Journal of Applied Botany and Food Quality 92, 378 - 387 (2019), DOI:10.5073/JABFQ.2019.092.050

[1]Laboratory for Analytical Chemistry and Industrial Analysis, Faculty of Chemistry and Chemical Engineering, University of Maribor, Slovenia
[2]Department of Agrochemistry and Brewing, Slovenian Institute of Hop Research and Brewing, Žalec, Slovenia
[3]Department of Chemistry and Biochemistry, Faculty of Chemistry and Chemical Technology, University of Ljubljana, Slovenia

Response surface methodology: An optimal design applied for maximum ultrasound-assisted extraction efficiency of phenolic acids from *Coriandrum sativum* L.

Milena Ivanović[1], Maša Islamčević Razboršek[1], Iztok Jože Košir[2], Mitja Kolar[3*]

(Submitted: May 20, 2019; Accepted: November 15, 2019)

Summary

In this study, a combined three-factors-three-level Box-Behnken design with a response surface methodology was used to optimize the ultrasound-assisted extraction of bound phenolic acids from coriander fruits. Temperature (X1, 20-60 °C), sonication time (X2, 15-45 min) and NaOH concentration (X3, 2-4 M) were studied as independent variables in order to obtain the optimal extraction conditions. For this purpose, a two-step analytical procedure was applied: first, alkaline hydrolysis and extraction under the influence of ultrasound was performed followed by a clean-up step using solid-phase extraction method. After derivatisation, the extracted phenolic acids were analysed using GC-MS. The interrelationship between the dependent and operational variables were well fitted (R2 >0.90) to the quadratic term models. The results obtained in this study confirmed that studied factors had a significant influence on phenolic acids extraction recovery. In favour of maximum extraction yields, the following experimental conditions are suggested: a sonication time of 17.4 min at 35.3°C and with a NaOH concentration of 2.02 M. These results can be utilized for further isolation of active phenolic compounds from other parts of coriander plant as well as for phenolic acids study over various plant materials from the Apiaceae family.

Keywords: coriander, phenolic acids, ultrasound-assisted extraction, hydrolysis, experimental design.

Introduction

Polyphenols represent a large class of chemical compounds, divided into sub-groups they include: phenolic alcohols, phenolic acids, phenylpropanoids, flavonoids, flavones, glycoflavonones, flavonones and biflavonyls, isoflavones, xanthones, stilbenes, tannins and quinines (Ferrazzano et al., 2011). The contents of those compounds were determined in different plant materials and plant products, such as: berries (Ćujić et al., 2016), aromatic plants (Roby et al., 2013; Kocak et al., 2016), tee plants (Nováková et al., 2010; Corbin et al., 2015), as well as beers, juices and wine (Abad-García et al., 2009; Ivanova-Petropulos et al., 2015; Moura-Nunes et al., 2016). In nature, polyphenols occur in free and conjugated forms, with one or more sugar residues linked to hydroxyl groups, whereby direct linkages of the sugar (polysaccharide or monosaccharide) to an aromatic carbon exist. However, free forms of phenolic acids are very rare in nature. Acidic, basic and enzymatic hydrolysis are the most commonly used methods for the extraction of phenolic acids from natural materials (Ross et al., 2009; Ahmad et al., 2016).

Despite current trends in sample handling, which focus on the development of faster, safer and more environmental friendly extraction techniques, both liquid-liquid extraction (LLE) and solid-phase extraction (SPE) are still useful and widely accepted techniques for the exhaustive extraction of polyphenols. The mentioned extraction techniques, with different organic solvents (methanol, ethanol, propanol, ethylacetate and acetone) and solvents mixtures, were developed for isolation of polyphenols from natural sources (Minuti et al., 2006; Irakli et al., 2012; Wang et al., 2013; Gültekin-Özgüven et al., 2015). Additionally, the efficiency of those extractions can be significantly improved by using different external effects; for example, a modern method is microwave-assisted extraction (MAE), which uses frequencies from 0.3 to 300 GHz and can be more suitable for the extraction of polyphenols as compared to traditional extraction methods. Recent studies also proved that the use of ultrasound can enhance the extraction efficiency through acoustic cavitation and mechanical effects (Carrera et al., 2012; Reboredo-Rodríguez et al., 2014; Corbin et al., 2015; Oniszczuk et al., 2015). Some of the ultrasound-assisted extraction (UAE) advantages for the extraction of plant bioactive components are shortened extraction time, lower solvent consumption and increased extraction yields (Oniszczuk et al., 2016).

Coriander (*Coriandrum sativum* L.) is a medicinal and aromatic plant belonging to the Apiaceae family, widely grown in North Africa and the Middle East, which has gained an increasing interest in Western Europe (Barros et al., 2012). Several authors have reported on the health benefits of consuming different parts of the coriander plant (flowers, leaves, stems and roots) (Randall et al., 2013; Duarte et al., 2016). The content of the important pharmaceutical potential compounds in coriander was reported in a review by Sahib et al. (2012). Methanolic, ethanolic and acetone coriander extracts were investigated by some authors, but polyphenol fractions have not been thoroughly studied (Kaiser et al., 2013; Msaada et al., 2013; Martins et al., 2016; Zeković et al., 2016). To the best of our knowledge, this is the first study regarding the bound phenolic acids content in coriander fruits, obtained after optimized alkaline hydrolysis.

The aim of the study was to examine the characterization of different polyphenols in coriander fruits. First, the total phenolic content (TPC) and total flavonoid content (TFC) in methanolic extracts of the coriander fruits were determined according to the standard spectrometric methods. Then, the Box-Behnken design (BBD) combined with a response surface experimental design methodology (RSM) was performed. In this way, the alkaline hydrolysis in combination with the UAE was optimized for the extraction of the trans-cinnamic acid, vanillic acid, syringic acid, p-coumaric acid, ferulic acid and caffeic acid from the coriander fruits. BBD was used to test the influence of three different factors (sonication time, temperature and concentration of NaOH) on the hydrolysis process and to determine the maximum phenolic acid yields. The extraction recoveries of active compounds, according to the UAE and hydrolysis conditions, were also taken into account.

* Corresponding author

Materials and methods

Reagents

Folin-Ciocalteu phenol reagent (2 N), sodium acetate (CH_3COONa), standard compounds; *trans*-caffeic acid (99%), vanillic acid (97%), syringic acid (97%), *trans*-p-coumaric acid (98%), *trans*-o-coumaric acid (98%), *trans*-ferulic acid (98%) and *trans*-cinnamic acid and solvents; tetrahydrofuran-THF (99.5%) and pyridine (99.9%) were supplied by Merck (Germany). The THF was distilled before use. The derivatisation reagent N-Methyl-N-(trimethylsilyl)trifluoroacetamide (MSTFA) as well as protocatechuic acid (99%), rutin (99%), HPLC-grade methanol (MeOH), sodium hydroxide (NaOH, 99%), aluminium chloride ($AlCl_3$) and sodium carbonate (Na_2CO_3) were purchased from Sigma (USA). Gallic acid, GC-grade toluene (99.5%) and hydrochloric acid (HCl, 36.5%) were purchased from Carlo Erba (Italy). Dichloromethane (DCM) was purchased from JT Baker (Germany), L-ascorbic acid (99.7%) was purchased from Alkaloid (Macedonia) and EDTA was purchased from Kemika (Croatia). Water (resistivity above 18 MΩ cm) used was obtained from a Milli-Q water purification system.

Methanolic extraction of polyphenols from coriander

Coriander samples (cultivated in Romania) were purchased from the local supermarket in Maribor, Slovenia. The fruits were milled in an electric blender (Gorenje, Slovenia), packaged in glass vessels and kept in a dark place at room temperature before analysis.

For the UAE, 1.00 g of homogenized sample was weighed into centrifuge tube. The sample was extracted separately three times by sonication with 10 mL of 80% or 100% MeOH for different lengths of time (15, 30 and 45 min). After each extraction, the extracts were centrifuged for 10 min at 6,000 rpm, and the supernatants were combined and evaporated to absolute dryness by rotary evaporation (Büchi, R-100). The dry extracts were kept at 4 °C until analysis.

Beside the UAE, a conventional extraction technique (CE) was also performed, and the results were compared. For the CE, 1.00 g of the homogenised sample was extracted with 80% or 100% MeOH in the way that homogenate was stirred with a magnetic stirrer at 900 rpm at room temperature for 30 min or for 24 h. Extractions were performed in triplicates.

Total phenolic content (TPC)

The TPC in the methanolic extracts of coriander fruits was determined according to the standard spectrometric method, with some modifications (Jiménez et al., 2015). Briefly, 40 µL of properly diluted methanolic extract was mixed with 3.160 mL of ultra-pure water and 200 µl of Folin-Ciocalteu's phenol reagent. After 6 min, 600 µL of Na_2CO_3 (0.2 g mL^{-1}) was added. The tubes were allowed to stand for 2 h in a dark place at room temperature. Standard solutions of gallic acid in the concentration range of 50-500 mg L^{-1} were prepared in the 80% methanol. For construction of the calibration curve, absorbances were measured at the wavelength of 765 nm (Shimadzu UV-VIS spectrophotometer, Kyoto, Japan). Samples were measured under the same conditions. The TPC in the coriander fruits was expressed as milligrams of gallic acid equivalents per gram of dry weight (mg GAE g^{-1} DW). All samples were analysed in duplicates.

Total flavonoid content (TFC)

The TFC was determined using the aluminium chloride colorimetric method (Milan, 2011). 500 µL of properly diluted crude methanolic extract was added to 1.5 mL of pure methanol and mixed well. After that, 0.1 mL of $AlCl_3$ (10 %), 0.1 mL of CH_3COONa (1 M) and 2.8 mL of ultra pure water was added. Standard solutions of rutin in the concentration range of 10-100 mg L^{-1} were prepared in the same way. The tubes were allowed to stand for 30 min in a dark place at room temperature, and the absorbances were measured at the 415 nm against a blank. The TFC was expressed as milligrams of rutin per gram of dry weight (mg RUT g^{-1} DW). All samples were analysed in duplicates.

Identification and quantification of phenolic acids by gas chromatography-mass spectrometry (GC-MS)

Experimental design

In order to optimize the hydrolysis conditions for the extraction of the target phenolic acids from the coriander fruits, an experimental design was applied. Design-expert software (Design Expert 10) was used for the experimental design and statistical analysis of the data. A three-level (-1, 0 and +1) three-factor Box-Behnken design (BBD) combined with a response surface methodology (RSM) was conducted to the design experimental project. The influence of three major factors: temperature (X_1), sonication time (X_2) and NaOH concentration (X_3) were tested as independent variables. The temperature extraction was evaluated in the range 20-60 ºC, sonication time covered the range of 15 to 45 min and NaOH concentration was evaluated between 2 M and 4 M. The actual and coded values of the operational variables are shown in Tab. 1. A total of fifteen experiments were carried out; of these, three were replications of the central point with different combinations of the temperature, sonication time and NaOH concentration. The extraction yields of caffeic acid (Y_1), ferulic acid (Y_2), vanillic acid (Y_3), p-coumaric acid (Y_4) and syringic acid (Y_5) as well as the extraction recoveries (%) of caffeic acid (Y_6), p-coumaric acid (Y_7), ferulic acid (Y_8) and trans-cinnamic acid (Y_9) were selected as dependent variables. The experimental data were fitted to a second-order polynomial model to obtain the regression coefficients. The generalized second-order polynomial model used in the response surface analysis was as follows:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{j=1}^{k} \beta_{ij} X_i X_j \quad (1.)$$

where Y is the response variable, X_i and X_j are the independent variables and k is the number of tested variables (k = 3). The regression coefficient is defined as β_0 for the intercept, β_i for the linear, β_{ii} for the quadratic and β_{ij} for the cross product term.

Hydrolysis and extraction of phenolic acids

The powdered sample (1.00 g) of coriander fruits was mixed with 20 mL of NaOH (which contained 1% L-ascorbic acid and 10 mM EDTA as stabilizers) at three different concentrations (2, 3 and 4 M) in a 100 ml round-bottom flask. These samples were mixed properly for 1–2 min and kept in an ultrasound bath (Model-LWB 106D,

Tab. 1: Experimental variables (factors and respective levels).

Independent variable	Unit	Symbol	Values (uncoded and coded)		
Temperature	°C	X_1	20 (-1)	40 (0)	60 (1)
Sonication time	min	X_2	15 (-1)	30 (0)	45 (1)
NaOH concentration	mol L^{-1} (M)	X_3	2 (-1)	3 (0)	4 (1)

Daihan Labtech Co. Ltd, Korea) for varying lengths of time (15, 30 and 45 min) at various temperatures (20, 40 and 60 °C). The temperature, sonication time and NaOH concentration were based on the experimental design (Tab. 2). After the hydrolysis, the samples were acidified to a pH of 2 using 6 M HCl. Prepared samples were added to pre-conditioned (2 × 3 mL of MeOH, and 2 × 3 mL of acidified water [pH=2]) HLB Supelco® SPE cartridges (Ivanović et al., 2016). Cartridges were washed with ultra pure water (2 × 3 mL) to remove sugars and other polar compounds. The free phenolic acids fraction was eluted with 2 × 2 mL of THF. The eluate was collected and dried in a rotary evaporator (at 40 °C) to absolute dryness. Then, the sample was derivatised by adding 100 µL of MSTFA and 50 µL pyridine, heated at 80 °C for 1h, diluted with toluene up to 1 mL and analysed using GC-MS. The analyses were carried out in duplicates. At the same time, the extraction recovery for every performed experiment was determined. For this purpose, 1.00 g of the powdered sample was spiked with a standard compounds mixture of an exactly known concentration. The spiked samples were exposed to the same conditions as the unspiked samples; thus, spiked and unspiked samples were used for the extraction recovery determination (%).

Preparation of calibration curves

Standard stock solutions of caffeic acid, ferulic acid, p-coumaric acid, vanillic acid, syringic acid and o-coumaric acid (internal standard-ISTD) were prepared by accurately weighing 10 mg of each into a 10 mL volumetric flask. Then, the standards were dissolved in THF. Working calibration solutions were prepared by combining various volumes (from 10 µL to 100 µL) of phenolic acids stock solutions with 50 µl of ISTD in 50 mL conical glass flasks. Each solution was derivatised by adding of 100 µL of MSTFA and 50 µL of pyridine for 1 h at 80 °C in a sand bath. After the derivatisation was finished, TMS derivatives were quantitatively transferred into 1 mL flasks and filled up to the mark with toluene. Five working solutions in concentrations ranging from 1 to 100 mg L^{-1} were injected in triplicates. The calibration curves were constructed by linear regression of the peak-area ratio of the individual phenolic acid (PA) standard to the ISTD (y), versus the concentration (mg L^{-1}) (x). The working solutions were prepared fresh daily.

GC-MS parameters

TMS derivatives of PAs were analysed with a Varian 3900 gas chromatograph, coupled to an MS/MS Saturn 2100 ion trap mass spectrometer. GC separation was performed using an Agilent Technologies, J&W scientific capillary column DB-5 (30 m × 0.25 mm × 0.25 µm). 1 µL of the sample was injected in split mode (split ratio 1:10). Carrier gas was He (6.0 UHP) at a flow rate of 1.0 mL min^{-1}. The initial oven temperature was 40 °C, held for 1 min, and then the temperature was raised up to 320 °C at a rate of 10 °C min^{-1}, held for 3 min (Ivanović et al., 2016). Total run time was 32 min. Mass spectra were recorded in SCAN or SIM mode in a range from 50 to 650 *m/z* using electron ionization energy at 70 eV. Peak identification was done by comparing retention times (tR) and spectral properties with those of standard compounds and by library matching from NIST MS library containing the mass spectra of TMS derivatives of phenolic acids (Ivanović et al., 2016).

Results and discussions

Determination of the TPC and TFC

In the first step of this study, two extraction methods (conventional-CE or ultrasound assisted extraction-UAE) were used to extract total polyphenols from the coriander fruits under the previously described conditions. Fig. 1 represents the extraction yields of the two mentioned extraction techniques for total phenolic (TPC) and total flavonoid content (TFC). Extraction techniques were compared regarding two influencing variables, namely the type of extraction solvent (80% aqueous MeOH solution and 100% MeOH) and sonication time (20, 30 and 45 min).

The results showed that the obtained extraction rates were affected by the type of the extraction as well as by the solvent used (Fig. 1). In general, the highest yields in total phenolics and total flavonoids from the coriander fruits were obtained by extraction using 80% MeOH under the 24 h long stirring and by 45 min of sonication using 100% MeOH, respectively.

Compared to the UAE, the CE method resulted in significantly lower contents of TFC, but this not was case for the TPC. These results are in agreement with the results, reported for other plants (Metrouh-Amir et al., 2015).

In the case of coriander fruits, it was confirmed that the UAE was not effective for TPC recovery. This can be explained by the fact that longer extraction time can lead to the degradation of unstable and sensitive natural compounds like phenolics (Da Porto et al., 2013; Qiao et al., 2013; Qu et al., 2017). Conversely, when compared to the CE, application of UAE may contribute to a lower solvent consumption and shorter extraction time. In this study by the 45 min long UAE at least 90% of TPC were extracted with 24 h stirring CE technique.

For the TFC, the 45 min sonication leads to the extraction of significantly higher concentration when compared with the 24h CE. The values for the TPC and TFC in the coriander fruits were varied among the extracts and ranged from 800 to 2900 mg GAE g^{-1} DW and from 540 to 850 mg RUT g^{-1} DW, respectively.

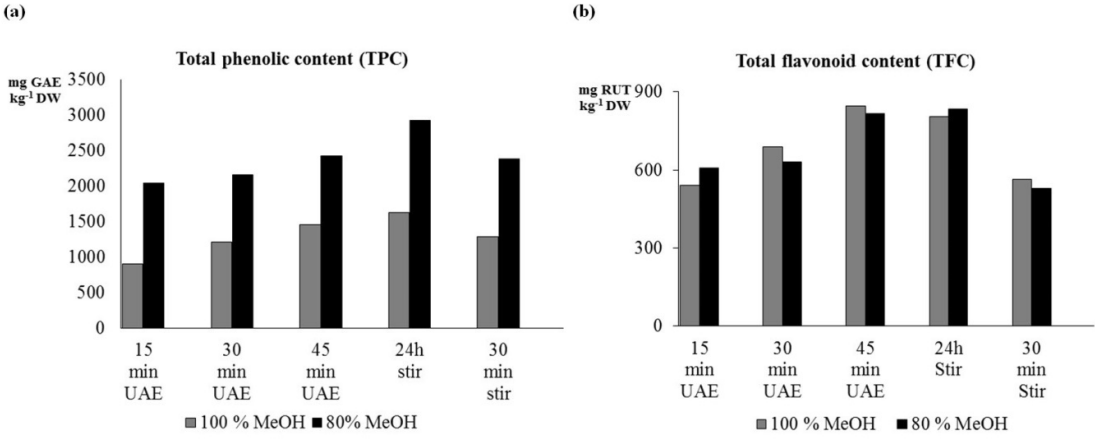

Fig. 1: Effect of the extraction solvent and extraction time on the TPC (a) and on the TFC (b) in *Coriandrum sativum* L. fruits.

Identification and quantification of bound phenolic acids by GC-MS

As previously mentioned, phenolic acids in the plant materials can be present in free or bound form. Free phenolic acid are extractable using different organic solvents, or their mixtures. Conversely, bound phenolic acids can be extracted after being released by alkaline, acidic and enzymatic hydrolysis. From the literature, it is known that the efficiency of a hydrolysis reaction can be affected by: the concentration of a hydrolysis reagent, temperature, reaction time, mass of analysed samples, application of microwaves or ultrasound, etc. (CHENG et al., 2014). Therefore, concentractions of identified phenolic compounds from similar samples in final extracts can be very different. In this study, six different phenolic acids (caffeic acid, ferulic acid, p-coumaric acid, vanillic acid, syringic acid and protocatechuic acid), including their geometrics isomers, were identified in the coriander fruits (Fig. 2).

Box-Behnken experimental design

In this section, a Box-Behnken design (BBD) combined with a response surface methodology (RSM) was used to optimize the alkaline hydrolysis and extraction conditions of the previously identified bound phenolic acids (Fig. 2). For optimization, the experiments were conducted by a 2^3 full factorial central composite design. All of the experimental data obtained from the 15-run experiments are shown in Tab. 2. The yields of caffeic acid (Y_1), ferulic acid (Y_2), vanillic acid (Y_3), p-coumaric acid (Y_4) and syringic acid (Y_5) as well as the extraction recoveries of caffeic acid

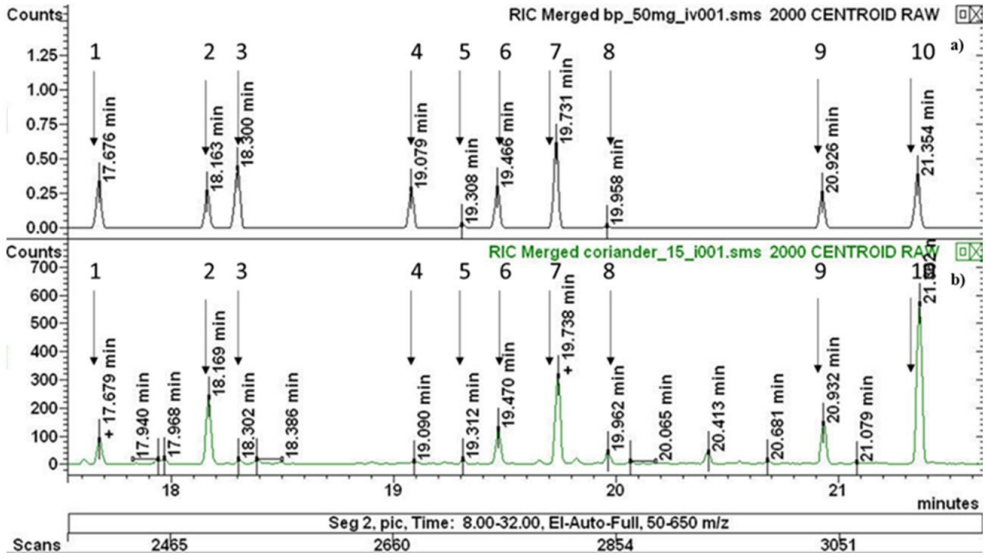

Fig. 2: GC chromatograms of: a) silylated standard mixture of phenolic acids (1. vanillic acid; 2. o-coumaric acid (ISTD); 3. protocatehuic acid; 4. syringic acid 5. *cis*-ferulic acid; 6. *trans*-p coumaric acid; 7. *trans*-cinnamic acid; 8. *cis*-caffeic acid; 9. *trans*-ferulic acid; 10. *trans*-caffeic acid); b) silylated phenolic acids present in *Coriandrum sativum* L. extract obtained after SPE (1. vanillic acid; 2. o-coumaric acid (ISTD); 3. protocatehuic acid; 4. syringic acid 5. *cis*-ferulic acid; 6. *trans*-p coumaric acid; 7. L-ascorbic acid (stabilizer); 8. *cis*-caffeic acid; 9. *trans*-ferulic acid; 10. *trans*-caffeic acid).

Tab. 2: Mean responses obtained for investigated phenolic acids from the experimental design.

Run	Temperature (°C)	Sonication time (min) Unit	NaOH con. (mol L^{-1})	Caffeic acid mg g^{-1}	Ferulic acid mg g^{-1}	Vanillic acid mg g^{-1}	p-coumaric acid mg g^{-1}	Syringic acid mg g^{-1}	Caffeic acid %	Ferulic acid %	p-coumaric acid %	*Trans*-cinnamic %
	X_1	X_2	X_3	Y_1	Y_2	Y_3	Y_4	Y_5	Y_6	Y_7	Y_8	Y_9
1	40 (0)	30 (0)	3 (0)	1.94	0.55	0.25	0.38	$5.13 \cdot 10^{-3}$	55	70	72	71
2	40 (0)	45 (+1)	4 (+1)	1.43	0.54	0.15	0.27	NQ	70	61	69	62
3	60 (+1)	45 (+1)	3 (0)	1.66	0.63	0.17	0.32	$2.13 \cdot 10^{-3}$	82	81	83	65
4	60 (+1)	30 (0)	4 (+1)	1.68	0.47	0.15	0.12	NQ	83	82	95	61
5	20 (-1)	30 (0)	2 (-1)	1.53	0.24	0.16	0.05	NQ	86	102	101	87
6	20 (-1)	45 (+1)	3 (0)	1.51	0.38	0.19	0.21	$1.33 \cdot 10^{-3}$	81	83	77	78
7	60 (+1)	30 (0)	2 (-1)	1.41	0.60	0.19	0.30	NQ	89	80	96	84
8	40 (0)	15 (-1)	2 (-1)	1.43	0.37	0.17	0.11	NQ	99	102	88	95
9	40 (0)	30 (0)	3 (0)	1.94	0.56	0.25	0.38	$5.13 \cdot 10^{-3}$	55	70	72	71
10	40 (0)	45 (+1)	2 (-1)	1.72	0.47	0.18	0.29	NQ	77	91	93	89
11	40 (0)	15 (-1)	4 (+1)	1.68	0.47	0.15	0.15	NQ	90	91	95	75
12	40 (0)	30 (0)	3 (0)	1.94	0.56	0.25	0.38	$5.13 \cdot 10^{-3}$	55	70	72	71
13	20 (-1)	30 (0)	4 (+1)	1.47	0.58	0.14	0.15	NQ	92	79	88	67
14	20 (-1)	15 (0)	3 (0)	1.52	0.32	0.17	0.12	$4.8 \cdot 10^{-4}$	100	105	102	76
15	60 (+1)	15 (-1)	3 (0)	1.40	0.52	0.19	0.27	NQ	94	96	97	74

NQ-not quantified

(Y_6), ferulic acid (Y_7), p-coumaric acid (Y_8) and *trans*-cinnamic acid (Y_9) were determined as the dependent variables. The concentration of protochatechuic acid in all obtained extracts was below LOQ and therefore, not used for method optimization.

The p-value and F-test were used to determine the significance of each coefficient. The high F-value and the small p-value mean significant corresponding variables. The results, values of "Prob > F" less than 0.05, indicates that the model terms are significant. The optimized conditions were validated for the maximum phenolic acids yield and extraction recovery based on the values obtained using RSM. The experimental values were compared with predicted values based on CV% in order to determine the validity of the model.

For the graphical presentation of the influence of tested conditions on the extraction yields, the three dimensional (3-D) surface response plots were generated by varying two variables within the experimental range and by holding one variable constant at the central point. Conversely, contour plots were generated for the graphical description of the influence of tested variables on the extraction recoveries. The test of statistical significance was based on the total error criteria with confidence levels of 95.0%, 99.0% and 99.9%.

Effect of the independent variables on the phenolic acids yield

To study the interactive effects of the operational parameters on the extraction yields, the three-dimensional (3D) profiles of multiple non-linear regression models were depicted in Fig. 3. The profiles present the interaction of two process factors (sonication time and temperature), while the third factor (NaOH concentration) was fixed at its middle level (3M).

Optimization of the extraction process for the phenolic acids yield was carried out by applying second-order polynomial equation. The analysis of variance (ANOVA) showed that this model adequately

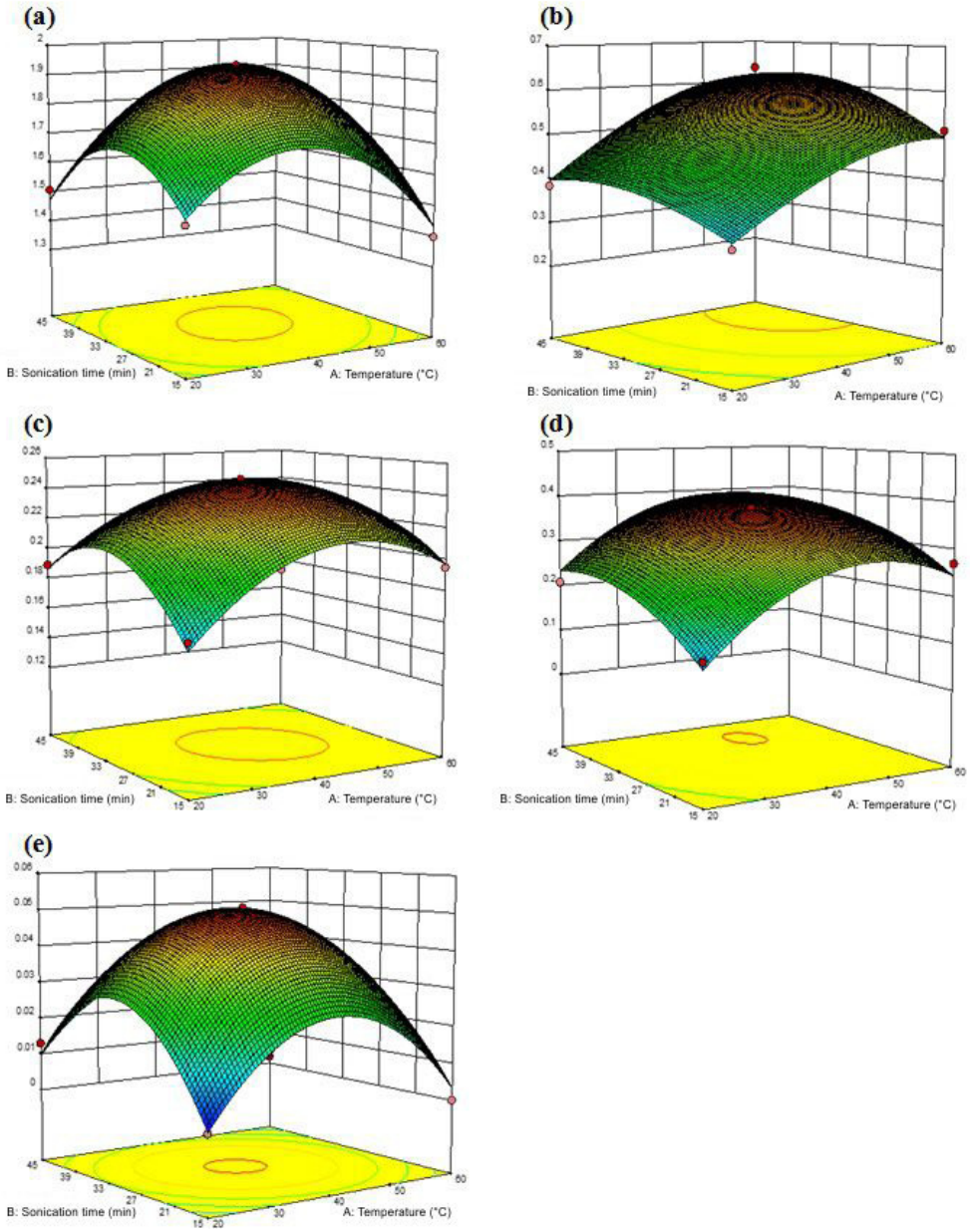

Fig. 3: 3D plots of ultrasound hydrolysis and extraction of bound phenolic acids (mg g^{-1} DW) from *Coriandrum sativum* L., varying sonication time and temperature (the concentration of NaOH is constant in the central point). (a) caffeic acid, (b) ferulic acid, (c) vanillic acid, (d) p-coumaric acid and (e) syringic acid.

represented the experimental data. The coefficient of multiple determination (R^2) for phenolic acid yields (caffeic acid, ferulic acid, p-coumaric acid, syringic acid and vanillic acid) was 0.92; 0.96; 0.94; 0.98 and 0.97, respectively. Analyses of variance for the response surface polynomial models are compiled in Tab. 3.

For caffeic acid, (Y_1), X_1X_2, X_1X_3, X_2X_3, X_1^2, X_2^2 and X_3^2 were significant model terms ($p < 0.05$) (Tab. 3). It means that only combinations of two factors influenced the extraction yield of caffeic acid significantly. Non-significant variables were removed and the following second-order polynomial equation was found to represent the extraction yield adequately:

$$Y_1=0.29+0.02X_1X_2+0.02X_1X_3-0.04X_2X_3-0.06X_1^2-0.05X_2^2-0.05X_3^2 \quad (2.)$$

The highest positive effect on the extraction yield of caffeic acid showed interactions between X_1X_3 and X_1X_2 with the maximums achieved when the factors were controlled to the ultrasound influence for 30 min at 40 °C and NaOH concentration of 3M. Caffeic acid was the most abundant among the phenolic acids presented in the coriander fruits with concentrations ranging from 1.4 to 1.9 mg g^{-1} DW.

The F-value of 36.02 for ferulic acid indicated that the model was significant. X_1, X_2, X_3, X_1^2, X_2^2 and X_3^2 were significant model terms ($p < 0.05$). It means that all tested parameters had a significant effect on the extraction yield of ferulic acid. Meanwhile, the P value of X_1X_3 was lower than 0.05, the interaction of the temperature and NaOH concentration also had a significant influence on the extraction yield of ferulic acid. The reduced second-order polynomail equation for ferulic acid was:

$$Y_2=1.34-0.17X_1-0.07X_2-0.11X_3+0.69\cdot10^{-3}X_1X_2+0.11X_1^2+0.06X_2^2+0.07X_3^2 \quad (3.)$$

The maximum yield of ferulic acid (0.634 mg g^{-1} DW) was achieved when the factors were adjusted to the central point values: temperature-60 °C; sonication time-45 min and NaOH concentration-3M.

The developed model was significant for vanillic acid, with the F-value of 53.60. There is only a 0.02% chance that an F-value this large could occur due to noise. In this case, X_1, X_3, X_1X_2, X_1^2, X_2^2 and X_3^2 were significant model terms, with probability values of less than 0.05. These results indicated that the sonication time only influences the extraction yield of vanillic acid when combined with temperature

Tab. 3: Analysis of variance (ANOVA) of response surface second order polynomial models for phenolic acids yield.

Variables	Responses (mg g^{-1} DW)					
	Caffeic acid			Ferulic acid		
	Mean of square	F value	*p* value	Mean of square	F value	*p* value
Model	0.04	18.00	0.003**	0.07	36.02	<0.001***
X_1	$8.76\cdot10^{-5}$	0.39	0.559	0.23	116.20	<0.001***
X_2	$7.59\cdot10^{-4}$	3.39	0.125	0.04	20.83	0.006**
X_3	$2.90\cdot10^{-4}$	1.30	0.307	0.09	48.22	0.001***
X_1X_2	$1.55\cdot10^{-3}$	6.90	0.047*	$1.92\cdot10^{-4}$	0.10	0.766
X_1X_3	$2.23\cdot10^{-3}$	9.95	0.025*	0.20	102.14	<0.001***
X_2X_3	$5.40\cdot10^{-3}$	24.13	0.004**	$2.68\cdot10^{-4}$	1.38	0.293
X_1X_1	0.01	57.38	< 0.001***	0.05	23.01	0.005**
X_2X_2	$8.46\cdot10^{-3}$	37.77	0.002**	0.01	7.28	0.043*
X_3X_3	$8.59\cdot10^{-3}$	38.35	0.002**	0.02	9.89	0.026*
R^2	**0.9701**			**0.9848**		
Adjusted R^2	**0.9162**			**0.9575**		
Adeq. precision	**12.162**			**21.713**		

Tab. 3: Continued.

Varibales	Responses (mg g^{-1} DW)								
	Vanillic acid			p-Coumaric acid			Syringic acid		
	Mean of square	F value	*p* value	Mean of square	F value	*p* value	Mean of square	F value	*p* value
Model	0.06	53.60	<0.001***	0.10	26.04	>0.001**	$6.80\cdot10^{-4}$	75.46	< 0.001***
X_1	0.02	13.96	0.014*	0.19	48.08	0.001***	$1.64\cdot10^{-5}$	1.82	0.236
X_2	$1.16\cdot10^{-3}$	1.10	0.343	0.12	31.37	0.003**	$2.87\cdot10^{-5}$	3.18	0.135
X_3	0.05	46.33	0.001***	$3.38\cdot10^{-3}$	0.87	0.393	$8.67\cdot10^{-19}$	$9.62\cdot10^{-14}$	1.000
X_1X_2	0.02	15.40	0.011*	$7.04\cdot10^{-3}$	1.82	0.235	$3.22\cdot10^{-5}$	3.57	0.117
X_1X_3	$8.71\cdot10^{-4}$	0.82	0.406	0.19	49.18	<0.001***	$8.67\cdot10^{-19}$	$9.62\cdot10^{-14}$	1.000
X_2X_3	$2.20\cdot10^{-3}$	2.07	0.210	$5.11\cdot10^{-3}$	1.32	0.302	0.00	0.00	1.000
X_1X_1	0.10	97.12	<0.001***	0.16	41.93	>0.001**	$2.08\cdot10^{-3}$	230.88	< 0.001***
X_2X_2	0.09	81.57	<0.001***	$5.23\cdot10^{-3}$	1.36	0.297	$2.08\cdot10^{-3}$	230.88	< 0.001***
X_3X_3	0.29	277.26	<0.001***	0.26	67.32	<0.001***	$2.80\cdot10^{-3}$	310.97	< 0.000***
R^2	**0.9897**			**0.9791**			**0.9927**		
Adjusted R^2	**0.9713**			**0.9415**			**0.9795**		
Adeq. precision	**20.904**			**17.059**			**21.697**		

Level of significance $^{*}p < 0.05$, $^{**}p < 0.01$, $^{***}p < 0.001$

(P<0.001). The following is a reduced second-order equation that represents the extraction yield of vanillic acid:

$$Y_3=-1.39+0.04X_1+0.08X_3-0.06X_1X_2-0.17X_1^2-0.15X_2^2-0.28X_3^2 \quad (4.)$$

The F-value of 26.04 for p-coumaric acid implies the model was significant. In this case, X_1, X_2, X_1X_3, X_1^2 and X_3^2 were significant model terms (equation 5):

$$Y_4=-0.42+0.15X_1+0.12X_2-0.22X_1X_3-0.21X_1^2-0.27X_3^2 \quad (5.)$$

The optimal conditions for the maximum p-coumaric acid extraction yield were those from the BBD central point (0.38 mg g^{-1} DW).

The high F-value (75.46) for the syringic acid implies the significance of the model. There is only a 0.01% chance that an F-value this large could occur due to noise. In this case, the influence of significant model terms (X_1^2, X_2^2 and X_3^2) can be represented by the following reduced second-order polynomail equation:

$$Y_5=-0.40-5.93\cdot10^{-5}X_1^2-1.06\cdot10^{-4}X_2^2-0.03X_3^2 \quad (6.)$$

Effect of the independent variables on the phenolic acids extraction recovery

Contour plots (Fig. 4), which are the graphical representations of the quadratic polynomial regression equation, illustrate the significant ($p < 0.05$) interaction effects of the sonication time and NaOH concentration on the recovery of the investigated compounds, with the temperature fixed at 45 °C (middle level).

The results of this study also confirm that the studied conditions have a significant influence on the phenolic acids extraction recoveries, especially those from the hydroxycinnamic acid derivative group (Qu et al., 2017). *Trans*-cinnamic acid was not identified in the tested coriander samples, but it has also been a subject of study. The coefficient of multiple determination (R^2) of caffeic acid, ferulic acid, p-coumaric acid and *trans*-cinnamic acid were 0.97, 0.93, 0.95 and 0.96, respectively (Tab. 4). The model showed high significant ($p < 0.001$) values with the experimental data for all tested responses. The analysis of variance (ANOVA) showed a significant ($p < 0.001$) negative linear (X_2) effect on the extraction recoveries (Tab. 4). It can be explained by the fact that the extended application of the ultrasound to the same matrix causes the degradation of phenolic acids with double-bounds in their structures (Da Porto et al., 2013).

The F-value of 52.43 implies the model was significant for the extraction recovery of caffeic acid. There is only a 0.02% chance that an F-value this large could occur due to noise. In this case, X_2, X_1^2, X_2^2 and X_3^2 are significant model terms and can be represented by the following equation:

$$Y_6=7.42-0.52X_2+1.14X_1^2+0.93X_2^2+0.80X_3^2 \quad (7.)$$

Represented equation means that only the sonication time ($p < 0.001$) has a significant influence on the extraction recovery of the caffeic acid. The negative influence of the NaOH concentration on the stability of caffeic acid was probably eliminated by adding L-ascorbic acid and EDTA as stabilisers (Narita et al., 2013). An adequate precision ratio greater than 4 is desirable. In this case, the value of 22.15 indicates an adequate signal, and this model can be used to navigate the design space.

Based on the regression coefficient (β) values, the influence of the ultrasound (X_2) had a significantly negative effect on the extraction recovery of ferulic acid followed by NaOH concentration (X_3), interaction (X_1X_3), and temperature (X_1). After removing the non-significant variables, the following second-order polynomial equa-

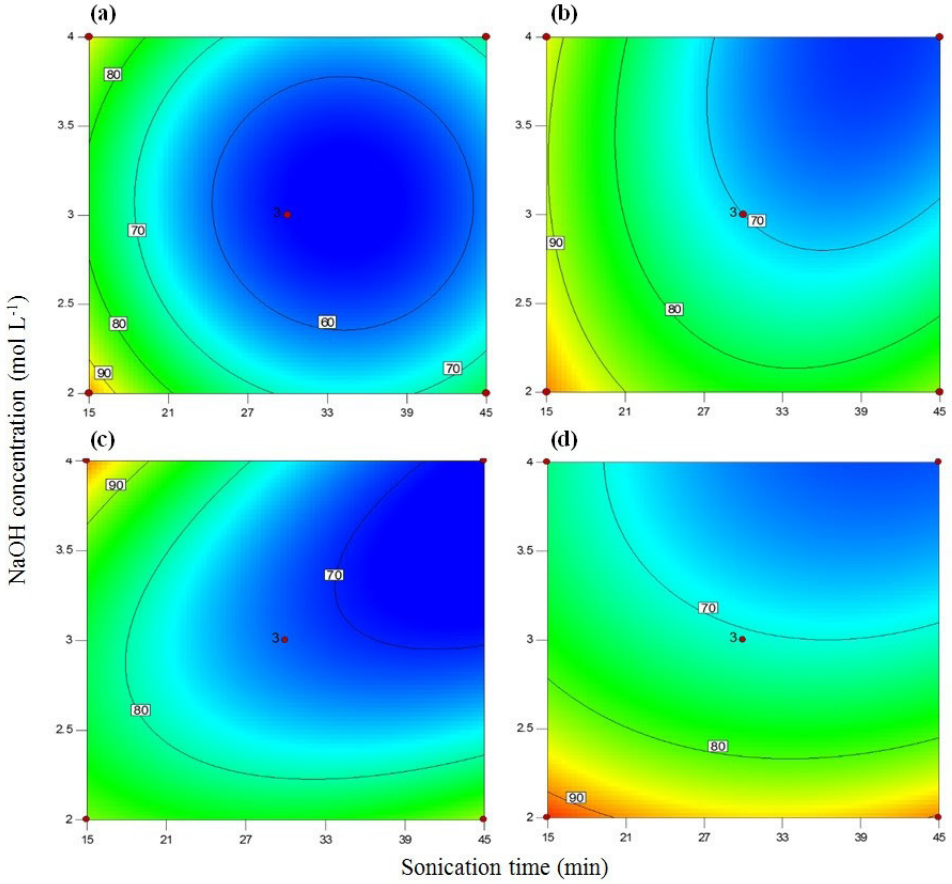

Fig. 4: Contour plots of extraction recoveries (%) for bound phenolic acids from *Coriandrum sativum* L., varying sonication time and NaOH concentration (the temperature is constant in the central point-45 °C). (a) caffeic acid, (b) ferulic acid, (c) p-coumaric acid and (d) *trans*-cinnamic acid.

Tab. 4: Analysis of variance (ANOVA) of response surface second order polynomial models for phenolic acids recovery.

Variables	Responses (%)					
	Caffeic acid			Ferulic acid		
	Mean of square	F value	*p* value	Mean of square	F value	*p* value
Model	1.28	52.43	<0.001***	271.38	22.61	>0.001**
X_1	0.07	3.03	0.142	112.50	9.38	0.028*
X_2	2.14	87.63	<0.001***	760.50	63.38	<0.001***
X_3	0.10	3.94	0.104	480.50	40.04	>0.001**
X_1X_2	0.08	3.20	0.134	12.25	1.02	0.359
X_1X_3	0.10	4.22	0.095	156.25	3.02	0.015*
X_2X_3	$7.47 \cdot 10^{-4}$	0.03	0.868	90.25	7.52	0.041*
X_1X_1	4.79	196.72	<0.001***	397.44	33.12	0.002**
X_2X_2	3.20	131.49	<0.001***	436.67	36.39	0.002**
X_3X_3	2.34	96.20	<0.001***	106.67	8.89	0.031*
R^2	**0.9895**			**0.9760**		
Adjusted R^2	**0.9706**			**0.9329**		
Adeq. precision	**22.150**			**21.713**		

Tab. 4: Continued.

Variables	Responses (%)					
	p-Coumaric acid			*Trans*-cinnamic acid		
	Mean of square	F value	*p* value	Mean of square	F value	P value
Model	0.03	32.93	<0.001***	0.03	40.67	<0.001***
X_1	$3.19 \cdot 10^{-4}$	0.36	0.573	0.02	22.62	0.005**
X_2	0.06	69.91	<0.001***	0.02	23.48	0.005**
X_3	0.02	19.47	0.006**	0.18	269.21	<0.001***
X_1X_2	$3.93 \cdot 10^{-3}$	4.46	0.088	$6.06 \cdot 10^{-3}$	9.15	0.029*
X_1X_3	$4.05 \cdot 10^{-3}$	4.60	0.085	$1.12 \cdot 10^{-3}$	1.69	0.250
X_2X_3	0.04	39.96	0.002**	$3.51 \cdot 10^{-3}$	5.30	0.070
X_1X_1	0.09	105.48	<0.001***	$1.50 \cdot 10^{-3}$	2.27	0.193
X_2X_2	0.01	12.86	0.016*	$8.85 \cdot 10^{-3}$	13.36	0.015*
X_3X_3	0.05	57.88	<0.001***	0.01	19.08	0.007**
R^2	**0.9834**			**0.9865**		
Adjusted R^2	**0.9536**			**0.9623**		
Adeq. precision	**16.626**			**21.044**		

Level of significance $^{*}p < 0.05$, $^{**}p < 0.01$, $^{***}p < 0.001$

tion was found to represent the extraction recovery of ferulic acid adequately:

$$Y_7=70-3.75X_1-9.75X_2-7.75X_3+6.25X_1X_3-4.75X_2X_3+10.38X_1^2+10.88X_2^2+5.37X_3^2 \quad (8.)$$

For p-coumaric acid, the F-value was 32.93. There is only a 0.06% chance that an F-value this large could occur due to noise. It was found that the major negative influence on this phenolic acid recovery has an interaction (X_2X_3) followed by the influence of the ultrasound (X_1) and NaOH concentration (X_3). Those interactions can be represented by following reduced equation:

$$Y_8=4.28-0.09X_2-0.05X_3-0.09X_2X_3+0.16X_1^2+0.06X_2^2+0.12X_3^2 \quad (9.)$$

Trans-cinnamic acid has also been a focus of this research. This study proved that stability of *trans*-cinnamic acid was also affected by the tested conditions of temperature, sonication time and NaOH concentration. The model was significant with an F-value of 40.67. The equation that described the influence of the independent variables on the *trans*-cinnamic acid recovery can be written as:

$$Y_9=4.26-0.04X_1-0.04X_2-0.15X_3-0.04X_1X_2+0.05X_2^2+0.06X_3^2 \quad (10.)$$

Choosing the best hydrolysis and extraction conditions must take into account both, phenolic acids yield and phenolic acids extraction recovery. Thus, the optimum conditions applied were 35.3 ºC, 2.02 M concentration of NaOH and a sonication time of 17.4 minutes.

Conclusions

This paper represents our contribution to the understanding of *Coriandrum sativum* L. polyphenol composition. To that end, the total phenolic content (TPC) and total flavonoid content (TFC) in the methanolic extract of coriander fruits were firstly determined. The maximum measured values for the TPC and TFC were 2900 mg GAE g^{-1} DW and 850 mg RUT g^{-1} DW, respectively. Additionally, a simple and fast ultrasound-assisted extraction (UAE) method involving GC-MS analysis for isolation and quantitative determination of total (free and bound) phenolic acids together with their geometric isomers was used for the first time. A response surface methodology and Box-Behnken design were successfully applied for the optimization of the most important UAE parameters (temperature, sonication time and NaOH concentration). Due to the satisfactory statistical parameters (R^2 and CV) and analysis of variance (ANOVA), it could be concluded that the developed second-order polynomial models

provided an adequate mathematical description of the UAE extraction yields. Furthermore, according to the results obtained, it could be concluded that all tested parameters had a significant impact on the extraction yields of phenolic acids, but sonication time was the most critical factor. With the aim to maximize the extraction yields of all independent variables, the following extraction conditions were determined to be the most optimal: sonication time of 17.4 min at 35.3 °C and NaOH concentration of 2.02 M. Finally, it can be concluded that coriander fruit is rich in polyphenols, including phenolic acids and can represent a potential natural source of antioxidants for food and pharmaceutical industries.

Acknowledgments

Authors thank financial support provided by the Slovenian Research Agency (ARRS), programmes P1-0153 and P2-006. M. Ivanović also acknowledge the financial support for PhD study provided by the Erasmus Mundus JoinEu-SEE Penta project.

References

Abad-García, B., Berrueta, L.A., Garmón-Lobato, S., Gallo, B., Vicente, F., 2009: A general analytical strategy for the characterization of phenolic compounds in fruit juices by high-performance liquid chromatography with diode array detection coupled to electrospray ionization and triple quadrupole mass spectrometry. J. Chromatogr. A. 1216, 5398-5415. DOI: 10.1016/j.chroma.2009.05.039

Ahmad, N., Zuo, Y., Lu, X., Anwar, F., Hameed, S., 2016: Characterization of free and conjugated phenolic compounds in fruits of selected wild plants. Food Chem. 190, 80-89. DOI: 10.1016/j.foodchem.2015.05.077

Barros, L., Dueñas, M., Dias, M.I., Sousa, M.J., Santos-Buelga, C., Ferreira, I.C.F.R., 2012: Phenolic profiles of in vivo and in vitro grown *Coriandrum sativum* L. Food Chem. 132, 841-848. DOI: 10.1016/j.foodchem.2011.11.048

Carrera, C., Ruiz-Rodríguez, A., Palma, M., Barroso, C.G., 2012: Ultrasound assisted extraction of phenolic compounds from grapes. Anal. Chim. Acta. 732, 100-104. DOI: 10.1016/j.aca.2011.11.032

Cheng, A., Yan, H., Han, C., Chen, X., Wang, W., Xie, C., Qu, J., Gong, Z., Shi, X., 2014: Acid and alkaline hydrolysis extraction of non-extractable polyphenols in blueberries: Optimisation by response surface methodology. Czech J. Food Sci. 32, 218-225.

Corbin, C., Fidel, T., Leclerc, E.A., Barakzoy, E., Sagot, N., Falguiéres, A., Renouard, S., Blondeau, J.P., Ferroud, C., Doussot, J., Lainé, E., Hano, C., 2015: Development and validation of an efficient ultrasound assisted extraction of phenolic compounds from flax (*Linum usitatissimum* L.) seeds. Ultrason. Sonochem. 26, 176-185. DOI: 10.1016/j.ultsonch.2015.02.008

Ćujić, N., Šavikin, K., Janković, T., Pljevljakušić, D., Zdunić, G., Ibrić, S., 2016: Optimization of polyphenols extraction from dried chokeberry using maceration as traditional technique. Food Chem. 194, 135-142. DOI: 10.1016/j.foodchem.2015.08.008

Da Porto, C., Porretto, E., Decorti, D., 2013: Comparison of ultrasound-assisted extraction with conventional extraction methods of oil and polyphenols from grape (*Vitis vinifera* L.) seeds. Ultrason. Sonochem. 20, 1076-1080. DOI: 10.1016/j.ultsonch.2012.12.002

Duarte, A., Luís, Â., Oleastro, M., Domingues, F.C., 2016: Antioxidant properties of coriander essential oil and linalool and their potential to control *Campylobacter* spp. Food Control. 61, 115-122. DOI: 10.1016/j.foodcont.2015.09.033

Ferrazzano, G.F., Amato, I., Ingenito, A., Zarrelli, A., Pinto, G., Pollio, A., 2011: Plant polyphenols and their anti-cariogenic properties: A review. Molecules. 16, 1486-1507. DOI: 10.3390/molecules16021486

Gültekin-Özgüven, M., Davarci, F., Pasli, A.A., Demir, N., Özçelik, B., 2015: Determination of phenolic compounds by ultra high liquid chromatography-tandem mass spectrometry: Applications in nuts. LWT - Food Sci. Technol. 64, 42-49. DOI: 10.1016/j.lwt.2015.05.014

Irakli, M.N., Samanidou, V.F., Biliaderis, C.G., Papadoyannis, I.N., 2012: Development and validation of an HPLC-method for determination of free and bound phenolic acids in cereals after solid-phase extraction. Food Chem. 134, 1624-1632. DOI: 10.1016/j.foodchem.2012.03.046

Ivanova-Petropulos, V., Hermosin-Gutierrez, I., Boros, B., Stefova, M., Stafilov, T., Vojnoski, B., Dornyei, A., Kilar, F., 2015: Phenolic compounds and antioxidant activity of Macedonian red wines. J. Food Compos. Anal. 41, 1-14. DOI: 10.1016/j.jfca.2015.01.002

Ivanović, M., Islamčević Razboršek, M., Kolar, M., 2016: Simultaneous GC-MS determination of free and bound phenolic acids in Slovenian red wines and chemometric characterization. Acta Chim. Slov. 63, 661-669. DOI: 10.17344/acsi.2016.2534

Jiménez, N., Carrillo-Hormaza, L., Pujol, A., Álzate, F., Osorio, E., Lara-Guzman, O., 2015: Antioxidant capacity and phenolic content of commonly used anti-inflammatory medicinal plants in Colombia. Ind. Crops Prod. 70, 272-279. DOI: 10.1016/j.indcrop.2015.03.050

Kaiser, A., Kammerer, D.R., Carle, R., 2013: Impact of blanching on polyphenol stability and antioxidant capacity of innovative coriander (*Coriandrum sativum* L.) pastes. Food Chem. 140, 332-339. DOI: 10.1016/j.foodchem.2013.02.077

Kocak, M.S., Sarikurkcu, C., Cengiz, M., Kocak, S., Uren, M.C., Tepe, B., 2016: Salvia cadmica: Phenolic composition and biological activity. Ind. Crops Prod. 85, 204-212. DOI: 10.1016/j.indcrop.2016.03.015

Martins, N., Barros, L., Santos-Buelga, C., Ferreira, I.C.F.R., 2016: Antioxidant potential of two Apiaceae plant extracts: A comparative study focused on the phenolic composition. Ind. Crops Prod. 79, 188-194. DOI: 10.1016/j.indcrop.2015.11.018

Metrouh-Amir, H., Duarte, C.M.M., Maiza, F., 2015: Solvent effect on total phenolic contents, antioxidant, and antibacterial activities of *Matricaria pubescens*. Ind. Crops Prod. 67, 249-256. DOI: 10.1016/j.indcrop.2015.01.049

Milan, S., 2011: Total phenolic content, flavonoid concentration and antioxidant actibity of *Marrubium peregrinum* L. Extracts. Kragujev. J. Sci. 33, 63-72. DOI: 581.19:582.929.4:577.164.3

Minuti, L., Pellegrino, R.M., Tesei, I., 2006: Simple extraction method and gas chromatography-mass spectrometry in the selective ion monitoring mode for the determination of phenols in wine. J. Chromatogr. A. 1114, 263-268. DOI: 10.1016/j.chroma.2006.02.068

Moura-Nunes, N., Brito, T.C., Fonseca, N.D. Da, Fernandez De Aguiar, P., Monteiro, M., Perrone, D., Guedes Torres, A., 2016: Phenolic compounds of Brazilian beers from different types and styles and application of chemometrics for modeling antioxidant capacity. Food Chem. 199, 105-113. DOI: 10.1016/j.foodchem.2015.11.133

Msaada, K., Jemia, M. Ben, Salem, N., Bachrouch, O., Sriti, J., Tammar, S., Bettaieb, I., Jabri, I., Kefi, S., Limam, F., Marzouk, B., 2013: Antioxidant activity of methanolic extracts from three coriander (*Coriandrum sativum* L.) fruit varieties. Arab. J. Chem. 10, 3176-3183. DOI: 10.1016/j.arabjc.2013.12.011

Narita, Y., Inouye, K., 2013: Degradation kinetics of chlorogenic acid at various pH values and effects of ascorbic acid and epigallocatechin gallate on its stability under alkaline conditions. J. Agric. Food Chem. 61, 966-972. DOI: 10.1021/jf304105w

Nováková, L., Vildová, A., Mateus, J.P., Gonalves, T., Solich, P., 2010: Development and application of UHPLC-MS/MS method for the determination of phenolic compounds in Chamomile flowers and Chamomile tea extracts. Talanta. 82, 1271-1280. DOI: 10.1016/j.talanta.2010.06.057

Oniszczuk, A., Podgórski, R., 2015: Influence of different extraction methods on the quantification of selected flavonoids and phenolic acids from *Tilia cordata* inflorescence. Ind. Crops Prod. 76, 509-514. DOI: 10.1016/j.indcrop.2015.07.003

Oniszczuk, A., Olech, M., 2016: Optimization of ultrasound-assisted extraction and LC-ESI-MS/MS analysis of phenolic acids from *Brassica oleracea* L. var. *sabellica*. Ind. Crops Prod. 83, 359-363.

DOI: 10.1016/j.indcrop.2016.01.015

Qiao, L., Ye, X., Sun, Y., Ying, J., Shen, Y., Chen, J., 2013: Ultrasonics Sonochemistry Sonochemical effects on free phenolic acids under ultrasound treatment in a model system. Ultrason. - Sonochemistry. 20, 1017-1025. DOI: 10.1016/j.ultsonch.2012.12.007

Qu, W., Masoud, R., Feng, Y., Shi, S., Wang, J., Ma, H., 2017: Ultrasonics - Sonochemistry Sonochemical effect of flat sweep frequency and pulsed ultrasound (FSF) treatment on stability of phenolic acids in a model system. Ultrason. - Sonochemistry. 39, 707-715. DOI: 10.1016/j.ultsonch.2017.05.034

Randall, K.M., Drew, M.D., Øverland, M., Østbye, T.K., Bjerke, M., Vogt, G., Ruyter, B., 2013: Effects of dietary supplementation of coriander oil, in canola oil diets, on the metabolism of [1-14C] 18:3n-3 and [1-14C] 18:2n-6 in rainbow trout hepatocytes. Comp. Biochem. Physiol. - B Biochem. Mol. Biol. 166, 65-72. DOI: 10.1016/j.cbpb.2013.07.004

Reboredo-Rodríguez, P., Rey-Salgueiro, L., Regueiro, J., González-Barreiro, C., Cancho-Grande, B., Simal-Gándara, J., 2014: Ultrasound-assisted emulsification-microextraction for the determination of phenolic compounds in olive oils. Food Chem. 150, 128-136. DOI: 10.1016/j.foodchem.2013.10.157

Roby, M.H.H., Sarhan, M.A., Selim, K.A.H., Khalel, K.I., 2013: Evaluation of antioxidant activity, total phenols and phenolic compounds in thyme (*Thymus vulgaris* L.), sage (*Salvia officinalis* L.), and marjoram (*Origanum majorana* L.) extracts. Ind. Crops Prod. 43, 827-831. DOI: 10.1016/j.indcrop.2012.08.029

Ross, K.A., Beta, T., Arntfield, S.D., 2009: A comparative study on the phenolic acids identified and quantified in dry beans using HPLC as affected by different extraction and hydrolysis methods. Food Chem. 113, 336-344. DOI: 10.1016/j.foodchem.2008.07.064

Sahib, N.G., Anwar, F., Gilani, A.H., Hamid, A.A., Saari, N., Alkharfy, K.M., 2012: Coriander (*Coriandrum sativum* L.): A potential source of high-value components for functional foods and nutraceuticals - A review. Phyther. Res. 1456, n/a-n/a. DOI: 10.1002/ptr.4897

Wang, L., Yao, Y., He, Z., Wang, D., Liu, A., Zhang, Y., 2013: Determination of phenolic acid concentrations in wheat flours produced at different extraction rates. J. Cereal Sci. 57, 67-72. DOI: 10.1016/j.jcs.2012.09.013

Zeković, Z., Kaplan, M., Pavlić, B., Olgun, E.O., Vladić, J., Canli, O., Vidović, S., 2016: Chemical characterization of polyphenols and volatile fraction of coriander (*Coriandrum sativum* L.) extracts obtained by subcritical water extraction. Ind. Crops Prod. 87, 54-63. DOI: 10.1016/j.indcrop.2016.04.024

ORCID:
Iztok Jože Košir https://orcid.org/0000-0002-2829-1335

Address of the authors:
Milena Ivanović; Maša Islamčević Razboršek, Laboratory for Analytical Chemistry and Industrial Analysis, Faculty of Chemistry and Chemical Engineering, University of Maribor, Smetanova ulica 17, SI-2000 Maribor, Slovenia
Iztok Jože Košir, Slovenian Institute of Hop Research and Brewing, Department of Agrochemistry and Brewing, Cesta Žalskega tabora 2, SI-3310 Žalec, Slovenia
Mitja Kolar, Department of Chemistry and Biochemistry, Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna pot 113, SI-1000 Ljubljana, Slovenia
E-mail: mitja.kolar@fkkt.uni-lj.si