Real-Time Authentication of Food and Beverages Using DART QDa LiveID Analysis

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INTRODUCTION

Currently there is no globally harmonized definition for "food fraud", however, there are initiatives coordinating action against fraudulent practices in the food supply chain. Food and beverages of higher commercial value are frequently subject to fraud. Analytical methods are required for process control, quality assurance and formulation. Direct Analysis in Real Time (DART) is an ambient ionization technique requiring minimal sample preparation and no chromatography. DART has been coupled to a single quadrupole mass detector (QDa) to produce spectral profile data for fingerprinting using chemometric model building software (LiveID 1.2). Here we investigate the potential for the DART QDa LiveID as a solution for the rapid screening of high value food and beverage samples with minimal sample preparation. Chemometric models for product verification have been generated using authentic reference samples of premium **whisky** (brand 1, brand 2 and adulterated), **palm oils** (including crude, sustainably produced crude and refined originating from different geographical locations) and ground **cinnamon and cassia**.

Experimental and Example Applications

The DART source linear X rail module with the QuickStrip cards were used for semi-automated sample introduction. The DART source was operated with a fixed helium gas flow of 1.5 L/min. The QDa was operated in full scan mode. The following parameters were optimized depending on the sample type; helium gas temperature; MS polarity; mass range and cone voltage (Table 1). The MS scan rate was fixed at 2 Hz with a DART rail speed of 0.5 mm/s. Multivariate statistical models were generated in LiveID using authentic characterized samples and subsequently the models were used for real-time classification of "unknown" samples as shown in the workflow below.

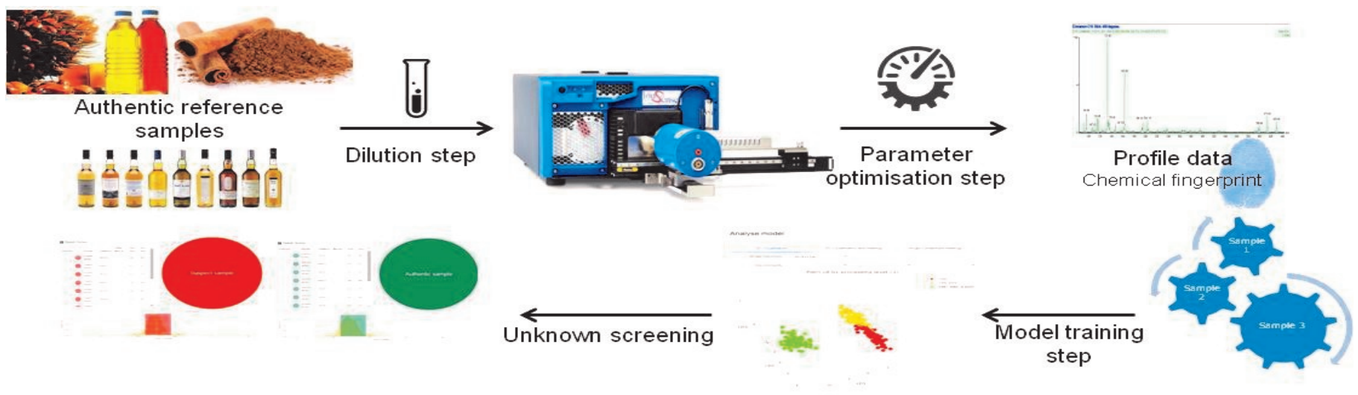
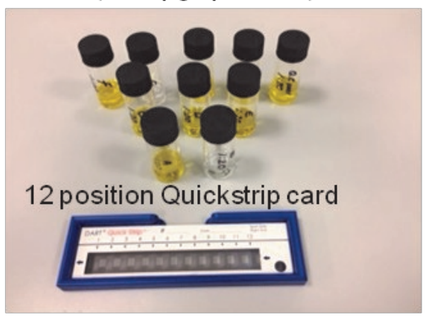


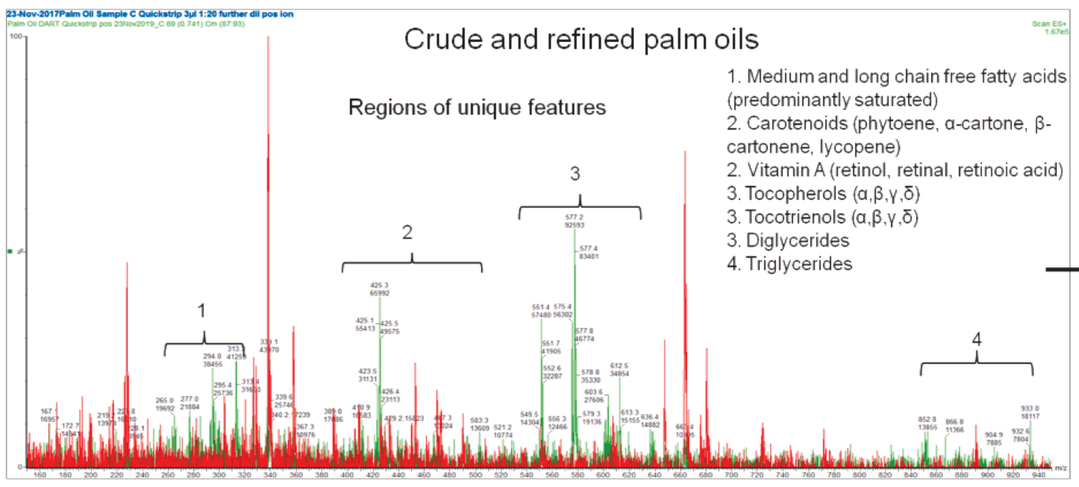
Table 1 Optimised method parameters

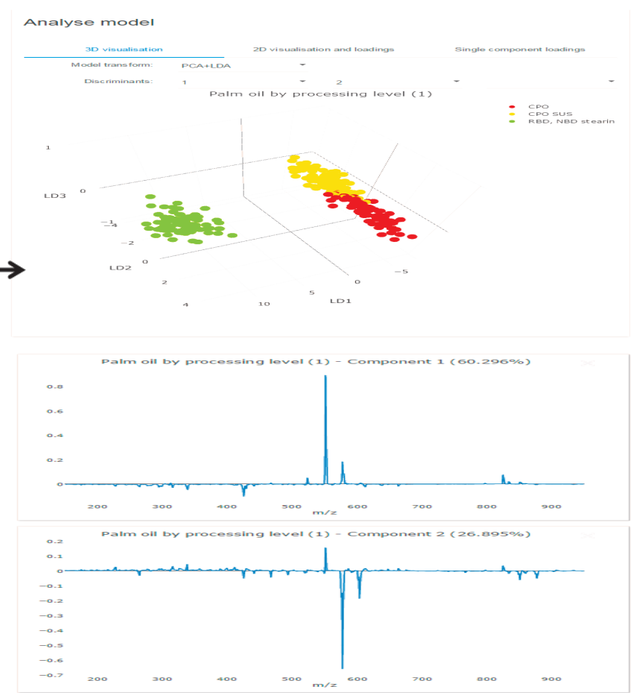
Parameter	Application		
	Palm Oil	Whisky	Cinnamon
Sample volume per measurement (µl)	3	10	3
DART helium temperature (°C)	350	300	150
QDa mass range (Da)	100-950	100-450	100-600
QDa cone Voltage (eV)	5	15	10
QDa polarity	Positive	Positive	Positive

Palm oil profiling

Palm oil samples diluted in dichloromethane (37.5 µg / position)

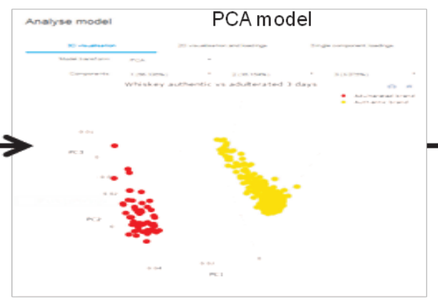


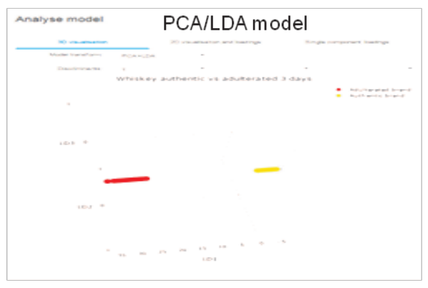


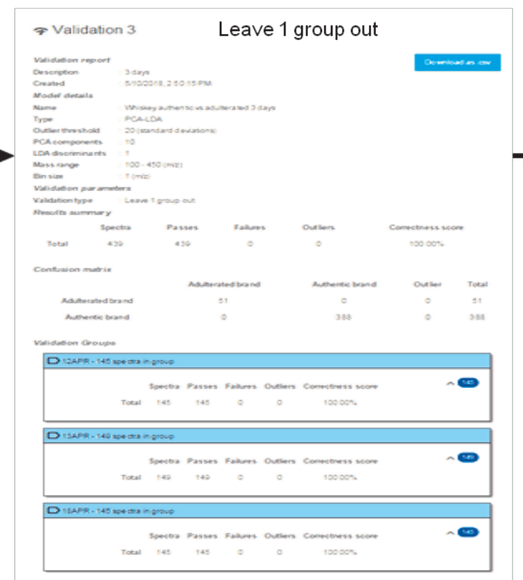


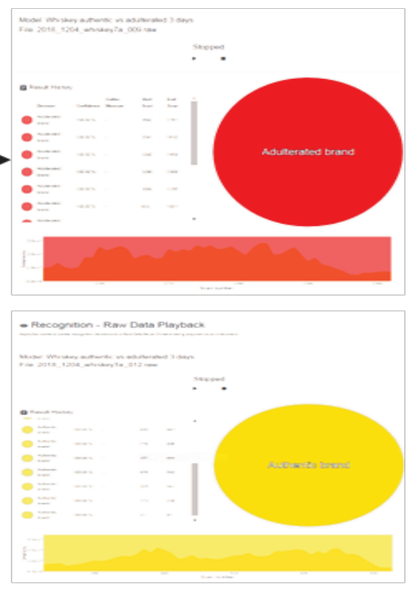
Palm oil samples were diluted in dichloromethane and spotted onto the Quickstrip cards for DART QDa analysis. Gross differences between the crude and refined oils observed in the region between *m/z* 220–950 are attributed to fatty acids, carotenoids, vitamins, diglycerides and triglycerides. The full scan data was used to train a multivariate model using PCA/LDA in LiveID 1.2. The scores plot shows tight grouping replicates and clear separation between the crude and refined oils (green and red circles), a weaker separation is also observed between crude and sustainable crude oil production (red and yellow circles, respectively). The loadings plots indicate that dyglyceride species in the *m/z* 550-600 region account for c.80% of the variance in the first two components.

Whisky adulteration



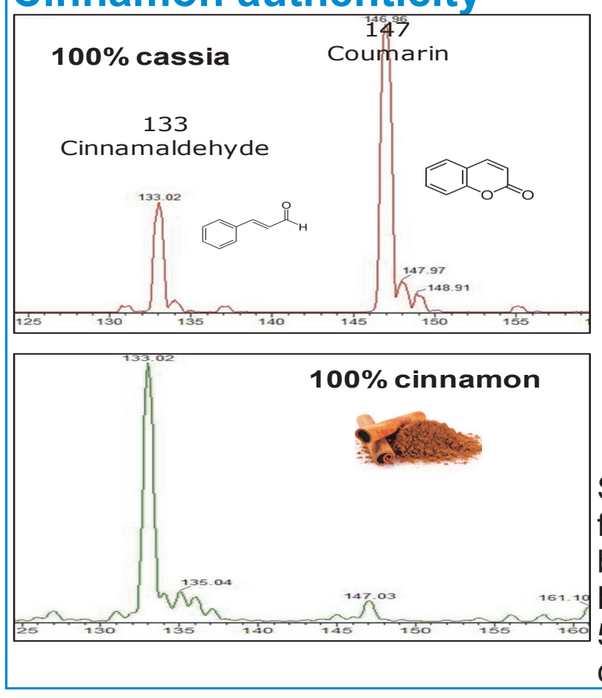


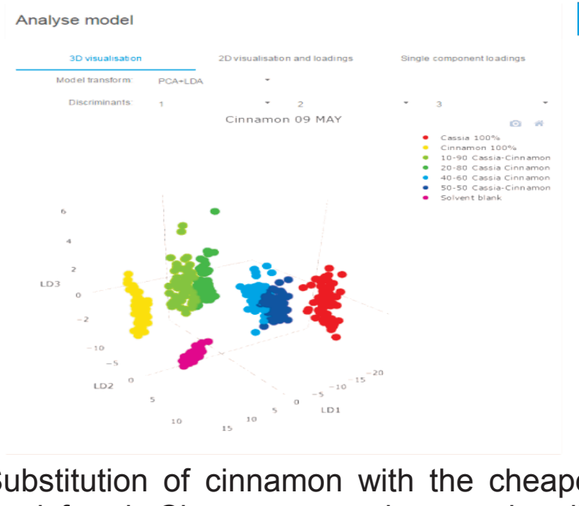




Authentic brand and adulterated brand whisky samples were analysed directly on the Quickstrip cards. The sample set was analysed on 3 separate days and the data combined to create a model. Leave 1 group out *in silico* validation was performed giving 100% correctness score. The model was challenged in real time recognition mode as an independent validation.

Cinnamon authenticity





Substitution of cinnamon with the cheaper species cassia is a common food fraud. Cinnamon species can be differentiated by ratio differences between cinnamaldehyde (ion at *m/z* 133) and coumarin (ion at *m/z* 147). Blends of cinnamon and cassia were prepared at 90:10, 80:20, 60:40 and 50:50 w/w mixes and used to train a model to recognise dilution with cassia. It is possible to detect blends to around 10% dilution.

CONCLUSIONS

- DART QDa LiveID is a rapid and powerful solution requiring minimal or no sample preparation and no chromatographic separation
- DART QDa LiveID shows great promise for profiling of gross differences *e.g.* authentic vs. adulterated product, production method and process control
- LiveID allows the analyst to easily generate, validate and curate bespoke chemometric models for their specific applications

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