



Work Package 10



## Industry Chemical Markers for Quality-Authenticity

Selection/evaluation of relevant chemical markers from the industrial perspective, which can be connected to specific quality/authenticity aspects of both raw materials/ingredients and corresponding finished products

RAW MATERIAL/ INGREDIENT/PRODUCT	TYPE OF RISK (fraud, sophistication, contamination)	TYPE OF ANALYSIS USUALLY ADOPTED	CHEMICAL MARKERS
Coffee	Blending with different coffee species	HPLC-DAD; LC-MS; LC-ECD; GC-HRMS	Chlorogenic acids determination; Unsaponifiable diterpens and sterols fraction characterization
	Sugars addition (soluble coffee)	LC-MS/IR/IEC	Saccharides profiles
	Origin mislabeling	IRMS; ICPMS	Stable isotope ratio $^2\text{H}/^1\text{H}$ $^{87}\text{Sr}/^{86}\text{Sr}$ , Trace elements profile
Cocoa products, chocolate-chocolate compounds	Addition of vegetable fats different from cocoa butter or hydrogenated fats	GC-MS; DART-HRMS	Fatty Acids/Triglycerides profiles
	Contamination: presence of cocoa shells over 5%	GC-FID; GC-MS	Fatty acid tryptamides
Eggs/Egg products	Addition of artificially colored eggs	HPLC-DAD; LC-MS	Extraneous pigments molecules. For instance, several banned dyes can be detected with a multiresidual method (e.g.: sudan, para red, toluidine red,...)
	Apparent increase of the protein content/dry matter	LC-MS	Melamine
	Apparent increase of fat content	GC-FID; GC-MS	Mineral/Vegetable oils profile

Eggs/Egg products	Addition of incubated and/or not fresh eggs	Enzymatic methods; HPLC; E-Nose	Organic acids such as 3-OH Butyric acid, Succinic Acid, Lactic Acid,...
	Use of synthetic fertilizers in organic agriculture	IRMS	Stable isotope ratio of N ( $^{15}\text{N}/^{14}\text{N}$ )
Fish	Temperature abuse during and/or after harvest	ELISA; HPLC	Histamine & other biogenic amines
	Mislabeled	IRMS	Stable isotope ratios $^2\text{H}/^1\text{H}$ , $^{12}\text{C}/^{13}\text{C}$ , $^{15}\text{N}/^{14}\text{N}$ , $^{34}\text{S}/^{32}\text{S}$ ;
	Adulteration/substitution with different species	ELISA; LC-MS	Specific protein markers
Fruit juices	Sugar addition (sugars, carbohydrate sweeteners e.g. HFCS, IS,...)	LC-MS/IR/IEC; GC; IRMS; SNIF-NMR	Saccharides profiles; Oligosaccharide profile; Stable isotope ratio of C ( $^{13}\text{C}/^{12}\text{C}$ ) and H ( $^2\text{H}/^1\text{H}$ ) in ethanol from sugars (AOAC methods 2004.01 and 995.17)
	Water addition	IRMS	Stable isotope ratio of O ( $^{18}\text{O}/^{16}\text{O}$ ) and of H ( $^2\text{H}/^1\text{H}$ ) in water
	Addition of citric-malic-ascorbic-tartaric acids	Enzymatic methods; HPLC; IRMS	Organic acids profiles; Stable isotope ratio of C ( $^{13}\text{C}/^{12}\text{C}$ )
	Addition of other cheaper fruits	HPAEC-PAD; GC-FID LC-MS	Polyphenols, Anthocyanins, Polymethoxylated flavones (PMFs), Carotenoids profiles
	Addition of synthetic aroma	Chiral GC, GC-IRMS	Racemic mixtures in the aroma/ flavor profile
	Geographical origin	IRMS, TIMS	$^{87}\text{Sr}/^{86}\text{Sr}$ -TIMS and multi-isotope testing
	Adulteration of acacia honey with rape one	HPLC-DAD; LC-MS; LC-ECD	Chlorogenic acid and ellagic acid
Honey	False floral origin	ICPMS; IRMS	Trace elements profile; Stable isotope ratios of C ( $^{13}\text{C}/^{12}\text{C}$ ) and H ( $^2\text{H}/^1\text{H}$ )

Honey	Addition of exogenous sugar	IRMS	Stable isotope ratios of C ( $^{13}\text{C}/^{12}\text{C}$ ) in honey and protein (AOAC 998.12)
Meat	Substitution of fresh meat with frozen-thawed one	Enzyme activity assay	Beta-hydroxyacyl-CoA dehydrogenase activity
	Mislabeling; origin mislabeling	IRMS; ICPMS	Stable isotope ratios $^2\text{H}/^1\text{H}$ , $^{12}\text{C}/^{13}\text{C}$ , $^{15}\text{N}/^{14}\text{N}$ , $^{34}\text{S}/^{32}\text{S}$ ; Trace element/mineral profiles
	Adulteration/substitution with different species	ELISA; LC-MS	Specific protein markers
Milk and Derivatives; Cheeses	Substitution of natural mozzarella cheese with imitation	HPLC	Lysinoalanine
	Apparent increase of the protein content/dry matter	LC-MS	Melamine
	Substitution of PDO cheese with others	HPLC; GC; LC-MS; IRMS, ICPMS	Free aminoacids / peptides profiles. Stable isotope ratios $^2\text{H}/^1\text{H}$ , $^{12}\text{C}/^{13}\text{C}$ , $^{15}\text{N}/^{14}\text{N}$ , $^{34}\text{S}/^{32}\text{S}$ ; Trace element profile
	Addition of other “non-milk” fats/oils	GC-MS; DART-HRMS	Fatty Acids/Triglycerides profiles
	Addition of pigments (e.g. beta-carotene,...) in order to increase color	HPLC-DAD	Carotenoids profile
Oils & Fats	Addition of foreign/refined/deodorized/... oil to EVO	GC-MS; LC-MS IRMS	Fatty Acids/Triglycerides profiles; Stable isotope ratio of C ( $^{13}\text{C}/^{12}\text{C}$ ) and H ( $^2\text{H}/^1\text{H}$ )
	Addition of pigments in order to improve the color	HPLC-DAD; LC-MS	Chlorophylls, pheophytins, carotenoids (...) profiles
	Mislabeling	IRMS	Stable isotope ratios $^{13}\text{C}/^{12}\text{C}$ $^2\text{H}/^1\text{H}$ $^{18}\text{O}/^{16}\text{O}$

Wine; Vinegar	Addition of cheaper sugar/alcohol	GC-FID/MS; LC-MS/IR/IEC IRMS, SNIF-NMR	Saccharides & Alcoholic profiles; Stable isotope ratio of C ( $^{13}\text{C}/^{12}\text{C}$ ) and H ( $^2\text{H}/^1\text{H}$ ) in ethanol and acetic acid (methods OIV-MA-AS311-05 and OIV-MA-AS312-07; OIV 510/2013, EN 16466-1 and EN 16466-2)
	Addition of water	IRMS	Stable isotope ratio of O ( $^{18}\text{O}/^{16}\text{O}$ ) in water (OIV-MA-AS2-12; OIV 511/2013 and EN 16466-3)
	Addition of industrial CO <sub>2</sub>	IRMS	Stable isotope ratio of C ( $^{13}\text{C}/^{12}\text{C}$ ) in CO <sub>2</sub> (OIV MA-F-AS314-03-CO2MOU)
	Geographical origin	IRMS, SNIF-NMR	Stable isotope ratio of C ( $^{13}\text{C}/^{12}\text{C}$ ) and H ( $^2\text{H}/^1\text{H}$ ) in ethanol and acetic acid and stable isotope ratio of O ( $^{18}\text{O}/^{16}\text{O}$ ) in water
Vegetables	Use of synthetic fertilizers in organic agriculture	IRMS	Stable isotope ratios of N ( $^{15}\text{N}/^{14}\text{N}$ ) in bulk tissue and of O ( $^{18}\text{O}/^{16}\text{O}$ ) in plant derived nitrate
Vanilla extracts	Substitution of natural vanilla flavor with artificial ones	GC-MS	4-hydroxybenzaldehyde
	Addition of exogenous vanilla	GC-IRMS	Stable isotope ratio of C ( $^{13}\text{C}/^{12}\text{C}$ ) (AOAC 2006.05)
Spirit Drinks	Addition of water	Density; IRMS	Ethanol/Water; Stable isotope ratio $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$ in water
	Addition of neutral alcohol/non-potable alcohol/cheaper alternative spirits	GC-FID; GC-MS; LC-UV	Volatile congener profiles, and maturation related compounds (for matured products)
	Addition of sweeteners and flavourings	LC-IEC; GC-MS; LC-UV	Sugar profiles and flavour compounds