Results obtained at Alpha MOS Laboratory (Toulouse, France) with nut mixes provided by an American consumer food producer and retailer.

Nuts are rich in polyunsaturated fats, which are particularly sensitive to lipid oxidation. In appetizer mixes, each type of nuts has a different contribution to potential overall rancidity. Therefore, it is important to identify the causes of possible rancidity to monitor the global sensory quality of these appetizers.

Objective

After having received a claim from a consumer about an unpleasant off-flavor in their product, an American manufacturer needed to explain the origin of the defect. This application note describes the analysis of the overall aroma profile of 5 mixes containing 6 types of nuts. The analysis was conducted using HERACLES Flash GC based E-Nose (fig. 1). The objective was to determine which nuts most contributed to bad quality.

Flash Gas Chromatography E-Nose

The HERACLES Electronic Nose (Alpha MOS, France) is based on the technology of ultra fast chromatography and includes two short columns of different polarities (DB5 apolar and DB1701 slightly polar), coupled to 2 Flame Ionization Detectors (FID). Therefore, 2 chromatograms are obtained simultaneously, allowing a sharper identification of the chemical compounds. The embedded Tenax trap located before the columns allows pre-concentration of the injected fraction prior to rapid thermo desorption, in order to improve analysis sensitivity. With high heating rates (up to 20°C/second), this reduces the time of analysis producing results in seconds and analysis can be run every 4 minutes.

AroChembase: Kovats Index library for chemical pre-screening & sensory characterization

The AroChembase (Alpha MOS, France) is an add-on module that can be used within the HERACLES E-Nose software, known as AlphaSoft. It consists of a library of chemical compounds with name, formula, CAS number, molecular weight, Kovats retention Index, sensory attributes and related bibliography. It allows to pre-screen the chemical compounds and give sensory features from the HERACLES chromatograms.

Aroma Analysis of Nut Mixes

Samples

Five appetizer samples of different sensory qualities were analyzed with HERACLES Electronic Nose. The nut mixes were composed of:

- peanuts (58% in weigh),
- almonds (22%),
- cashew nuts (9%),
- brazil nuts (6%),
- pecan nuts (3%)
- hazelnuts (2%).

The five samples were previously assessed by the company internal sensory panel (table 2).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Assessed Quality</th>
<th>Detected Off-flavors</th>
<th>Nuts with off-flavors</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>Good</td>
<td>None</td>
<td>/</td>
</tr>
<tr>
<td>M2</td>
<td>Medium</td>
<td>Slightly rancid</td>
<td>Peanuts</td>
</tr>
<tr>
<td>B3</td>
<td>Bad</td>
<td>Rancid</td>
<td>Peanuts, cashews, pecans</td>
</tr>
<tr>
<td>B4</td>
<td>Bad</td>
<td>Rancid</td>
<td>Peanuts, cashews, pecans</td>
</tr>
<tr>
<td>B5</td>
<td>Bad</td>
<td>Slightly rancid</td>
<td>Peanuts</td>
</tr>
</tbody>
</table>

Table 2: samples designation and sensory panel results
Detailed information can be found in literature about chemical and lipidic composition of nuts (tables 3 & 4). This information gives first indications on the tendency of each nut to oxidize:

- Unsaturated fatty acids are known to be more likely to oxidize than saturated fatty acid.
- Conversely, the tocopherols are known to protect against lipid oxidation, δ- and γ-tocopherol being more protective against oxidation than α- and β-tocopherol.

From the lipidic and chemical composition, it could be suspected that almonds or cashew nuts would develop a lower rancidity than pecan or hazelnuts for example.

However, these data on the chemical composition do not give a direct and global sensory information on the product.

That is why HERACLES E-Nose analysis (table 6) was conducted to get both an overall sensory profiling and chemical composition information.

In this study, the use of large vials (100mL) was particularly suitable to analyze entire nuts (easier sample preparation with no cutting) and larger quantities of product therefore more representative of the samples (fig. 5).
Chromatograms
The comparison of chromatograms showed significant differences in volatile compounds profile between the different nut mixes (fig. 7).

Bad products clearly show higher contents in volatile compounds. The characterization of these volatile compounds will help find and explain their origin and the possible causes of defects.

Characterization of volatile compounds
The nature of the main volatile compounds detected in the headspace of nut mix samples was investigated using their Kovats retention indices (Table 7) and the AroChemBase library. The main volatile compounds mostly correspond to secondary oxidation molecules: aldehydes, ketones and alkanes, which confirms that the presence of volatile compounds is strongly related to an oxidation phenomenon.

<table>
<thead>
<tr>
<th>Retention time</th>
<th>Kovats Index</th>
<th>Possible matching compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>DB5</td>
<td>DB1701</td>
<td>DB5</td>
</tr>
<tr>
<td>4.8</td>
<td>4.7</td>
<td>491</td>
</tr>
<tr>
<td>6.3</td>
<td>7.4</td>
<td>630</td>
</tr>
<tr>
<td>6.9</td>
<td>8.4</td>
<td>667</td>
</tr>
<tr>
<td>8.7</td>
<td>11.4</td>
<td>749</td>
</tr>
<tr>
<td>9.7</td>
<td>11.7</td>
<td>786</td>
</tr>
<tr>
<td>12.9</td>
<td>15.3</td>
<td>883</td>
</tr>
<tr>
<td>13.3</td>
<td>15.3</td>
<td>892</td>
</tr>
<tr>
<td>13.3</td>
<td>19.3</td>
<td>892</td>
</tr>
</tbody>
</table>

Table 7: characterization of nut mix volatile compounds based on their Kovats Index

Odor Map
To globally compare products’ aroma, a general odor map based on Principal Component Analysis (PCA) was generated using all chromatograms peaks (Figure 8). E-Nose analysis confirmed the sensory panel results, since samples were clearly differentiated based on the 3 odor qualities linked to rancidity.

The next step would consist of evaluating each type of nut individually to determine which ones mainly contribute to the global rancidity defect.

Individual Aroma Analysis of Each Nut Type
In each mix, the nuts were separated by type (peanuts, almonds, cashew nuts, brazil nuts, pecan nuts, hazelnuts). Then each type of nuts was analyzed individually with the E-Nose and their aroma profiles compared with the corresponding mix. The analytical conditions were the same as the ones previously applied for the mixes analysis (table 6).

Figure 9 represents the odor map of bad B3 mix and its different nut components. The same odor maps built for the 2 other bad samples (B4, B5) and the medium quality sample (M2) showed a similar distribution of the nuts. In bad and medium quality samples, peanuts were the nuts having the volatile profile closest to nut mix aroma.

The distance between a blank and each mix, then between the same blank and each type of nuts isolated, was calculated based on HERACLES E-Nose measurement (fig. 10). The distance for hazelnuts, which was very low, is not presented in the graph.
Figure 10: Odor distance between a blank and each mix or each individual nut type of the mixes (calculated from E-Nose measurement)

Peanuts and cashew nuts are the most concentrated in volatile compounds, which are linked with lipid oxidation and rancidity. Thus, peanuts are by far the most responsible for the off-odor in bad mixes. Cashew nuts could also have an important impact on final flavor of nut mix.

Even in the good mix (G1), the different nuts show the same ranking based on volatile compounds content, but with much lower concentrations. This may indicate that the oxidation rate is the same in the various mixes.

Conclusion

The global aroma analysis performed thanks to HERACLES E-Nose showed that peanuts are the most critical ingredients in the development of rancidity off-flavors in nuts mixes. Indeed, among the 5 types of nuts contained in the appetizer, peanuts contain the highest level of volatile compounds. Moreover, as this nut accounts for approximately 60% of the mix mass, the quality of this constituent must be carefully and strictly monitored.

Pecans and cashew nuts also present a relatively high concentration of rancidity off-odors. However, the relatively low proportion of these nuts in the final mix (especially for pecan nuts) make them less critical towards rancidity. As for brazil nuts, almonds and hazelnuts, that contain relatively lower amounts of volatile compounds, they have a low impact on the overall mix aroma.

The same classification of odor intensities was observed between the different nuts in the various mixes. Every nut seem to undergo lipid oxidation with proportional rates. This could be explained by an oxidation kinetics dependent upon the fatty acid and tocopherol contents and the nut geometry. For example, the relatively higher level of γ-tocopherol observed in brazil nuts compared to peanuts could compensate the higher proportion of polyunsaturated fatty acids in the former. Furthermore, as the size of brazil nuts is relatively important compared with peanuts, the deep lipid content of these nuts may be better protected against oxygen and light, factors that accelerate oxidation.

Globally, in order to guarantee the quality of nuts mixes, a quality control of each ingredient should be achieved before blending. This quality control should be conducted in priority on peanuts and cashew nuts, but the analysis of other minority nuts should not be neglected either.


2 USDA National Nutrient Database for Standard Reference

http://www.nal.usda.gov/fnic/foodcomp/search/