



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

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Waters Corporation

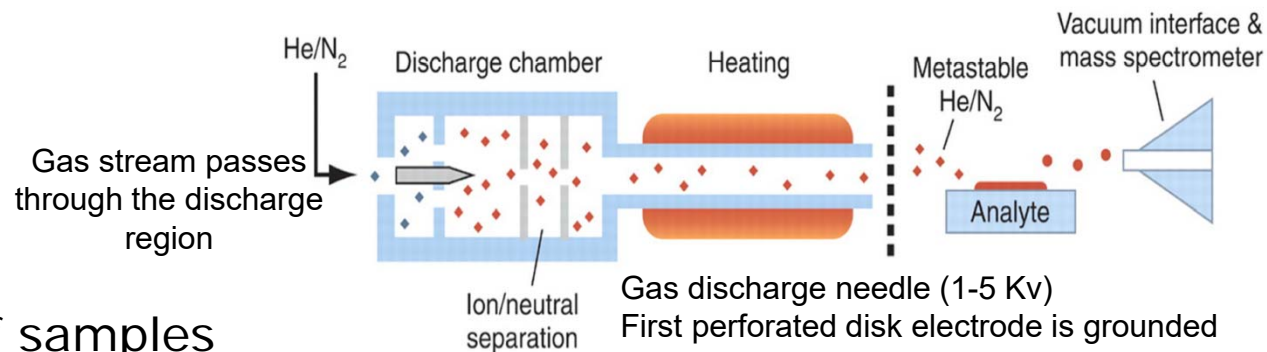
NEMC 2019

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Introduction to the DART QDa LiveID system

- What is happening in **DART ion source**?
 - Thermal desorption of analytes by hot gas stream
 - APCI-like ionization from corona discharge

The gas temp varies from ambient to 600°C. The width of the gap between the DART source exit and sampling cone varies from c. 5 – 25 mm.



Gas discharge needle (1-5 Kv)
First perforated disk electrode is grounded
Second disk electrode & the grid electrode are ± 100 & ± 250 V, respectively
Gas flow rate is typically at least 0.55 L/min⁻¹

- Why use DART?
 - Direct analysis of samples
 - Little to no sample prep required
 - No chromatography needed

DART QDa sample introduction techniques

Direct analysis of;

- Solids and powders
- Liquids
- Tablets
- Vapour / aroma

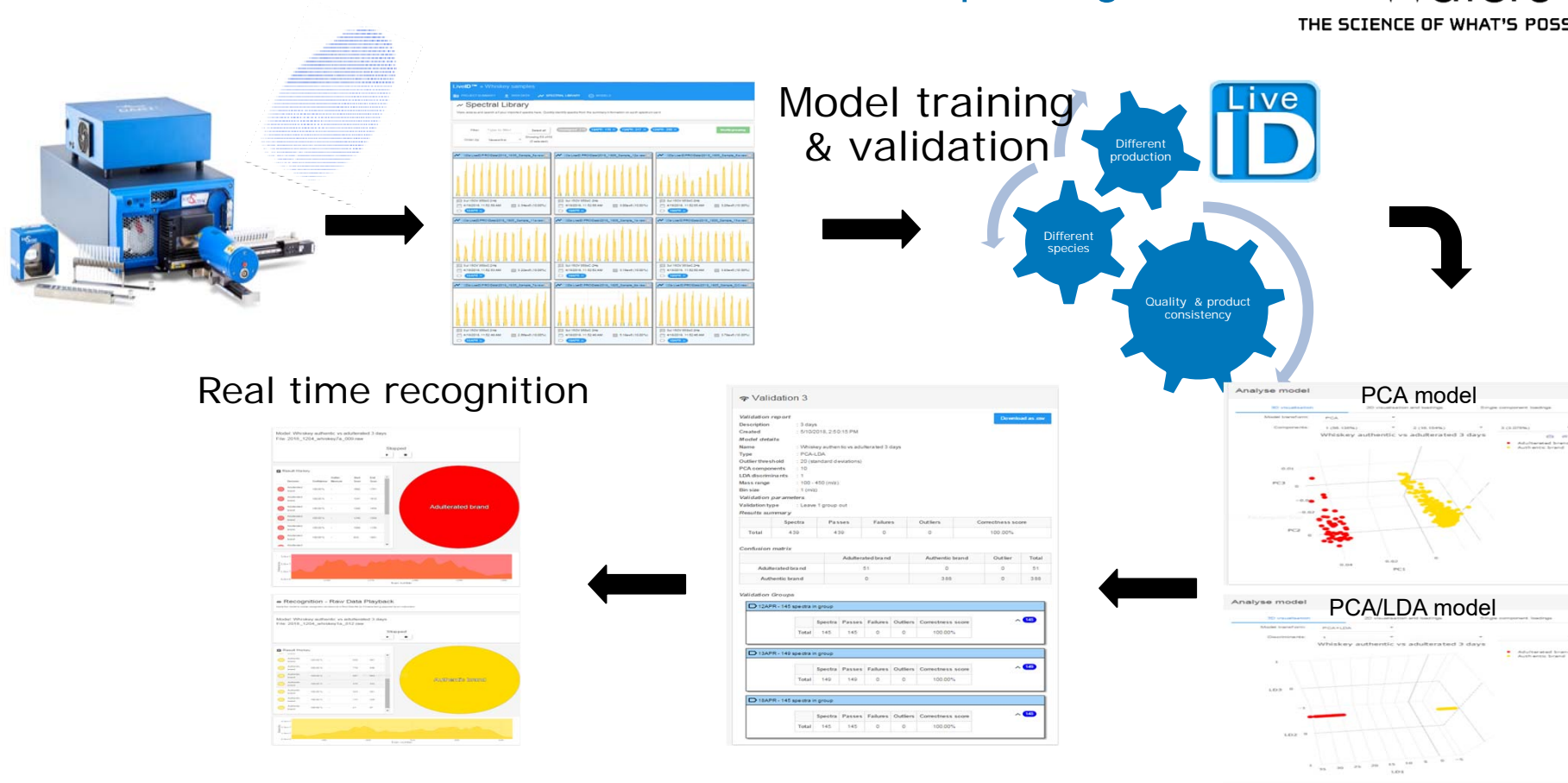


Automation using 12 position
Quickstrip cards and Dip-it tips



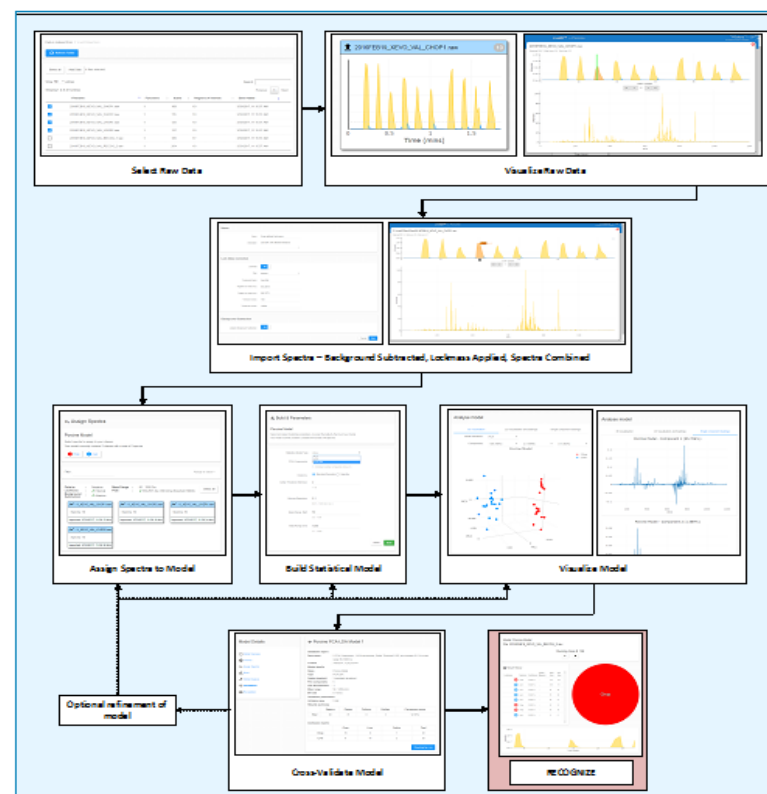
DART QDa LiveID workflow for chemometric profiling

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LiveID v1.2 Work Flow – for model training

- Full scan profile data acquired in MassLynx
- Each region of interest is combined into a single spectrum
- Pre-processing user configurable, mass range selection & data binning
- PCA (Principal Components Analysis), LDA (Linear Discriminant Analysis) or combined PCA-LDA model types
- Model cross-validation and analysis capability to iteratively refine the model
- Real time recognition from a MassLynx .Raw file that is being actively acquired
- Clear instant results at point-of-use



DART QDa LiveID for food research

Finished foods (authenticity/research)

- Ground herbs & spices
- Alcoholic beverages
- Edible oils (e.g. EVOO)
- Fruit juices
- Coffee & tea



Raw ingredients and processed foods

- Quality profiling
- Flavour & taste profiling
- Supplier verification testing
- Label claim verification
- Nutritional content (e.g. vitamin fortification)
- Composition and consistency [$\pm 20\%$]

DART QDa LiveID applications

- Edible oil authenticity & quality
 - Palm oil production
 - EVOO authenticity
- Black tea authenticity
- Whiskey adulteration and brand authenticity
- Spice authenticity (cinnamon, black pepper* & cocoa*)
- Milk quality*

*Collaborator research

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DART QDa LiveID for Palm Oil Production and Processing



Palm Oil Sample Set

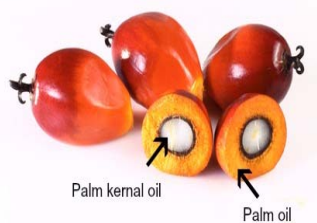
Sample ID	Geographical origin	Description	Descriptor code
A	Indonesia	Crude palm oil	CPO
B	Indonesia	Refined, bleached and deodorised crude palm oil	RBD
C	Indonesia	Crude palm oil	CPO
D	Bialla-PNG	Sustainable crude palm oil	SCPO
E	Indonesia	Sustainable crude palm oil	SCPO
F	Indonesia Padang	Crude palm oil	CPO
G	Indonesia Padang	Refined, bleached and deodorised crude palm oil	RBD
H	Malaysia	Neutralised, bleached and deodorised	NBD
I	Bialla-PNG	Sustainable crude palm oil	SCPO
J	Indonesia-Padang	Sustainable crude palm oil	SCPO

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Palm Oil Sample Preparation

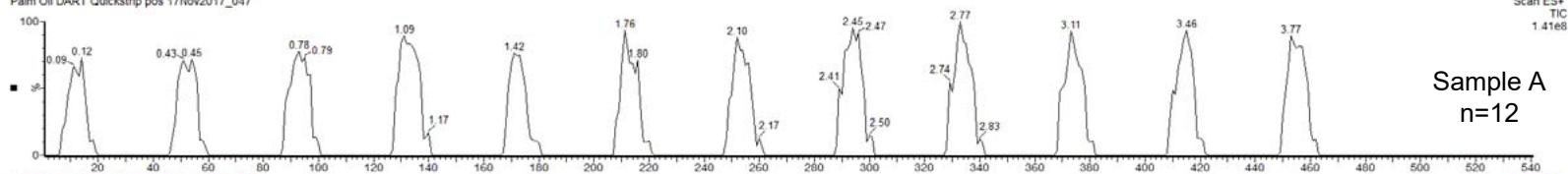
- 1 g material weighed into a 20 ml glass vial
- 4 ml of dichloromethane added to the vial
- Vortex mix for 30 s to dissolve
- 3 μ l extract spotted on Quickstrip gauze and allowed to completely dry under ambient conditions [~5 mins]



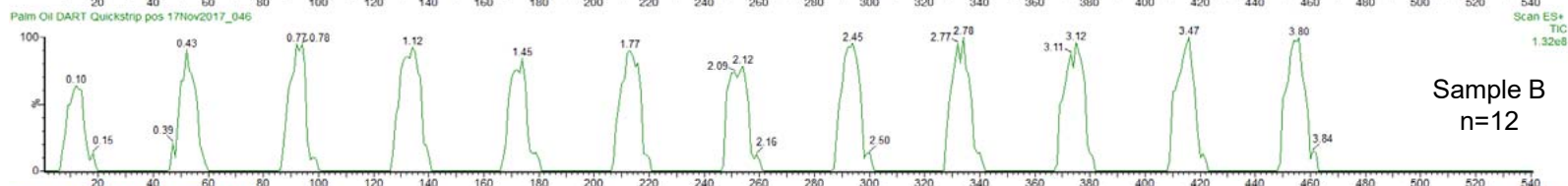
DART QDa Data – example TIC repeatability across 12 Quickstrip sampling events

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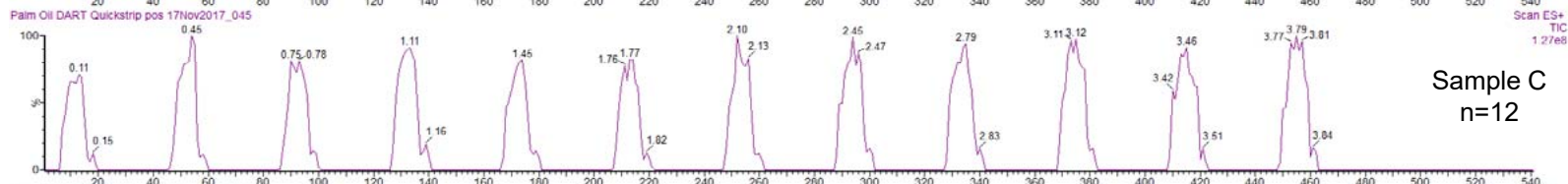
Palm Oil Sample E Quickstrip 3µl 1:20 further dil pos ion
Palm Oil DART Quickstrip pos 17Nov2017_047



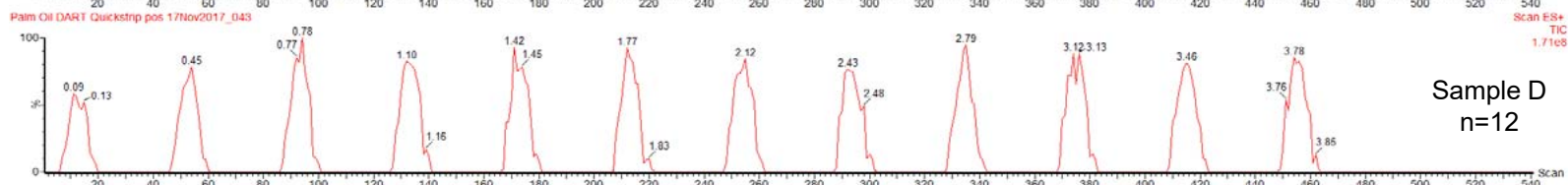
Palm Oil DART Quickstrip pos 17Nov2017_046



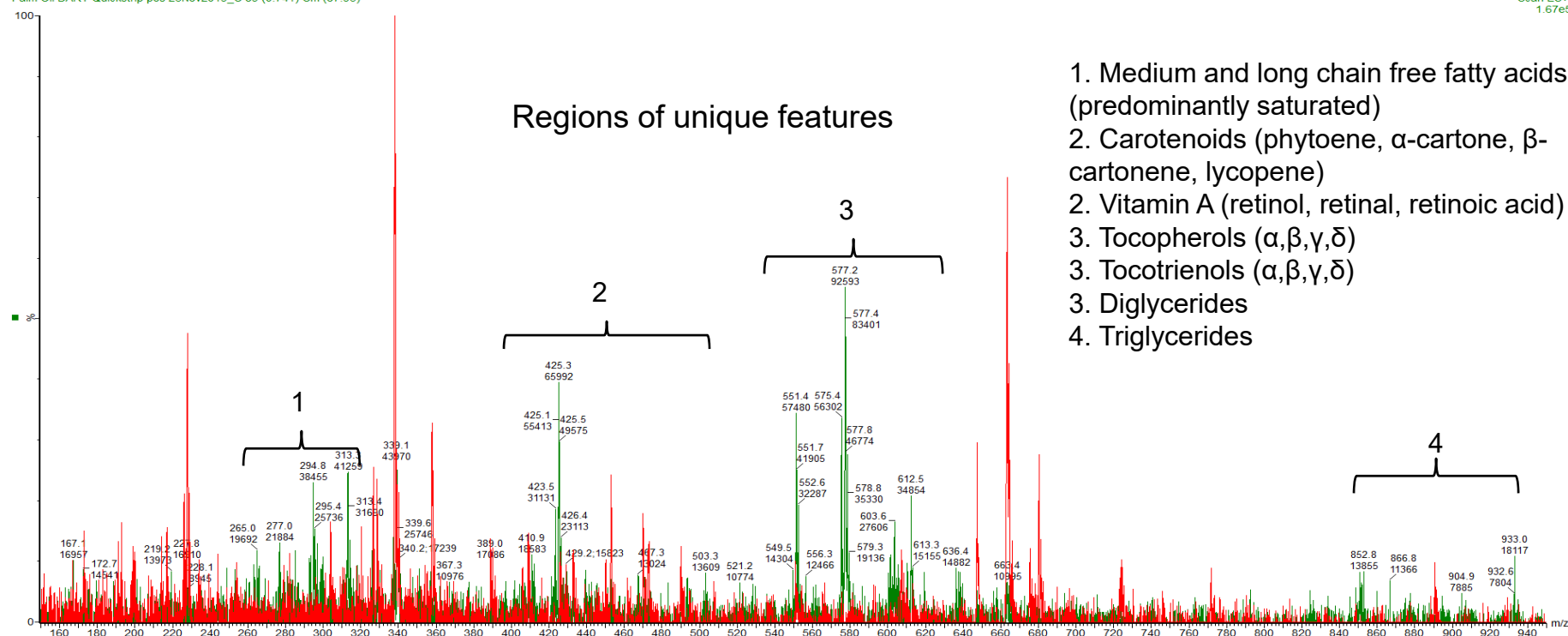
Palm Oil DART Quickstrip pos 17Nov2017_045



Palm Oil DART Quickstrip pos 17Nov2017_043

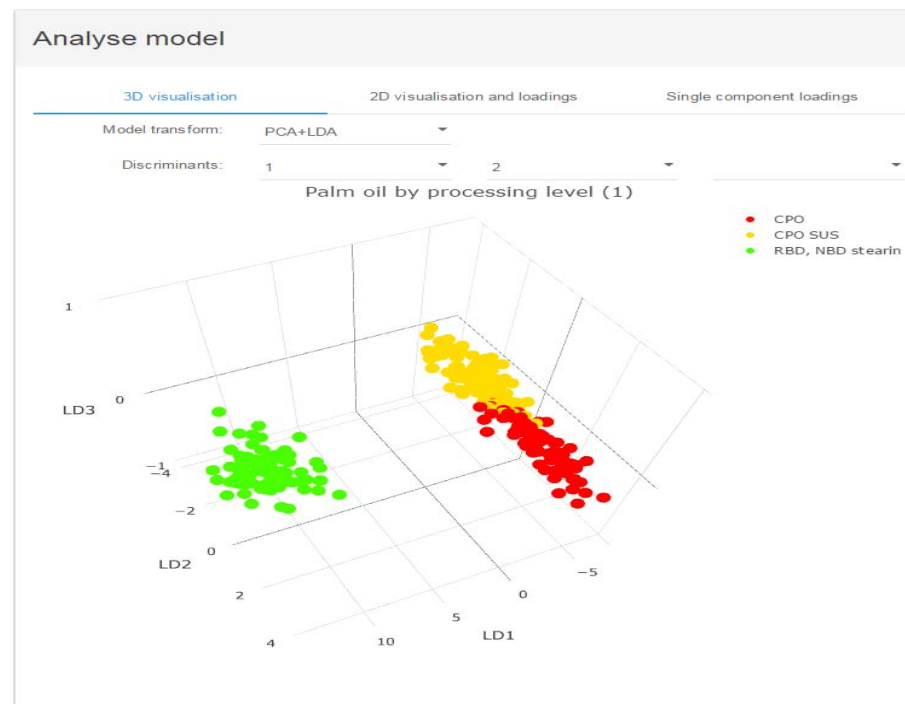


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Scan ES+
1.67e5

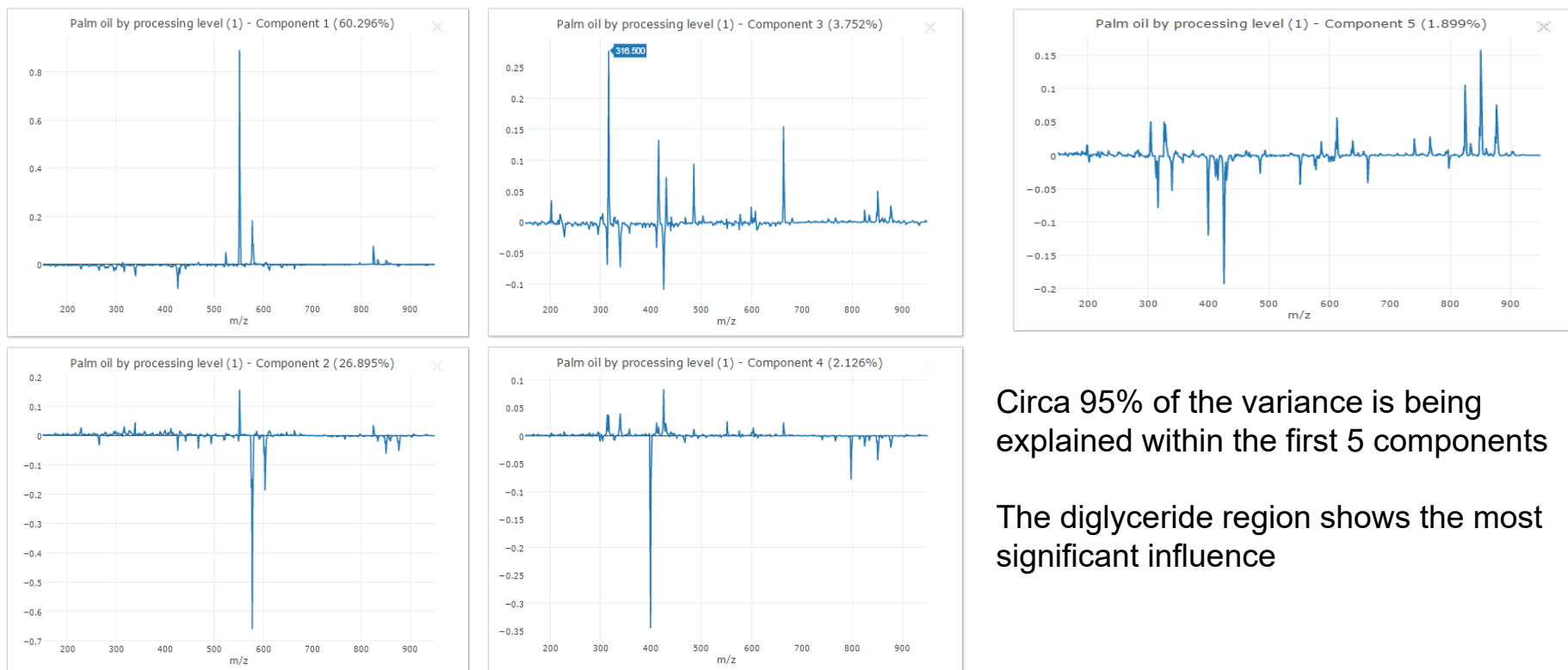
LiveID model

Grouped by processing level, 2 instruments, 3 days data combined, positive ion mode



Weak differentiation between production methods

LiveID model grouped by processing level – loadings plot view showing the first 5 components



Circa 95% of the variance is being explained within the first 5 components

The diglyceride region shows the most significant influence

Herbs and spices authenticity

Cinnamon

Collaboration with British Spice and Pepper Board

Facts about Cinnamon

- Cinnamon is commonly adulterated
- Cinnamon is obtained from the inner bark of several tree *spp.* of *Cinnamomum* genus
- Common species of cinnamon
 - ***C. Verum* or *Ceylon*** → “**True Cinnamon**” Sri Lanka produces 80-90% of global supply
 - *C. Burmannii* → “Indonesian cinnamon”
 - *C. Loureiroi* → “Saigon cinnamon”
 - *C. Cassia* → “Chinese cinnamon” → This is the adulterant commonly used
- Ceylon is the only cinnamon that **does not** contain high levels of **coumarin**
 - EU Regulations describe maximum limits for coumarin
 - Hepatotoxic compound & possible carcinogen



Analysis of ground cinnamon - controlled samples

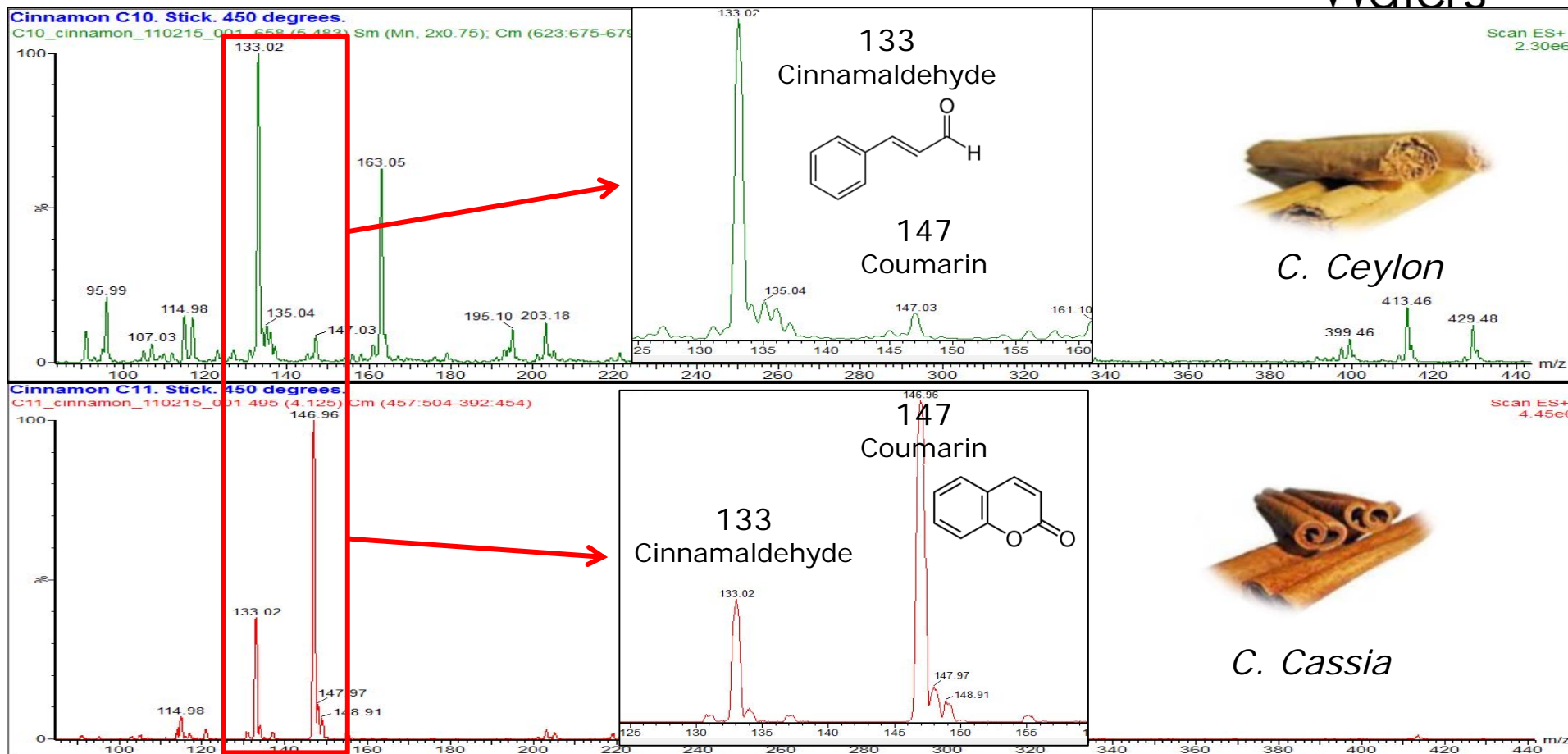
Ceylon vs. Cassia

Sample preparation

- 1 g of ground cinnamon mixed with 15 ml of EtOH:water 1:1
- Vortex for 1 min
- Sonicate 15 min
- Centrifuge at 6000 rpm for 5 min
- Load 3 ml of supernatant on HLB prime pass through (60 mg capacity 3cc)
- Elute analytes with 1 ml of 100 % methanol
- 3 µl spot on Quickstrip and analyzed by DART-Qda

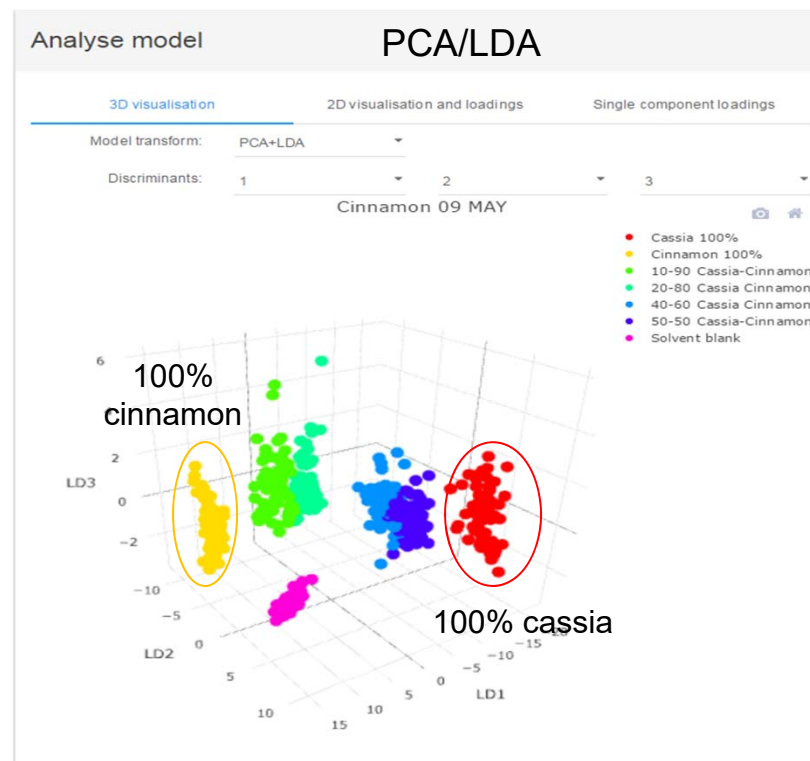
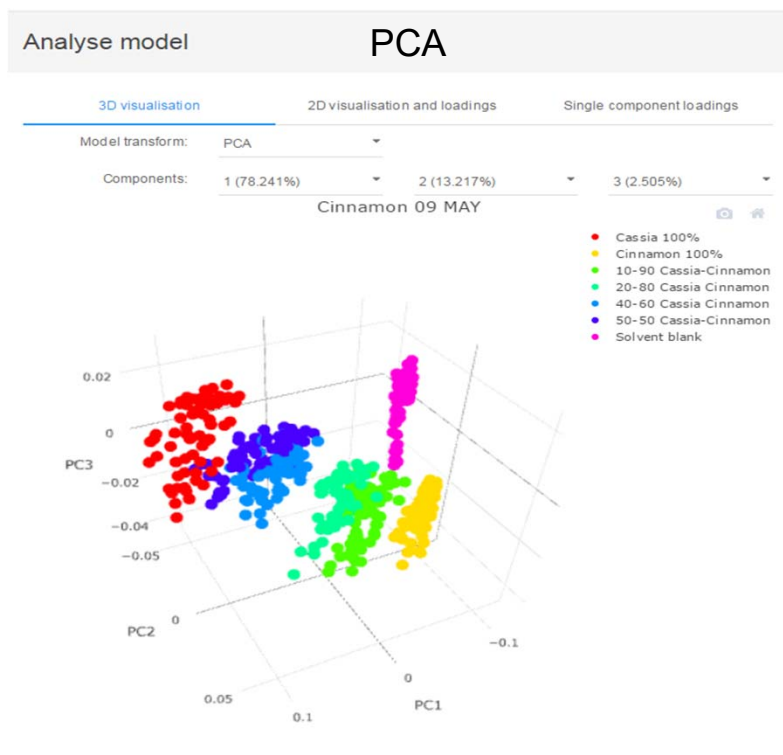
Cinnamon vs. Cassia

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Cinnamon vs. Cassia blends

LiveID model constructed on 1 instrument, 3 days repeatability



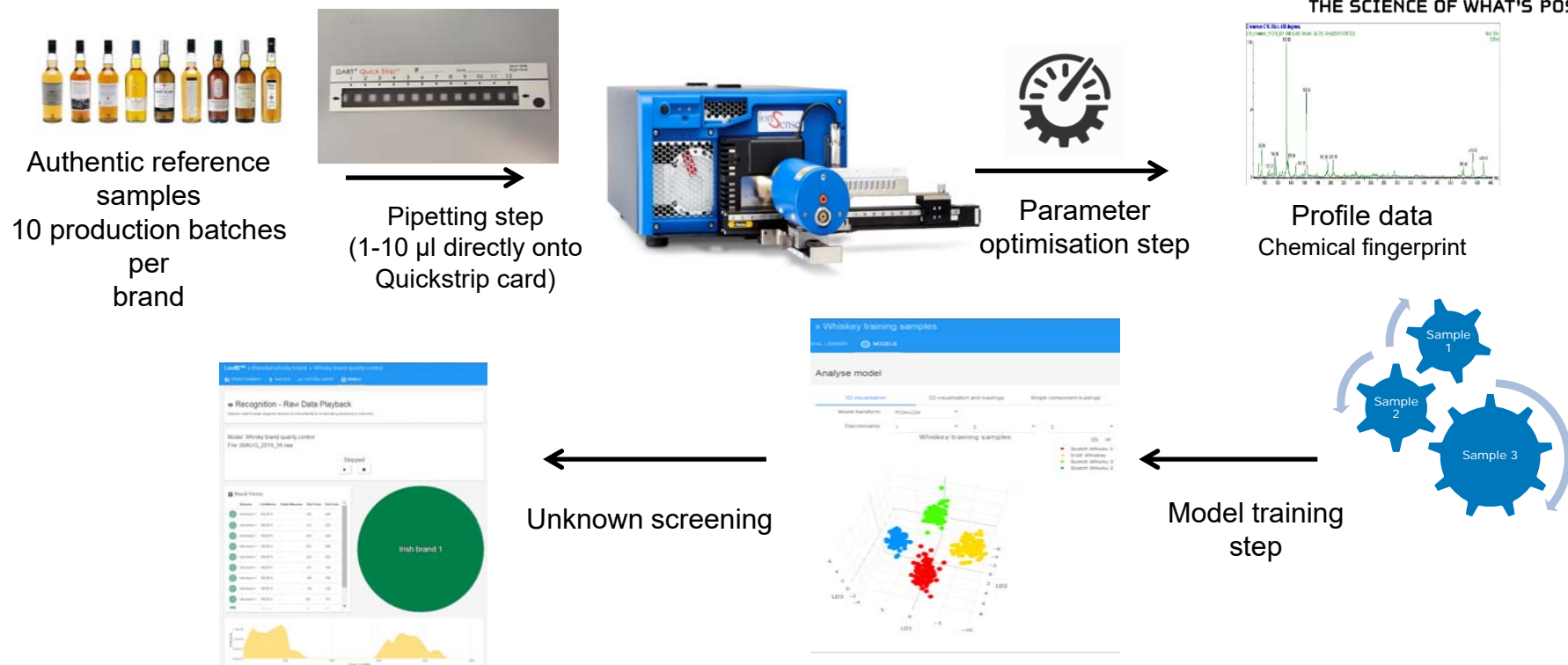
Whisky brand authenticity

Collaboration with SWRI

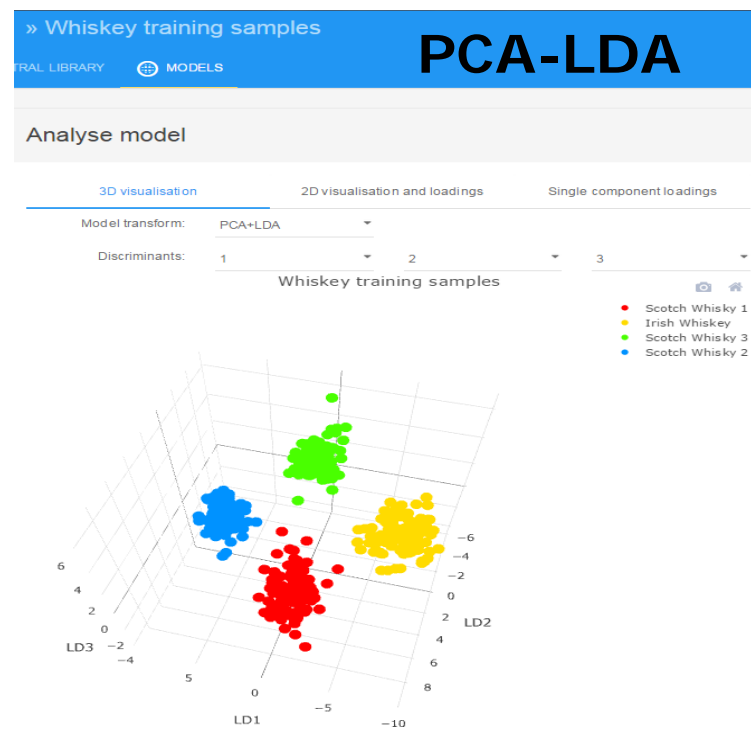
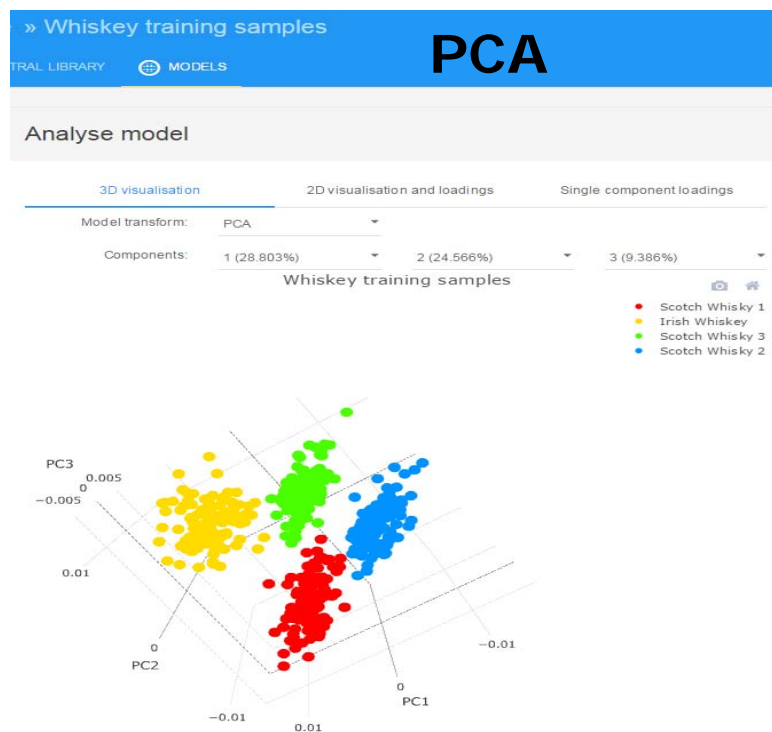


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LiveID Chemometric model



LiveID *In silico* validation – leave one file out

Model parameters

Statistical Model Type PCA-LDA

PCA Components 10
1 - 439 (total number of spectra minus 1)

Linear Discriminants 3
1 - 3

Outlier by ☒ Standard Deviation ☐ Quantile

Outlier Threshold (Std Dev) 20
≥ 0

Binning Resolution 1.00
0.10 - 5.00 (to 2 d.p.)

Mass Range: Start 100
100 - 499

Mass Range: End 430
101 - 500

Reset

Build

Validation_LOFO

Validation report

Download as .csv

Description :
Created : 12/7/2018, 2:40:29 PM

Model details

Name : Whisky brand quality control
Type : PCA-LDA
Outlier threshold : 5 (standard deviations)
PCA components : 10
LDA discriminants : 3
Mass range : 100 - 450 (m/z)
Bin size : 1 (m/z)

Validation parameters

Validation type : Leave 1 file out

Results summary

	Spectra	Passes	Failures	Outliers	Correctness score
Total	436	436	0	0	100.00%

Confusion matrix

	Scottish brand 1	Irish brand 1	Scottish brand 3	Scottish brand 2	Outlier	Total
Scottish brand 1	109	0	0	0	0	109
Irish brand 1	0	109	0	0	0	109
Scottish brand 3	0	0	109	0	0	109
Scottish brand 2	0	0	0	109	0	109

Single blind samples independent validation run on a second day

Sample Identifier code (40% ABV)	Classification result (<i>replicates</i>)	LiveID % Confidence match score	True Identity
S16 -3331	Scottish brand 3 (11)	100	Scotch brand 3
S16-0143	Scottish brand 1 (11)	100	Scotch brand 1
S16-0155	Scottish brand 1 (11)	100	Scotch brand 1
S15-1390	Irish brand 1 (11)	100	Irish brand 1
S15-1391	Irish brand 1 (11)	100	Irish brand 1
S15-1424	Irish brand 1 (11)	100	Irish brand 1
S15-3338	Scottish brand 3 (11)	100	Scotch brand 3
S15-3737	Scottish brand 2 (11)	100	Scotch brand 2
S15-3025	Scottish brand 3 (11)	100	Scotch brand 3
S15-3029	Scottish brand 3 (11)	100	Scotch brand 3

Single blind samples independent validation run on a second day

Sample Identifier code (40% ABV)	Quick strip card position	True Identity	Classification result
S15-1088	1	Scotch whisky brand 1	
S15-1102	2	Scotch whisky brand 2	
S15-0911	3	Irish whiskey brand 1	
S15-1518	4	Scotch whisky brand 3	
S15-3737	5	Scotch whisky brand 2	
S15-1391	6	Irish whiskey brand 1	
S16-0155	7	Scotch whisky brand 1	
S16-0155	8	Scotch whisky brand 1	
S15-3331	9	Scotch whisky brand 3	
S15-3338	10	Scotch whisky brand 2	
S15-1424	11	Irish whiskey brand 1	
S15-1391	12	Irish whiskey brand 1	

Summary

- DART QDa combines the simplicity of minimal or no sample preparation, speed of no chromatography with the power of mass spectral profiling
- LiveID converts the mass spectra into data to train multi-variant statistical models that is used in real time to classify unknown samples
 - Provides the user with tools to create a database for their specific application
- Fit for purpose as a rapid screening tool for the identification of differences *e.g.* authentic vs. adulterated product or process monitoring
- Often not possible to solve these industry challenges using alternative methods
 - NIRS, FTIR, RAMAN etc.
- DART QDa LiveID offers a quick, powerful and low sample preparation solution

Acknowledgements

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