HALLENGING ODOR ZONES IN COCOA NIBS: THE KEY-ROLE OF MULTIDIMENSIONAL GAS CHROMATOGRAPHY COUPLED WITH MASS SPECTROMETRY AND OLFACTOMETRY

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The complex volatile fraction from high quality cocoa samples was studied by combining Headspace Solid Phase Microextraction (HS-SPME) with comprehensive two-dimensional gas chromatography coupled with Time of Flight Mass Spectrometry (GC×GC-TOFMS) using a combined Targeted and Untargeted approach for the most inclusive fingerprinting. Five different processing steps, across the chocolate production chain, were taken in consideration: fermented raw beans, roasted and steamed beans, nibs, and cocoa mass. Cocoa origins, selected on the basis of their peculiar sensory profiles, were: Colombia, Venezuela, Sao Tomé, Ecuador and Mexico.

Cocoa nibs showed interesting fingerprints in terms of quali-quantitative distribution of informative volatiles (odorants and technological markers) and were selected for potent odorants screening by GC-Olfactometry. In particular a multidimensional heart-cut (H/C) MDGC-MS/Olfactometry platform (H/C MDGC-MS/O) was adopted with an investigation strategy that collects odor qualities, based on the frequency detection technique (FD), from two panelists for every single run.

Aromagrams from cocoa nibs, based on the results collected from at least 9 panelists, clearly indicated several odor-active zones with univocal qualities/descriptors. In addition, 1D-GC-MS parallel analyses enabled identity confirmation for most of the targeted odorants. However, some olfactive zones resulted ambiguous or not univocally described by panelists due to co-elutions.

Critical regions were therefore re-analyzed by H/C-MDGC-MS/O that enables the full chromatographic resolution of sensory active compounds, univocal description of resulting odor qualities and in most cases, identity confirmation by EI-MS spectra. When H/C-MDGC-MS was not sensitive enough to provide suitable S/N for MS interpretation, the beneficial effect of band-compression in space produced by thermal modulated GC×GC-TOFMS can be exploited and odorants confirmed through their EI-MS spectrum.

The olfactory zones elucidated using the multidimensional approach have revealed the presence of unique potent odorants.