Volatiles profiling from high quality cocoa samples at early stages of technological treatment by two-dimensional comprehensive gas chromatography - mass spectrometry

Federico Magagna[1], Erica Liberto[1], Stephen E. Reichenbach[2], Qingping Tao[3], Carlo Bicchi[1] and Chiara Cordero[1]

[1] *Dipartimento di Scienza e Tecnologia del Farmaco, Università degli Studi di Torino, Via Pietro Giuria 9, Torino, Italy*
[2] *Computer Science and Engineering Department, University of Nebraska, 1400 R Street, Lincoln, NE, USA*
[3] *GC Image LCC, Lincoln NE, USA*

Comprehensive two-dimensional gas chromatography (GC×GC) coupled with mass spectrometry (MS) is one of the most powerful techniques for the detailed analysis (quali-quantitative profiling and fingerprinting studies) of medium-to-high complexity mixtures of volatiles as those produced during food processing practices [1]. This study investigates the characteristic distribution of technologically informative and sensory active volatiles included in the unique profile of "high quality" varieties of cocoa (*Theobroma cacao)*. Samples of different botanical origin (*Trinitario*, *Forastero* and *Criollo*), geographical provenience (Mexico, Ecuador, Venezuela, Colombia, Java, Trinidad, Sao Tomè) and analyzed at different technological stages (raw, roasted, steamed, nibs and mass) have been characterized by combining the effectiveness of HS-SPME sampling technique, the high separation and detection power of GC×GC-MS and automated fingerprinting based on *peak-regions features* approach [2].

Among the 450 detectable volatiles, a group of 180 target analytes has been identified and relative distribution assessment, and monitored across the investigated samples (origin) and technological stages. Experimental results show that some analytes undergo significant changes during the early stages of processing. As expected, most of them increase their relative distribution after roasting and steaming with clear changes on the 2D separation patterns. Interestingly some markers, diagnostic of thermal processing and fermentation, as for example alkyl-pyrazines, already detectable in the raw matrix (fermented cocoa beans), show a constant increase across technological steps. The steaming stage, implemented after roasting, conversely induces a decrease of some Strecker aldehydes (potent odorants) and 2-methyl ketones, although hot water promotes the hydrolysis from their precursors [3].

The study proposes an investigation strategy capable to exploit the full potential of GC×GC-MS in defining an informative chemical signature within complex mixtures of volatiles and illustrates how effective and automated data mining might improve food quality assessment and authentication process.

[1] Cordero C, Kiefl J, Schieberle P, Reichenbach SE, Bicchi C. Comprehensive two-dimensional gas chromatography and food sensory properties: potential and challenges. Anal Bioanal Chem. 2015 Jan;407(1):169-91

[2] Reichenbach SE, Tian X, Boateng AA, Mullen CA, Cordero C, Tao Q. Reliable peak selection for multisample analysis with comprehensive two-dimensional chromatography. Anal Chem. 2013 May 21;85(10):4974-81

[3] Granvogl M, Beksan E, Schieberle P. New insights into the formation of aroma-active strecker aldehydes from 3-oxazolines as transient intermediates. J Agric Food Chem. 2012 Jun 27;60(25):6312-22