Rapid and Accessible Mass Detection Tools for the Identification of Substitution Fraud in Dried Herbs

Emily Rose Britton[1], Sara Stead[1], Nicola Dreolin[1] and Tito Damiani[2]
[1]Waters Corporation, Milford, MA, USA and Wilmslow, UK
[2]University of Parma, Department of Food and Drug, Parco Area delle Scienze

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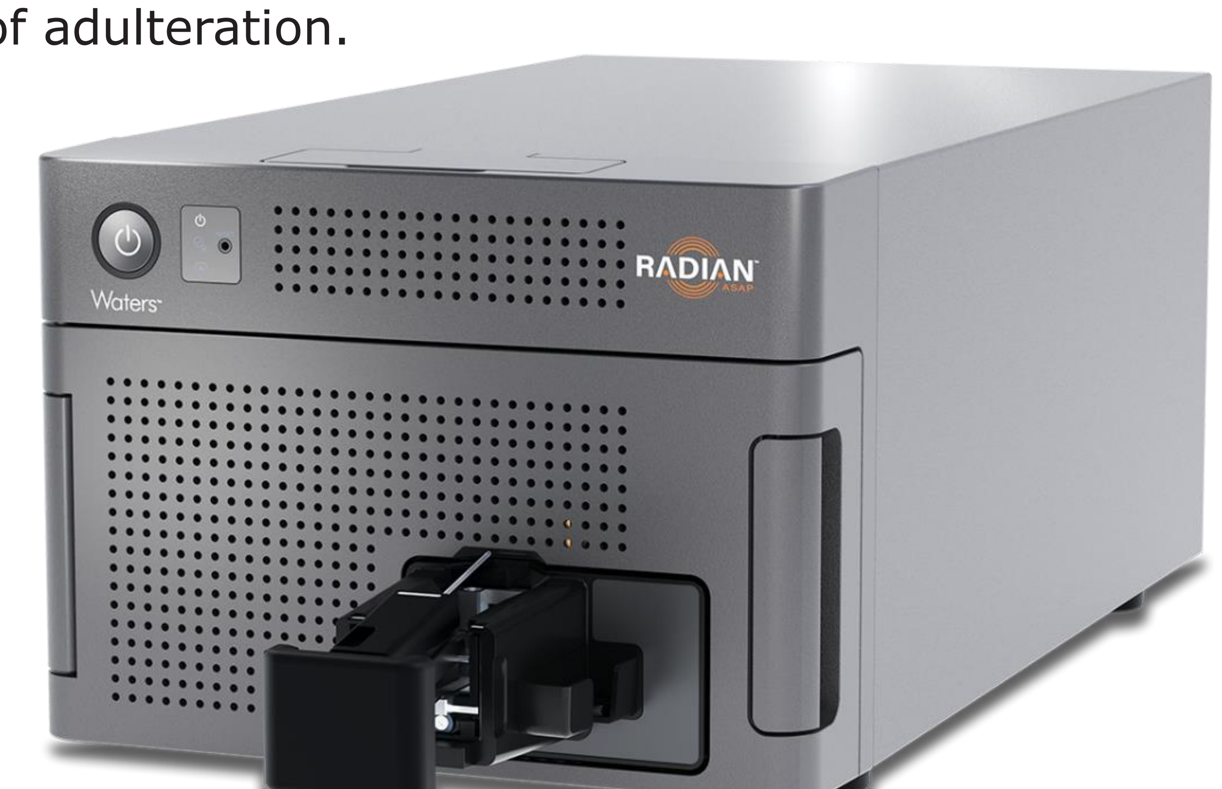
INTRODUCTION

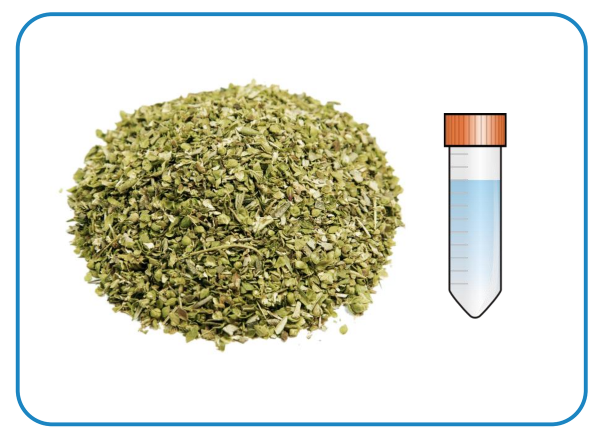
Economically motivated adulteration is a growing issue in the food supply as consumer demand for products increases and supply chains are consequently strained. A common form of economically motivated adulteration is substitution fraud, where lesser valued ingredients are blended with higher value items and misrepresented as pure or authentic. Many of the methods currently employed within the food manufacturing industry for quality control purposes are based on spectroscopic techniques. By comparison, direct mass spectrometry has shown to offer comparable speed and ease-of-use, alongside the advantages of higher selectivity, sensitivity, and diagnostic chemical information.

Existing mass spectrometry-based methods have proven effective in identifying substitution fraud but can require existing knowledge of ingredient and adulterant biomarkers, advanced training in mass spectrometry, and experience with multivariate analysis tools. One solution to these challenges is the use of the RADIAN ASAP system with LiveID, an easy to use and fit-for-purpose mass detection system which enables rapid and direct sampling of materials for untargeted analysis and classification. Further, the RADIAN ASAP hardware and software are simple to learn and use, thus lowering the barrier to entry for those who want to implement fraud screening workflows into their laboratories and facilities.

Mediterranean oregano is one of the most appreciated culinary herbs and is also used as a functional ingredient in food preparations, perfumes and cosmetic products. Its substitution with lower economical value plant leaves having similar visual properties (e.g. sumac, cistus, myrtle, olive leaves) has been previously reported in scientific literature. Therefore, oregano was chosen as a representative herb to evaluate the capability of the RADIAN ASAP to detect varying levels of adulteration.



SAMPLE PREPARATION & WORKFLOW

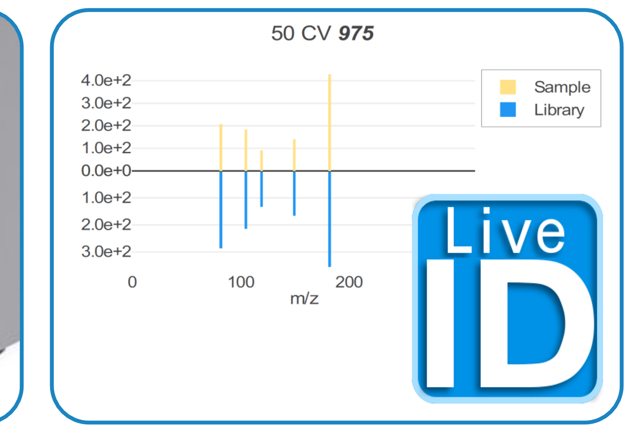


1. Extract with MeOH at 20 mg/mL

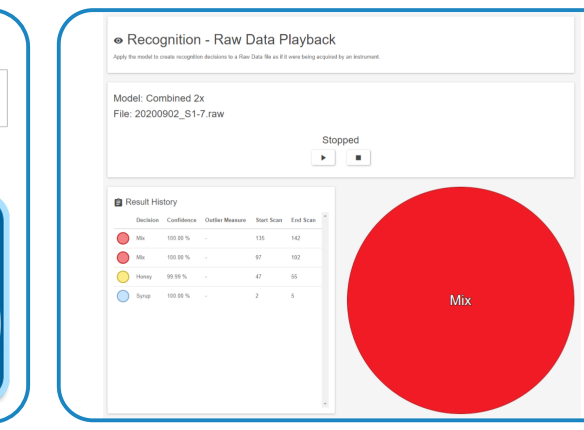
2. Clean the capillary

3. Load sample on capillary

4. Insert capillary to start acquisition



5. Real-time data visualization



6. Unambiguous identification

HARD/SOFTWARE SETTINGS

RADIAN ASAP PARAMETER	SETTING
Ionization mode	ASAP+
Corona pin	3 µA (default)
Desolvation gas (N_2) temperature	450°C
Sampling cone	12 V (default)
Acquisition mode	Full scan (continuum)
Mass range	100-1000 Da
Scan speed	2 Hz
Sampling technique	Capillary dip (5 sec hold)

LiveID 2.0 PARAMETER	SETTING
Relative peak detection threshold applied for model training and recognition	50%
Model algorithm	PCA/LDA
PDA components	3
LDA components	1
Outlier method	Standard deviation
Outlier distance	3
Binning resolution	1 Da
Mass range	300-750 Da

LiveID MODEL TRAINING

A training set of samples containing 35 different authentic oregano and 18 different olive leaf samples was selected to create the LiveID authenticity model. The samples were analyzed in a randomized order by a single analyst on a single instrument over two different days to generate two technical replicates per sample giving a population of 70 oregano and 36 olive leaf samples. The RADIAN ASAP spectra generated for the authentic oregano and other herb samples showed repeatable (from technical replicates), reproducible (from biological replicates), feature rich profiles. LiveID (v.2.0) was employed to create and validate chemometric models for discrimination between the authentic and adulterated oregano samples.

MULTIVARIATE ANALYSIS RESULTS

A PCA/LDA training model was generated from 35 authentic oregano samples and 18 authentic olive leaf samples. A random selection of 7 authentic oregano and 2 olive leaf samples (representing 20% of the model training sets) were tested on 1 of 4 instruments by 1 of 3 analysts. In all cases, LiveID recognition returned the correct classification result with a 100% confidence score. Representative samples of 4 different herbs not present in the model (marjoram, thyme, cistus, and mint) were also included in the validation study. The model returned an "outlier" classification indicating the chemical profile was not recognized as matching either authentic oregano or the single adulterant class (olive leaf) included in this model within the defined outlier distance.

SUBSTITUTION SPECIES	FAMILY & GENUS	% SUBSTITUTION IN OREGANO	LIVEID CLASSIFICATION & %OCCURRENCE (N=6)	DECISION
Olive *Olea europaea*	Oleaceaea *Olea*	10	Outlier 30% Oregano 70%	< SDL
		30	Outlier 100%	≥ SDL
		100	Outlier 100%	≥ SDL
Cistus *Cistus incanus*	Cistaceaea *Cistus*	10	Oregano 100%	< SDL
		30	Outlier 100%	≥ SDL
		100	Outlier 100%	≥ SDL

To estimate the assay blends containing an Screening Detection Limit (SDL), individual adulterant species in authentic oregano at 10 and 30% (*w/w*) were used. The blends were analyzed on the same instrument on two different days (n=6) and classified *via* LiveID real-time recognition.