GC and Sensory Techniques Coupled in Caramel Flavor Analysis

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Aromatic caramel is a complex moisture of saccharides (glucose, fructose and sucrose) and numerous degradation substances which contribute to its aroma and taste. Two complimentary methods have been used for its study:

- *Sensory Analysis*—Identification and quantification of organoleptic attributes by sensory analysis techniques. The general practice of sensory analysis is described elsewhere in the literature.[1] In our labs we use the "objective map method," which involves direct smelling and tasting evaluation by a panel.
- *GC/MS*—Determination of components by capillary gas chromatography coupled with mass spectroscopy (GC/MS).[2] In our labs we use a "column sniffing method" based on sniffing at the outside of a GC column after separation of components.

Materials and Methods

Industrial caramel is prepared by heating a mixture of sucrose in water in the presence of citric acid. Solvent extraction and analysis by GC/MS have been described elsewhere.[2]

Direct sensory analysis: Direct sensory analysis of caramel odor requires evaluation of a complex mixture of information in a setting that changes over time. That is, it takes the brain time to identify the sample's components, and during that time the sample has changed.

Our objective map method is a formal procedure for identifying the odor attributes of a flavor and estimating their intensity. This method produces graphs which we call "Distribution of Intensity of Attributes versus Time curves," or D.I.C.T. curves.[3]

Examination of these graphs allows a coherent and detailed comparison of various samples and the opportunity to follow their time-dependent transformation.

The first step in the objective map method is to train subjects to note and analyze the smell of complex flavors so the components can be described by six easily identifiable attributes. Our method is advantageous because it allows the use of smelling reference attributes that have been carefully defined,[4,5] so various members of the panel can evaluate the same attributes by coupling similar smelling components. From the responses of the various panel members, a single approximation of relative intensity is expressed for each of the six attributes on a scale from zero to nine.

To enhance the analysis, various paths of presentation and perception have to be checked:

- Smelling of raw caramel via both the nose (inhalation) and the back of the mouth (exhalation).
- Smelling of an aqueous solution of raw caramel via both the nose and the back of the mouth.
- Tasting of an aqueous solution of caramel.

The panel is composed of 20 trained subjects and the methodology involves the following steps:

1. Prepare a solution of the sample in odorless water and adjust the sample concentration (in the range between the absolute odor threshold and saturation) to achieve the best perception level. Typically, this is achieved at a dilution of about 15% of dry matter, so we would take 15 g of caramel and add enough water to make 100 ml.
2. Identify the various smelling attributes of the solution. Here we are selecting the attributes that we'll use to describe the olfactory sensations for caramel. This is done by individual evaluations followed by a common run. Then the panel gets together to obtain a common answer.
3. Determine the order in which the selected attributes peak during the period of olfaction. This is done individually by each panelist.
4. Estimate the intensity of each attribute by ranking it on a relative scale. Again, this is done individually by each panelist.
5. Plot the D.I.C.T. curves. This takes all the data col-

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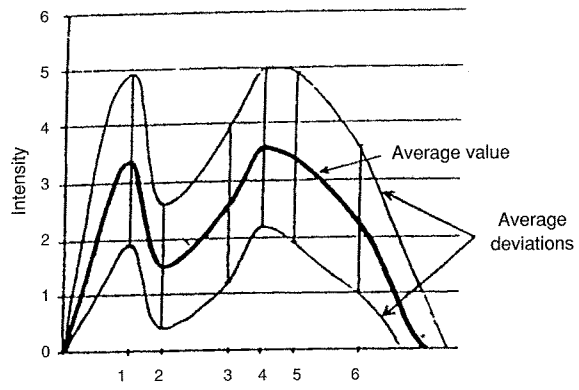

Figure 1. Inhalation (nasal) D.I.C.T. curves for six attributes of 15% caramel solution (industrial mixture) smelled via the nose

1 = milky butter
2 = ethered fruit
3 = lactoned fruit
4 = sweet
5 = caramel
6 = roasted

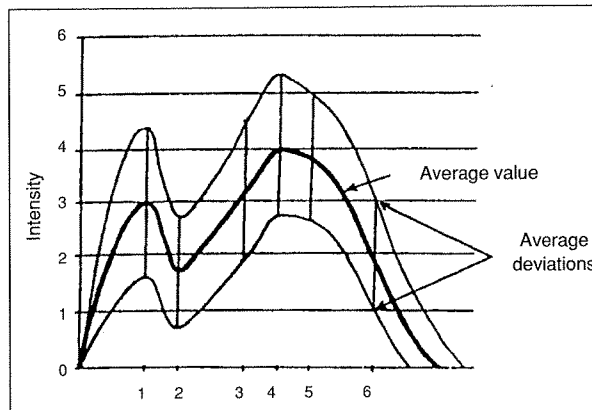

Figure 2. Exhalation (retronasal) D.I.C.T. curves for six attributes of a 15% caramel solution (industrial mixture) smelled via the back of the mouth

1 = milky butter
2 = ethered fruit
3 = lactoned fruit
4 = sweet
5 = caramel
6 = roasted

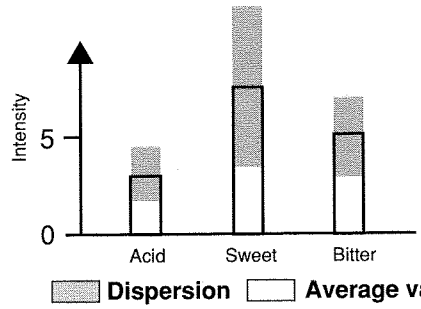

Figure 3. Histogram of taste descriptors for a 15% caramel solution (industrial mixture)

lected individually by the panelists and combines it in one curve.

Sensory analysis after separation of components in a packed column: Gas chromatography allows a separation of components by time and by other criteria that are functions of the liquid phase and the vapor phase. Using more than one criterion can improve the knowledge of a complex mixture, although there is no reason to claim that this will identify all components. Solvent extraction is achieved in the same fashion as with GC/MS.

In order to understand fully the effect of each component on the aroma of caramel, it is necessary to have a finer identification of the main components. The "sniffing method" is well suited for that. It uses gas chromatography coupled to two parallel detectors—a flame ionization detector (FID) and a human nose. Subjects who perform this analysis should be well qualified or expert.

The advantage of the "sniffing method" is that it allows the sample to be fractionated and the olfactive data displayed versus time, which results in more precise identification than by direct sensory analysis. (However, direct sensory analysis has the advantage of reporting on the sample's olfactive picture as a whole.)

Effective identification of the various substances present in caramel (mainly at trace level) requires the use of a packed column; the high concentration of fragrance at the outside of the column makes the olfaction easy.

The chromatograph (Girdel 3000) was equipped with a packed column (Carbowax 20M 10%—Chromosorb 60/80 WAW) of 5 m length with an inner diameter of 6.5 mm. At the column outlet, the odorous vapor flow was divided as follows: 15% to the FID and 85% to the nose.

The evaluation is performed through an analyzer that is not connected to the FID, but has an identical paper speed. The subject smells every eight to ten seconds, sampling the flow and noting impressions regardless of the FID machine readings. Both results are then compared and show that:

- One or several odors can be present at one peak.
- Some peaks are odorless.

The olfaction process is designed not to damage the mucous membrane (when the nose is directly exposed at the outside of the column) and avoids too high a concentration of products when using a hydrating device, thus maximizing the available information.

The link between the FID response and olfactive sensations has been established from retention times, from tasters' experience and from previously published literature.[6]

Results and Discussion

Six smelling attributes (or descriptors) were selected by the panel as representative of the odor range, and their order of perception in time was as follows:

1. Milky butter
2. Ethered fruit
3. Lactoned fruit
4. Sweet
5. Caramel

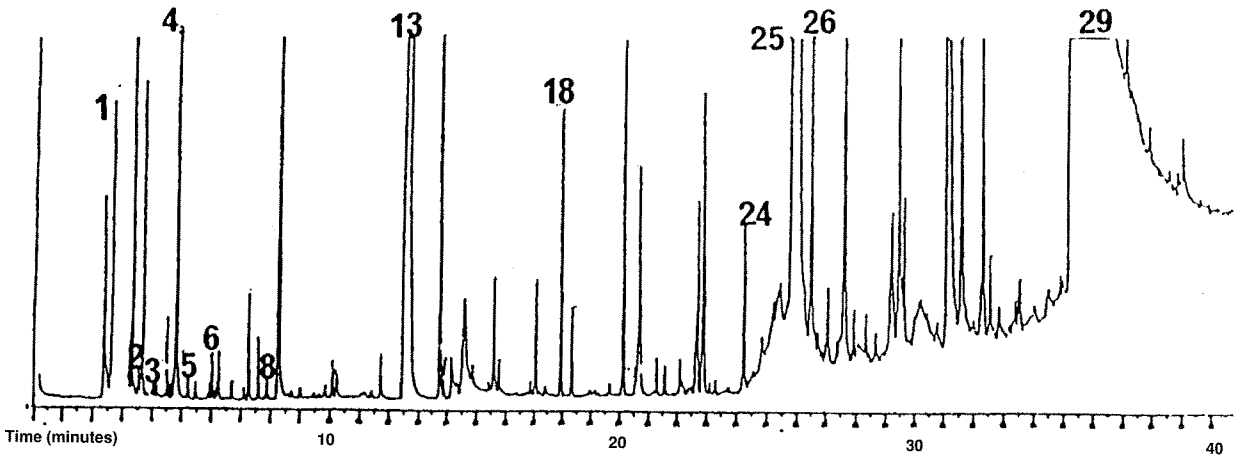

Figure 4. Gas chromatogram of caramel extract (an industrial mixture) in CH_2C_{12}. The extract was made by countercurrent extraction with 100 cm³ of caramel solution (30% dry matter). Then the solvent was evaporated down to 0.1 cm³ and this mixture was analyzed.

1 = 2-propanone
2 = 3-methyl-2-oxobutanoic acid, methyl ester
3 = 2-methyl-1-propanol
4 = 1-butanol
5 = 3-methyl-3-butene-2-ol
6 = 1,2-butanediol
8 = 3-hydroxy-2-butanone (acetoin)
13 = furfural
18 = furfuryl alcohol
24 = 5-hydroxy-2-methyl(4H)4-pyranone (allo maltol)
25 = 2-furancarboxylic acid, methyl ester
26 = 3-furancarboxylic acid, methyl ester
29 = 5-hydroxymethyl-furfural

6. Roasted

(Of course, each of these attributes was related to a reference substance. For instance, the reference for "caramel" was ethyl maltol.)

The results are shown in Figures 1 and 2. Examination of the two curves shows that the two presentation paths lead to similar results. The panelists generally distinguished more head notes when smelling via the nose and more background or heavy notes when smelling via the back of the mouth.

Results obtained for the 15% solution exhibit a good homogeneity (mean deviation is 1.2) and the treatment of various curves allows one to plot a coherent mean curve. As we expected, when sample concentration was adjusted, high concentrations (beyond saturation level) of the aromatic substance in pure caramel do not allow for reliable results.

Plots exhibit a variety of attributes (milky butter, ethered fruit, lactoned fruit and sweet) which are not limited to nuances of pyrogenation. All the attributes are perceived via either the nose or the back of the mouth and they are perceived in the same relative order. A given attribute is seen to have roughly the same intensity (average value and average deviations) via either nose or back of mouth. The weakness of the ethered fruit character (which corresponds to substances derived from furfurals expected from the thermal degradation of sucrose) confirms the aromatic attractiveness of the sample; the panel had expressed a hedonic opinion that a high level of the ethered fruit note reduced the aromatic attractiveness of the sample.

The three taste descriptors—acid, sweet and bitter, shown in Figure 3—coincide well with the expected attributes in Figures 1 and 2. Caramel sweet taste exhibits the largest variation, while bitterness is a fast sensation which is sensed forward in the mouth.

Similar analysis of aromatic caramel samples from another process—continuous heating by microwaves—has shown other organoleptic attributes. However, these attributes did not show up when the microwaved samples were submitted to classical analysis such as GC/MS.

A caramel gas chromatogram is shown in Figure 4, and the results of column sniffing are shown in Table I. Twenty-nine components were identified in caramel extracts by GC/MS.[2] One sees numerous cases of good agreement between the detector peaks and the nose; examples include 1-butanol, 3-hydroxy-2-butanone, and furfuryl alcohol. One also sees that column sniffing can sometimes detect aromatic data where the experimental detector sees none; for example, during the first two minutes the experimental detector sits on the baseline while the nose has already detected diacetyl (and furan, in the case of dark caramel).

Conclusion

We have been able to correlate chemical nature and generated flavor by smelling or tasting food products, in particular by analyzing the organoleptic characteristics of caramel. The originality of our work was to correlate instrumental analysis and several new approaches to sensory analysis by systematic connections between the similarities of the two sets of results.

The use of such results has the following advantages:

Table I. Sniffing analysis of caramel extract (an industrial mixture) in CH_2C_{12} separated in a gas chromatograph

GC Peak (Fig 4.)	Product	Descriptors: Light Caramel	Dark Caramel	Industrial Caramel Mixture	Microwaved Caramel
	diacetyl	butter	butter	butter	butter
	furan		ether		
1	2-propanone	fruit			
	3-methyl-2-oxobutanoic acid, methyl ester		fruit		
3	2-methyl-1-propanol	fruit			
4	1-butanol	fat	fat	fat	
5	3-methyl-3-butene-2-ol	fat	fat	fat	
6	1,2-butanediol			butter	
8	3-hydroxy-2-butanone (acetoin)	fat acid	fat acid	fat acid	fat acid
	-				burned
	-				caramel
13	furfural		fresh		
	-		rum/ether	rum/ether	
	-	methional	methional		methional
	-	burned		roasted	
18	furfuryl alcohol		fruit	fruit	
	-		furan alcohol	furan alcohol	furan alcohol
	-	sweet			
	-	floral			
	-		floorcloth		floorcloth
	-	lactoned			
24	5-hydroxy-2-methyl(4H)4-pyranone (allo maltol)	burned	burned	burned	
25	2-furancarboxylic acid, methyl ester	fruit			
26	3-furancarboxylic acid, methyl ester	fruit			
29	5-hydroxymethyl-furfural	herbaceous	herbaceous	herbaceous	herbaceous
	-	ether	ether	ether	ether

- Relationships are drawn between bodies of information.
- Organoleptic data identifies fractions which were not detected by the gas chromatograph.
- There are industrial applications. For example, our aim was to achieve certain flavors in microwaved caramel,[7] and we found we could do that by changing the caramel's overall composition so that when the caramel was microwaved, it would generate the fruited or buttered notes we wanted to obtain.

Finally, our results are based on an original scheme of coupling advanced gas chromatographic analysis with sensory analysis. This allows us to establish a relationship between identification of compounds and the smell and taste attributes of a given product.

Odor and fragrance are the main reason to produce caramel. So it is obvious that they should be identified in the first place using the most adequate instrument, which is the nose. On the other hand, this detector being apt to err due to human subjectivity, it is equally important to compare with the machine, as long as both sets of data retain some common points.

References

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