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## RECENT ADVANCES USING GC × GC-TOFMS WITH CHEMOMETRICS TO FOOD QUALITY AND METABOLOMICS

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We have previously developed methods that use the multi-way chemometric technique Parallel Factor Analysis (PARAFAC) [Chemom. Intell. Lab. Syst., 38 (1997) 149–171] for automated mathematical resolution of both known (target) peaks [Anal. Chem., 79 (2007) 1611–1619], and unknown (non-target) peaks [Anal. Chem., 80 (2008) 6677–6688] in relatively small subsections of data using comprehensive two-dimensional gas chromatography with time-of-flight mass spectral detection (GC × GC-TOFMS). These PARAFAC based techniques take advantage of the three-way structure of GC × GC-TOFMS data from a single run to resolve peaks from baseline, noise, and other peaks, all without requirements for completely selective m/z for each peak or signal source. We have recently developed an extended non-target method to handle much larger sections of a GC × GC-TOFMS chromatogram up to a full chromatogram [J. Chemom., 23 (2009), 421–431]. Useful analytical information for all peaks resolved is provided by this extended automated PARAFAC method: apparent retention times on both separation dimensions, peak height, peak volume, identity of compounds of highest mass spectral match from a mass spectral library and associated match values, etc.

We developed and evaluated a method to analyze volatile compounds in the headspace above cacao beans that employs PARAFAC and other chemometric techniques [J. Sep. Sci. 32 (2009), 2289–2295]. The method utilizes solid phase micro extraction (SPME) sampling at an experimentally determined optimal temperature followed by GC × GC-TOFMS. Cacao beans from four geographical origins (Ivory Coast, Ghana, Ecuador, and Costa Rica) were studied under two storage conditions, either dry (no surface mold on the beans) or high moisture (surface mold present on beans). Using the Fisher-ratio statistical method [Anal. Chem. 78 (2006), 5068–5075] to discover significant differences, many peaks were found that either increased or decreased in intensity as a function of the two storage conditions. The results indicate that bean surface chemistry metabolism plays a role in the concentration of analytes, and this information can be readily determined using this analytical technology and methodology.

Another recently developed method employs GC × GC-TOFMS with isotope dilution mass spectrometry to obtain isotope ratios and achieve absolute quantitative measurements from a single sample injection [Anal. Chem. 2009, accepted]. For method validation,  $^{13}\text{C}$  isotopically labeled analytes were spiked into a sample at known concentrations. Unlike the partial separation seen when using deuterated analyte spikes, the isotopically labeled compounds behaved essentially the same as the unlabeled compounds and coelute with them;  $^{13}\text{C}$  labeled compounds also react much more like the  $^{12}\text{C}$  compounds, avoiding the potentially much larger biases introduced by using deuterated analytes in derivatization. PARAFAC was used to resolve the combined  $^{12}\text{C} + ^{13}\text{C}$  spectrum, which was then subjected to classical least squares (CLS) to obtain relative concentrations of the  $^{12}\text{C}$  analyte and  $^{13}\text{C}$  standard. Although  $^{13}\text{C}$  labeled standards may not be currently available for many analytes, technologies are emerging for quantitatively generating widespread  $^{13}\text{C}$  compounds for use in biological studies i.e. biosynthesis.