

# DETECTION OF ADULTERATION OF GROUND COFFEE USING NEAR-INFRARED SPECTROSCOPY AND CHEMOMETRICS

Antonia Zeman, Davor Valinger, Ana Jurinjak Tušek, Jasenka Gajdoš Kljusurić, Maja Benković, Tamara Jurina\*

University of Zagreb, Faculty of Food Technology and Biotechnology, Pierottijeva 6, 10000 Zagreb, Croatia

\*tamara.jurina@pbf.unizg.hr

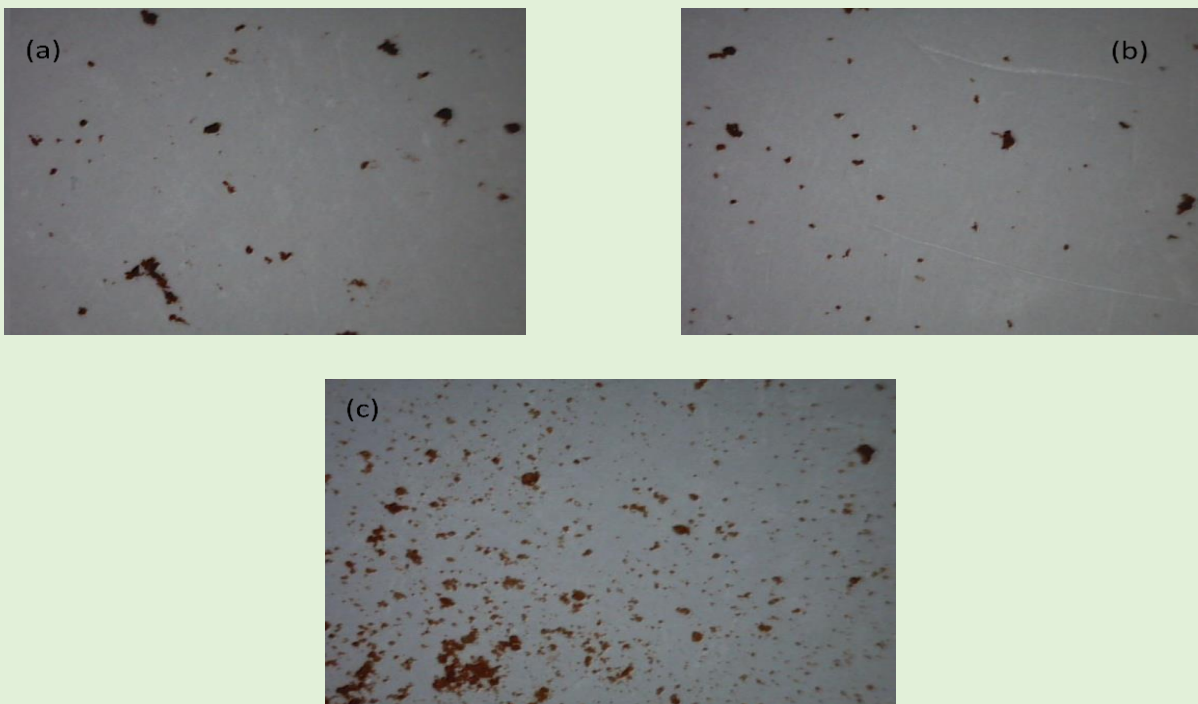
## INTRODUCTION

Coffee authenticity has become a challenging issue in the food industry, due to the fact that coffee is among the most consumed beverages globally. When considering coffee's market value, the main problem represents an illegal practice of adulterating coffee with less expensive and inferior ingredients, due to greater financial profit. Therefore, the purpose of this work was to investigate if Near Infrared Spectroscopy (NIRs), in combination with chemometrics, could be used in detection of the adulteration of ground coffee with malt coffee.

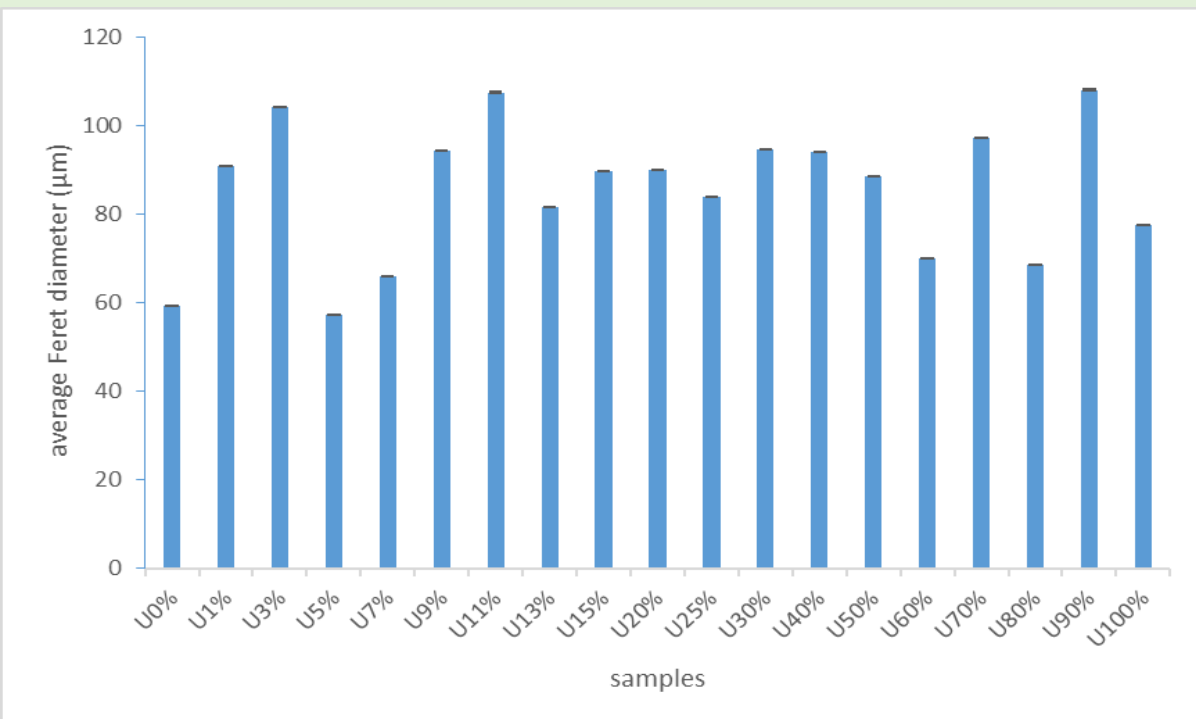
## MATERIALS AND METHODS

- adulteration: pure coffee samples were adulterated with corresponding amounts of malt coffee (U1%, U3%, U5%, U7%, U9%, U11%, U13%, U15%, U20%, U25%, U30%, U40%, U50%, U60%, U70%, U80%, U90%)
- determination of physical properties: dry matter content (105 °C/3 h, Inkolab convection oven, Zagreb, Croatia), color change (CIELab color scale), average Feret's particle diameter (camera (AM2111, Dino-Lite, USA) and image analysis (ImageJ, version 1.8.0. NIH, Maryland, USA))
- NIR spectroscopy: (1) NIR spectrometer Control Development, Inc., NIR-128-1.7-USB/6.25/50 µm with installed software SPEC 32 (South Bend, IN, USA);  $\lambda = 904 \text{ nm} - 1699 \text{ nm}$   
(2) portable NIR spectrometer NIR-S-G1 with installed software ISC-NIRScan (InnoSpectra, Taiwan);  $\lambda = 900 \text{ nm} - 1700 \text{ nm}$
- chemometrics (Principal Component Analysis (PCA) and Artificial Neural Networks (ANNs) (Statistica 14.0, TIBCO, USA))
- extraction: solid-liquid extraction with water as a solvent; results were expressed as mg of caffeine per gram of dry matter of the prepared adulterated sample
- determination of chemical properties: concentration of caffeine measured by two methods: spectrophotometric with UV-Vis spectrophotometer at  $\lambda = 260 \text{ nm}$  (Thermo Fisher Scientific, USA) and HPLC (1260 Infinity II, Agilent, Santa Clara, CA, USA) with diode array (UV/DAD, 1260 Infinity II, Agilent, USA)

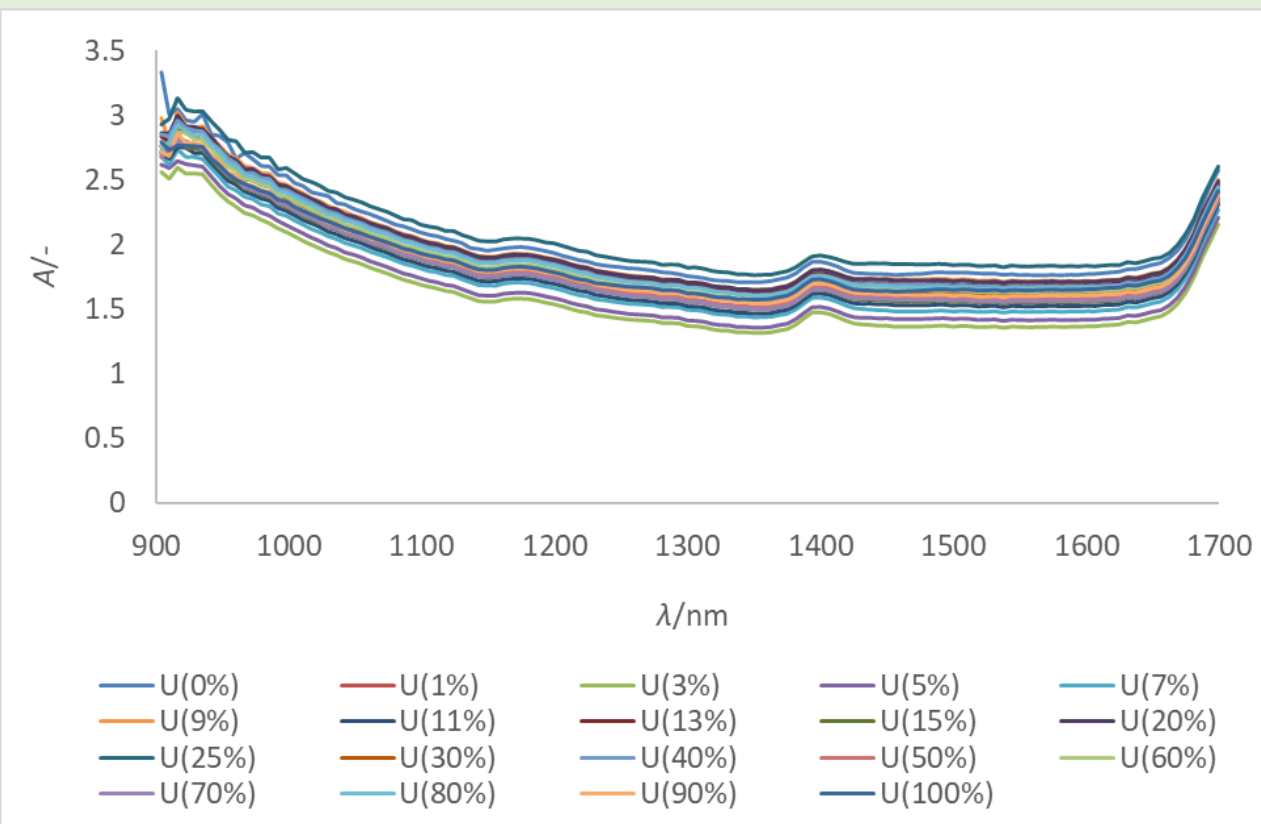
## RESULTS AND DISCUSSION



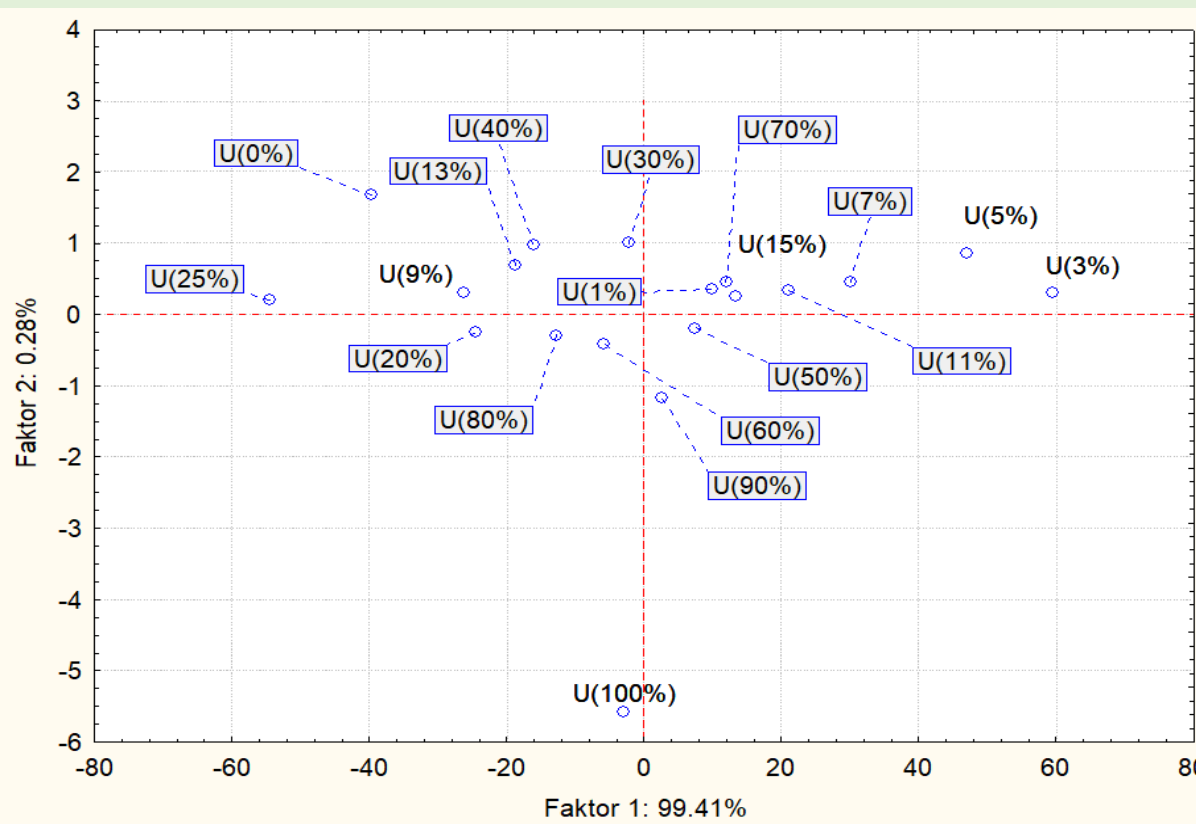
**Fig.1** Microscopic presentation of particles of adulterated coffee samples: (a) ground coffee (U0%), (b) coffee adulterated with 50% of malt coffee (U50%), (c) malted coffee (U100%)



**Fig.2** Average Feret's particle diameter of ground coffee (U0%), malt coffee (U100%) and adulterated coffee samples



**Fig.4** Raw NIR spectra, recorded with NIR 128 spectrometer, of ground coffee, malt coffee and adulterated coffee samples (left) and corresponding Principal Component Analysis (PCA) (right)



**Table 2** Artificial neural networks for prediction of physical-chemical characteristics of ground coffee, malt coffee and adulterated coffee samples

		Network characteristic	$R^2_{\text{training}} / \text{RMSE}_{\text{training}}$	$R^2_{\text{test}} / \text{RMSE}_{\text{test}}$	$R^2_{\text{validation}} / \text{RMSE}_{\text{validation}}$	Hidden activation function	Output activation function
NIR 128	Caffeine concentration determined by spectrophotometric method	10-7-1	0.9694 / 0.0015	0.9666 / 0.0028	0.9644 / 0.0071	Tanh	Logistic
	Caffeine concentration determined by HPLC method	10-9-1	0.9589 / 0.0019	0.9183 / 0.0085	0.9179 / 0.0056	Tanh	Exponential
	Color change ( $\Delta E$ )	10-8-1	0.9939 / 0.0003	0.7630 / 0.0011	0.7471 / 0.0232	Tanh	Logistic
	Average Feret's particle diameter	10-4-1	0.3135 / 0.0407	0.5761 / 0.0292	0.2520 / 0.0440	Tanh	Tanh
	Dry matter	10-9-1	0.9620 / 0.0015	0.9766 / 0.0021	0.1951 / 0.0033	Logistic	Identity
NIR S-G1	Caffeine concentration determined by spectrophotometric method	10-11-1	0.9928 / 0.0004	0.9758 / 0.0025	0.9659 / 0.0025	Tanh	Tanh
	Caffeine concentration determined by HPLC method	10-8-1	0.9684 / 0.0014	0.9626 / 0.0032	0.8088 / 0.0076	Exponential	Exponential
	Color change ( $\Delta E$ )	10-11-1	0.9993 / 0.0001	0.9539 / 0.0004	0.9791 / 0.0020	Tanh	Tanh
	Average Feret's particle diameter	10-5-1	0.9962 / 0.0001	0.9950 / 0.0004	0.7363 / 0.0013	Exponential	Exponential
	Dry matter	10-12-1	0.5672 / 0.0394	0.3379 / 0.0258	0.2481 / 0.0430	Identity	Identity

**Table 1** Color change ( $\Delta E^*$ ) of ground coffee, malt coffee and adulterated coffee samples

SAMPLE*	$\Delta E^*$
U1%	2.26 ± 0.29
U3%	1.48 ± 0.01
U5%	0.63 ± 0.01
U7%	0.70 ± 0.01
U9%	1.64 ± 0.01
U11%	0.47 ± 0.03
U13%	1.43 ± 0.01
U15%	2.13 ± 0.06
U20%	2.37 ± 0.04
U25%	1.42 ± 0.18
U30%	1.19 ± 0.55
U40%	2.75 ± 0.21
U50%	4.04 ± 0.14
U60%	1.66 ± 0.07
U70%	2.60 ± 0.00
U80%	3.26 ± 0.22
U90%	2.47 ± 0.27
U100%	10.13 ± 0.06



**Fig.3** Caffeine concentration in ground coffee, malted coffee and adulterated coffee samples determined (a) spectrophotometric and (b) HPLC method

Average Feret's particle diameter of the adulterated coffee samples mostly exhibited increasing trend with the addition of the higher amount of the malt coffee (Fig.2). The average Feret's diameter for the sample U90% is 108.2 µm while the lowest value was measured for the sample U5% (57.25 µm). Based on the results from Table 1, the highest deviation from the reference sample (ground coffee) was observed for the malted coffee (U100%) ( $\Delta E^* = 10.13 \pm 0.06$ ), while the smallest was observed for the sample U11% ( $\Delta E^* = 0.47 \pm 0.03$ ). Caffeine concentrations in the adulterated samples determined by the spectrophotometric method were significantly higher, compared to the caffeine concentrations obtained by the HPLC method (Fig.3). Caffeine concentrations didn't show decreasing trend with increasing amount of the malt coffee. This was probably due to the sticking of the particles during the homogenization of the samples. According to Fig.4. it is clear that the raw spectra correspond to a single absorbance pattern. The wavelength range from 1100 to 1200 nm corresponds to  $\text{CH}_3$  and  $\text{C=O}$  bonds, which are associated with the structure of the caffeine molecule. Principal Component Analysis (PCA) (Fig.4) successfully distinguished prepared adulterated samples with the eigenvalues of 99.41% and 0.28% for the first and second factor, respectively. Based on the recorded NIR spectra, Artificial Neural Network models (ANNs) were developed in order to predict physical (dry matter content, color change, average Feret's particle diameter) and chemical (concentration of caffeine measured by two methods: spectrophotometric and HPLC) characteristics of the adulterated samples (Table 2). The developed ANN models, with values of  $R^2_{\text{validation}} = 0.8088 - 0.9659$  for caffeine concentration of the prepared mixtures and values of  $R^2_{\text{validation}} = 0.7471 - 0.9791$  for color change ( $\Delta E$ ), showed the potential for industrial application of NIRs in detection of adulteration of ground coffee.