa varieties by GC-MS and corroborated by Kovats' retention indices [4]

Functional Group	#	Volatile Compounds	Kovats Indices		Quality	Sensory Perception
			Author	Literature		
Acids	1	Acetic acid	625	622	97	Vinegar, rancid, Acid
	2	Propanoic acid	710	702	77	Rancid
	3	2-methylpropanoic acid	779	785	80	butter, rancid
	4	3-methylbutanoic acid	854	848	93	Pungent, rancid cheese
	5	2-methylbutanoic acid	864	858	85	Cheese, rancid
	6	Octanoic acid	1197	1201	74	Cheese, rancid, butter
Alcohols	7	3-methyl-2-butanol	698	700	85	Floral
	8	2,3-butanediol	792	793	90	Floral
	9	2-heptanol	894	894	95	Floral, grass
	10	β-linalool	1090	1092	97	Floral
	11	2-nonanol	1094	1098	88	Floral
	12	2-phenylethanol	1108	1110	93	Floral, roses
	13	2-methylbutanal	642	640	93	Malt, sweet, chocolate
Aldehydes	14	Benzaldehyde	955	959	96	Sweet, almonds
	15	Phenylacetaldehyde	1029	1029	81	Sweet, nutty
	16	Decanaldehyde	1185	1188	88	Roasted, walnut
	17	2-phenyl-2-butenal	1277	1281	97	Sweet, cocoa, almonds
	18	4-methyl-2-phenyl-2-pentenal	1378	1383	74	Cocoa, sweet
	19	5-methyl-2-phenyl-2-hexenal	1475	1483	81	Cocoa, sweet
Ketones	20	2,3-Butanedione	590	591	88	Floral, fruity
	21	3-hydroxy-2-butanone	705	710	95	Butter, fruity
	22	2-heptanone	882	889	82	Floral, fruity
	23	1-phenylethanone	1060	1062	92	Floral, almond
	24	2-nonanone	1087	1087	90	Floral, fruity
Esters	25	3-methylbutyl acetate	867	867	95	Banana, frutal
	26	Benzyl acetate	1154	1161	87	Pear, fruity, floral
	27	Ethyl benzoate	1162	1168	93	Fruity, floral
	28	Ethyl octanoate	1184	1192	89	Apple, sweet
	29	2-phenylethyl acetate	1258	1264	90	Fruity, sweet
	30	Ethyl decanoate	1594	1591	81	Fruity
Pyrazines	31	2,3-dimethylpyrazine	909	911	94	Nutty, cocoa, roasted
	32	2,3,5-trimethylpyrazine	993	991	94	Nutty, almonds
	33	2,3,5,6-tetramethylpyrazine	1081	1086	98	Nutty, hazelnut, peanut
Others	34	2-furancarboxaldehyde	815	820	74	Floral, sweet
	35	Dihydro-2(3H)Furanone	906	910	79	Floral
	36	B-pinene	964	968	87	Pine, floral
	37	2-acetylpyrrole	1062	1060	90	Toasted, Pop corn
	38	Alpha-terpineol	1174	1179	81	Floral, lilac

• Sensory profiles of cocoa liquors

Figure 2. Sensory profiles of each cocoa variety with their respective liquor AZ and BF. a) Var1, b) Var2, c) Var3, d) Var4



• Correlation between Volatile Compounds and sensory attributes

Figure 3. Correlation loading between volatile compounds (blue) and sensory attributes (red)

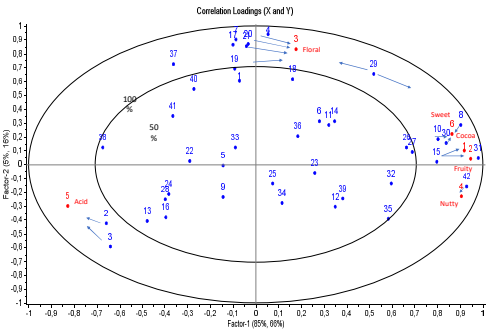


Table 2. Volatile compounds for the structuring of mathematical models

Functional Group	No.	Volatile Compounds
Acids	X_1	3-methylbutanoic acid
	X_2	2-methylbutanoic acid
Alcohols	X_3	2-heptanol
	X_4	2-nonanol
	X_5	2-phenylethanol
Aldehydes	X_6	Benzaldehyde
	X_7	5-methyl-2-phenyl-2-hexenal
Ketones	X_8	2-heptanone
	X_9	2-nonanone
	X_{10}	2-undecanone
Esters	X_{11}	Ethyl octanoate
	X_{12}	2-phenylacetate ethyl
	X_{13}	2-phenylethyl acetate
	X_{14}	Ethyl dodecanoate
Others	X_{15}	B-pinene
Pirazynes	X_{16}	2,3,5,6-tetramethylpyrazine

• Structuring of mathematical models

Equation 1. Cocoa attribute regression model

$$Cocoa\ (X) = 2.224 - 0.006X_1 - 0.008X_2 + 0.005X_3 + 0.008X_4 + 0.014X_5 + 0.005X_6 + 0.005X_8 + 0.001X_9 + 0.002X_{11} + 0.001X_{12} + 0.021X_{13} - 0.001X_{14} + 0.013X_{15} \qquad R^2: 0.85$$

Equation 2. Floral attribute regression model

$$Floral\ (X) = -0.317 - 0.035X_1 - 0.048X_2 + 0.044X_3 + 0.076X_4 + 0.061X_5 + 0.017X_6 + 0.041X_8 + 0.005X_9 + 0.014X_{11} + 0.001X_{13} - 0.036X_{14} - 0.020X_{15} + 0.002X_{16} \qquad R^2: 0.70$$

Equation 3. Fruity attribute regression model

$$Fruity\ (X) = 0.538 - 0.005X_1 - 0.006X_2 + 0.002X_3 + 0.003X_4 + 0.013X_5 + 0.005X_6 + 0.002X_8 + 0.001X_{11} + 0.001X_{12} + 0.027X_{13} + 0.002X_{14} + 0.019X_{15} \qquad R^2: 0.89$$

Equation 4. Nutty attribute regression model

$$\text{Nutty}\ (X) = 0.962 + 0.007X_1 + 0.012X_2 - 0.014X_3 - 0.026X_4 - 0.008X_5 - 0.001X_6 - 0.014X_8 - 0.002X_9 - 0.004X_{11} + 0.002X_{12} + 0.028X_{13} + 0.016X_{14} + 0.031X_{15} - 0.001X_{16} \qquad R^2: 0.87$$

Equation 5. Sweet attribute regression model

$$\text{Sweet}\ (X) = 1.458 - 0.009X_1 - 0.012X_2 + 0.009X_3 + 0.015X_4 + 0.019X_5 + 0.006X_6 + 0.008X_8 + 0.001X_9 + 0.003X_{11} + 0.001X_{12} + 0.017X_{13} - 0.005X_{14} + 0.009X_{15} \qquad R^2: 0.79$$

Equation 6. Acid attribute regression model

$$Acid\ (X) = 4.840 + 0.015X_1 + 0.020X_2 - 0.016X_3 - 0.027X_4 - 0.030X_5 - 0.009X_6 - 0.015X_8 - 0.002X_9 - 0.005X_{11} - 0.001X_{12} - 0.021X_{13} + 0.010X_{14} - 0.009X_{15} - 0.001X_{16} \qquad R^2: 0.77$$

5. Conclusions

- SPME, GC-MS, GC-FID and sensory analysis techniques were implemented to study the aroma characteristics of 10 promising cocoa varieties from the department of Santander. The effect of temperature and extraction time of volatile compounds associated with aroma characteristics was observed, finding a temperature of 60°C and 40 minutes as optimal points to extract volatiles from cocoa liquors; these values were similar to those found in other researches. In addition, through chromatography and sensory analysis techniques, it was possible to identify and quantify 77 volatile compounds in the 20 cocoa liquors and 6 sensory attributes perceived in them. These results made it possible to determine the chemical and sensory profile of each of the liquors.
- The PLSR method was able to mathematically model the 6 sensory attributes from the chemical profile of volatile compounds obtained. The predictor variables (volatile compounds) contributing to the modelling of the sensory attributes were reduced from 77 compounds to 16 volatile compounds. Although the prediction accuracy (R^2) of the models is reduced on average from 87% to 81%, the models are more accessible and manipulable with 16 variables. However, the prediction accuracy obtained by the models proposed in this work (R^2=81%) was of similar orders of magnitude to those obtained in other matrices such as cheeses (R^2=81%), wines (R^2=75%) , meats (R^2=72%), coffee (R^2=84%) and juices (R^2=82%); inferring that the proposed models largely describe the analysed data and predict the studied sensory perceptions with a good level of confidence.

7. References

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[4] C. Palencia-Blanco et al., "Proposal for a semi-quantitative method for the determination of volatile compounds in cocoa liquors," Respuestas, vol. 25, no. 1, 2020, doi: https://doi.org/10.22463/0122820X.2406.

6. Acknowledgement

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