Industrial Crops and Products 61 (2014) 377–381

Contents lists available at ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop

Extraction methods for the determination of phenolic compounds from *Equisetum arvense* L. herb

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ARTICLE INFO

Article history:
Received 4 April 2014
Received in revised form 15 July 2014
Accepted 17 July 2014
Available online 9 August 2014

Keywords:
Ultrasound assisted extraction
Accelerated solvent extraction
Matrix solid-phase dispersion
Equisetum arvense L.
Polyphenols
High performance liquid chromatography

ABSTRACT

Polyphenols are a very important group of pharmacologically active compounds. The extraction yield of selected phenolic acids and flavonoids from *Equisetum arvense* L. herb has been determined by use different methods of extraction – Soxhlet extraction, ultrasound assisted extraction (USAE), and accelerated solvent extraction (ASE). Methanol and 80% aqueous methanol were used as extractants. The crude extracts were evaporated to dryness and prepared for fractionation of the analyzed compounds by solid-phase extraction (SPE). An alternative method used for the isolation and purification of analyzed polyphenols was matrix solid-phase dispersion (MSPD). Samples containing the phenolic fraction were analyzed by RP-HPLC. Quantitative analysis was performed by the external standard method and use of a calibration plot for each standard. The most effective technique was ultrasound assisted extraction. Only for caffeic acid the highest yield gave exhaustive extraction in a Soxhlet apparatus. The methods were validated in terms of accuracy, precision LOD and LOQ.

1. Introduction

Equisetum arvense L. (horsetail), belonging to Equisetaceae family, is a plant showing aerial stems, branched with regular verticilies 2–23 mm in diameter, terminal strobile in the branches and in the main stem (10 mm long and 4 mm in diameter). This plant grows in several regions of Europe and North, Central, and South America (Dos Santos et al., 2005; Garcia et al., 2013).

Studies of *E. arvense* have reported on its antioxidant constituents (i.e. caffeic acid, chlorogenic acid, ferulic acid, kaempferol, quercetin, isoquercetin, apigenin, and luteolin) (Garcia et al., 2012). Moreover horsetail is rich in many kinds of vitamins, such as B1, B2, B6, nicotinic acid, folic acid, pantothenic acid, and vitamins C, E, K, silicic acid, saponins, and trace elements such as Na, K, Ca, Mg, P, Fe, Zn, Cu, Mn, Si, Sr, and Ti. In conclusion this medical plant may be useful to protect against the various diseases (Nagai et al., 2005). Horsetail has traditionally been used as a diuretic agent, and sometimes is suggested for the following diseases: kidney stones, urinary tract infections, brittle nails, minor wounds, and burns (applied topically) (Nagai et al., 2005).

The antioxidant activities of the plant extracts largely depend on the extraction efficiency of bioactive components, and composition of the extracts. The extraction yield of active compounds from plant materials is affected by different factors, such as the extraction techniques, solvents, time, temperature, solvent-to-plant material ratio, and many others. However, a suitable extracting method, and solvent are crucial to ensuring an efficient extraction of the targeted nutraceuticals from plant material (Karabegović et al., 2014).

Various solvents, such as methanol, ethanol, acetone, ethyl acetate, and their combinations have been used in previous studies for the extraction of phenolic compounds from plant materials, often with different proportions of water, in order to establish their extractive efficiency (Nour et al., 2014; Dai and Mumper, 2010; Fernandez-Agullo et al., 2013; Vongsak et al., 2013). The extraction of these compounds may be performed by traditional or by modern methods (such as: accelerated solvent extraction (ASE), ultrasound assisted extraction (USAE), microwave assisted solvent extraction (MASE) etc. The novel methods require shorter extraction time, use of low amount of solvents, allow for simultaneous parallel processing of several samples, and are automatic, but are more expensive. The important step in sample preparation is

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http://dx.doi.org/10.1016/j.indcrop.2014.07.036
0926-6690/

clean-up of crude extract. The most used purification technique is the solid-phase extraction (SPE) (Chen et al., 2008).

An alternative, introduced for sample preparation is matrix solid-phase dispersion (MSPD) (Capriotti et al., 2010; Visnevschi-Necrasov et al., 2009; Barker, 2000; Oniszczuk et al., 2013). It is a simple, and cheap preparation technique that combines sample homogenization, extraction, and purification of the analyzed compounds in one step (Barker, 2007; Kristenson et al., 2006; Dopico-Garcia et al., 2007). MSPD may selectively elute a single compound, several classes of compounds or fractions (Capriotti et al., 2010; Garcia-Lopez et al., 2008). This method can eliminate many complicated steps in classical liquid–solid extraction (LSE) and/or solid phase extraction (SPE), allows for the reduction of organic solvent consumption, exclusion of sample component degradation, improvement of extraction efficiency, and selectivity (Abhilash et al., 2007; Dawidowicz and Rado, 2010; Dawidowicz et al., 2011).

Theoretically, the optimal extraction method should be simple, safe, reproducible, inexpensive, and suitable for industrial application (Vongsak et al., 2013).

The aim of this paper was comparison of ultrasound assisted extraction, accelerated solvent extraction, Soxhlet extraction, and matrix solid-phase dispersion in the determination of selected phenolic compounds from *E. arvense* by HPLC-DAD.

In case of all liquid–solid extraction methods solid-phase extraction for the purification of crude extracts was used.

2. Materials and methods

2.1. Materials and chemicals

Field horsetail (*E. arvense* L.) herb was purchased from "*Flos*" herbal industrial (Mokrsko, Poland). Before the extraction dry plant material was milled, and sieved.

All standards were purchased from Sigma Aldrich (Steinheim, Germany). HPLC-grade methanol, acetonitrile, and formic acid were purchased from J.T. Baker (Netherlands), water was purified using a Millipore laboratory ultra pure water system (Simplicity™ system, Millipore, Molsheim, France). Methanol used for preparation, and purification of the extracts was of analytical grade, and obtained from the Polish Reagents (POCH, Gliwice, Poland). The solid phase used for MSPD was Alltech bulk high capacity C 18 sorbent, 50 μM (Alltech, Deerfield, IL, USA), end-capped, 17% C. The columns used for SPE were Bakerbond C 18, 3 mL columns, packed with 500 mg reversed phase, 40 μM (J.T. Baker, Deventer, Netherlands), end-capped, 17.5% C.

2.2. Sample preparation

2.2.1. Soxhlet extraction

2 g of dried *E. arvense* herb powder was placed to the filter paper, and extracted with applicable solvent (methanol or 80% aqueous solution of methanol) for 48 h in Soxhlet apparatus. Extracts were evaporated to dryness. The residues were dissolved in 25 mL of 80% aqueous solution of methanol. The whole procedure was repeated three times for each solvent.

2.2.2. Ultrasound assisted extraction (USAE)

2 g of dried *E. arvense* herb powder was extracted with 50 mL of applicable solvent (methanol or 80% aqueous solution of methanol) in ultrasonic bath with temperature regulation (Bandelin Electronic, Sonorex RK 100H, Germany) at 60 °C for 30 min. Extract was filtered, and plant material was extracted afterwards with two portions of the solvent by the same way. Extracts were filtered, combined, and evaporated to dryness. The residues were dissolved in 25 mL of 80% aqueous solution of methanol. The whole procedure was repeated three times for each solvent.

2.2.3. Accelerated solvent extraction (ASE)

ASE was performed with a Dionex (Sunnyvale, CA, USA) ASE 200 instrument with solvent controller. Plant material (2 g) was placed in a stainless-steel extraction cell, and extracted with applicable solvent (methanol, and 80% aqueous solution of methanol). The extractions were performed at three temperature ranges (80, 100, and 120 °C) for 30 min (three cycles for 10 min at the same temperature, for every sample) at a pressure of 60 bar. Extracts were combined, and evaporated to dryness. The residues were dissolved in 25 mL of 80% aqueous solution of methanol. The whole procedure was repeated three times for each solvent.

2.2.4. Solid phase extraction (SPE)

All crude extracts (obtained by Soxhlet, USAE, and ASE) were purified by SPE. 10 mL of every sample was passed through a Bakerbond C 18 SPE column (previously conditioned). The retained polyphenols were eluted with 15 mL of 80% aqueous solution of methanol using a SPE vacuum. Fractions for analysis were transferred into volumetric flask, filled up to their volume with 80% aqueous solution of methanol, and injected into the HPLC system. The whole procedure was repeated three times for each solvent.

2.2.5. Matrix solid-phase dispersion (MSPD)

0.25 g of dried *Equisetum* herb powder was placed in a glass mortar, and mixed with 0.5 g of sorbent (previously conditioned), and 1 mL of 80% aqueous solution of methanol. The mixture was then homogenized in the glass mortar using a pestle to obtain a homogenous mixture. The blend was then transferred into a 3 mL syringe with a paper frit on the bottom. The sample was covered with another paper frit, and compressed using the syringe plunger. Polyphenols were eluted with 5 mL of 80% aqueous solution of methanol. Fractions for analysis were transferred into volumetric flask, filled up to their volume with 80% aqueous solution of methanol, and injected into the HPLC system. The whole procedure was repeated three times for each solvent.

2.3. HPLC conditions

Analysis was performed with a liquid chromatograph equipped Elite LaChrom VWR Hitachi DAD L-2455 (column oven Elite LaChrom L-2300, Autosampler Elite LaChrom L-2200, Pump Elite LaChrom L-2130), on the Merck LiChrocart 250-4 HPLC column (250 mM × 4.0 mM) packed with 5 μm (LiChrosper 100 RP-18 end-capped). The sample injection volume was 10 μL. The mobile phase was acetonitrile (A), and water containing 0.5% formic acid (B). The A% was changed as follow: 0 min (10%); 25 min (20%); 45 min (30%); 47 min (100%). The flow rate was 1 mL/min, the column temperature was 25 °C. The identification was performed by comparing retention times, and UV-DAD spectra with those analyzed under the same conditions for appropriate standards. The qualitative, and quantitative determination was performed in following wavelengths: λ = 255, and 323 nM.

The flavonoids, and phenolic acids content in the extracts were determined by use of calibration plots constructed for every standard. Standard solutions were prepared by dissolving the compounds in methanol.

2.4. Validation of the methods

The methods were validated in terms of accuracy, precision LOD, and LOQ. Moreover, the linear ranges of calibration curves were determined.

Table 1
Yield of extraction of investigated polyphenols from *Equisetum* herb by different methods and extractants ($n = 3$).

Method and extractant	Yield ± SD[a] (mg mg g^{-1} of dry weight)				
	Chlorogenic acid	Caffeic acid	Ferulic acid	Isoquercetrin	5-Glucoside luteolin
ASE 80 °C 80% MeOH	0.2441 (±0.0060)	0.2941 (±0.0077)	0.1355 (±0.0052)	0.2055 (±0.0025)	0.1245 (±0.0067)
RSD%[b]	2.4390	2.6326	3.8459	1.2385	5.3596
ASE 100 °C 80% MeOH	0.2415 (±0.0092)	0.2881 (±0.0052)	0.1093 (±0.0006)	0.1909 (±0.0003)	0.1050 (±0.0009)
RSD%	4.2951	1.7922	0.5314	0.1393	0.8387
ASE 120 °C 80% MeOH	0.1333 (±0.0061)	0.4350 (±0.0147)	0.0797 (±0.0011)	0.1901 (±0.0044)	0.0670 (±0.0013)
RSD%	4.6113	3.3699	1.4011	2.3092	1.9117
ASE 80 °C 100% MeOH	0.0418 (±0.00001)	0.0847 (±0.0034)	0.0263 (±0.0006)	0.1056 (±0.0011)	0.0136 (±0.0004)
RSD%	0.3346	4.0041	2.2591	1.0005	2.6980
ASE 100 °C100% MeOH	0.0691 (±0.0001)	0.1081 (±0.0060)	0.0281 (±0.0015)	0.1422 (±0.0052)	0.0175 (±0.0001)
RSD%	1.6744	5.5659	5.4847	3.6576	0.8181
ASE 120 °C 100% MeOH	0.1020 (±0.0002)	0.1172 (±0.0038)	0.0240 (±0.0003)	0.1564 (±0.0002)	0.0129 (±0.0001)
RSD%	1.8391	2.2015	0.1261	0.1017	0.6116
USAE 80% MeOH	0.5631 (±0.0227)	0.4739 (±0.0536)	0.2120 (±0.0004)	0.2629 (±0.0010)	0.2485 (±0.0045)
RSD%	4.0289	5.3152	0.2106	0.3662	1.7954
USAE 100% MeOH	0.1225 (±0.0030)	0.1902 (±0.0057)	0.1313 (±0.0025)	0.1282 (±0.0034)	0.1217 (±0.0017)
RSD%	2.4371	2.9899	1.8854	2.6819	1.3757
Soxhlet 80% MeOH	0.3526 (±0.0030)	0.5175 (±0.0304)	0.0943 (±0.0008)	0.1498 (±0.0015)	0.0910 (±0.0009)
RSD%	0.8383	5.8835	0.8542	1.0179	0.9548
Soxhlet 100% MeOH	0.2501 (±0.0016)	0.1668 (±0.0015)	0.0880 (±0.0001)	0.2102 (±0.0009)	0.0867 (±0.0001)
RSD%	0.6559	0.9141	0.1040	0.4158	0.1022
MSPD	0.2425 (±0.0005)	0.3250 (±0.0071)	0.1562 (±0.0006)	0.1559 (±0.0018)	0.1653 (±0.0016)
RSD%	0.2103	2.1992	0.4119	1.1591	0.9393

[a] SD – standard deviation.
[b] RSD% – relative standard deviation in percent.

The method precision was evaluated by intra-day, and inter-day tests. Intra-day experiments were performed by replicate analysis of six aliquots of the same sample within one day. Inter-day tests were carried out on three consecutive working days in the same way as intra-assay experiments. Three measurements of every peak area for the extract components were carried out. Limit of detection (LOD), and limit of quantification (LOQ) were established at a signal-to-noise ratio (S/N) of 3, and 10, respectively.

The accuracy of the solid phase extraction for all extracts, and for solid-phase dispersion was evaluated through recovery studies. Pre-analyzed samples (crude extracts in the SPE, and plant material in the mortar in the MSPD) were spiked with known amounts of the each standard solution (three concentration levels – 48, 60, and 72 μg mL^{-1}), then SPE, and MSPD were performed by using the same methods employed in the quantitative determination of flavonoids, and phelolic acids in the plant samples. The experiment was conducted three times.

3. Results and discussion

Different methods of classical extraction such as: shaking with methanol or water (Nagai et al., 2005), maceration with aqueous solution of ethanol (Dos Santos et al., 2005; Garcia et al., 2012, 2013), and extraction with water at 100 °C in a water bath (Li et al., 2013) were developed for isolation of active compounds from *E. arvense* L. herb.

In our experiment modern extraction method – accelerated solvent extraction, ultrasound assisted extraction, and traditional extraction in Soxhlet apparatus were used for the isolation of polyphenols from horsetail herb. The cinnamic acid derivatives – caffeic, and ferulic acids, the depside – chlorogenic acid, and flavonoids: isoquercetrin, and 5-glucoside luteolin were identified in the all extracts from *E. arvense*. The quantitative composition of extracts obtained by a variety of extraction methods was different, however (Table 1). For most of the analyzed compounds the highest yields were obtained by ultrasound assisted extraction. Only for caffeic acid the most efficient method was exhaustive extraction in Soxhlet apparatus.

The results of recent study confirm that ultrasound-assisted extraction is an effective, easy in operation, reliable, and feasible method for extraction of polyphenols from plant material (Muñiz-Márquez et al., 2013; Wang et al., 2013; Melecchi et al., 2006).

The comparison between the ultrasound-assisted extraction, and different extraction methods developed by other researches showed the superiority of USAE for extracting phenolic compounds for example from *Phlomidoschema parviflorum* L. leaves (Majd et al., 2014), *Thymus vulgaris* L. herb, *Verbena officinalis* L. flowers (Bajerová et al., 2014), and *Vitis vinifera* L. seeds (Da Porto et al., 2013).

In all the cases, accelerated solvent extraction, irrespective of the temperature applied (80, 100, and 120 °C), did not give the highest yield of analyzed compounds. High efficiency of the USAE may be associated with the fact, that destruction of the compact, hard structures of *E. arvense* stems (which are rich in silicic acid), and diffusion of solvent into this material requires drastic extraction conditions. Phenolic compounds can, moreover, form strong bonds with lignin, a component of the cell walls of stems, and leaves (Kohlmunzer, 2003). Such lignin complexes are difficult to break down, and then classic extraction methods are less efficient (Waksmundzka-Hajnos et al., 2008). In such circumstances techniques which destroy the cell structure e.g. ultrasound assisted extraction results in higher yields of the phenolic acids. Matrix solid-phase dispersion-method which gave high yields of furanocoumarins (Oniszczuk et al., 2013) was in this case poorly effective. This is probably caused by the fact, that coumarins (playing the role phytoalexins) are located not too deep inside plants tissues, even on the surface of plant organs. In order to extract them, only mechanical destruction of the structure of plant tissue is then necessary.

In the experiment methanol, and 80% aqueous solution of methanol were used as extractants. Because of the polar nature of the analyzed polyphenols higher yields gave 80% aqueous solution of methanol, in all the cases. Exemplary HPLC chromatograms of polyphenols isolated by USAE techniques are shown in Fig. 1.

Validation of the methods was performed in terms of accuracy, precision LOD, and LOQ. The concentration of all standards in calibration plots was in range 1–500 μg mL^{-1}. The calibration

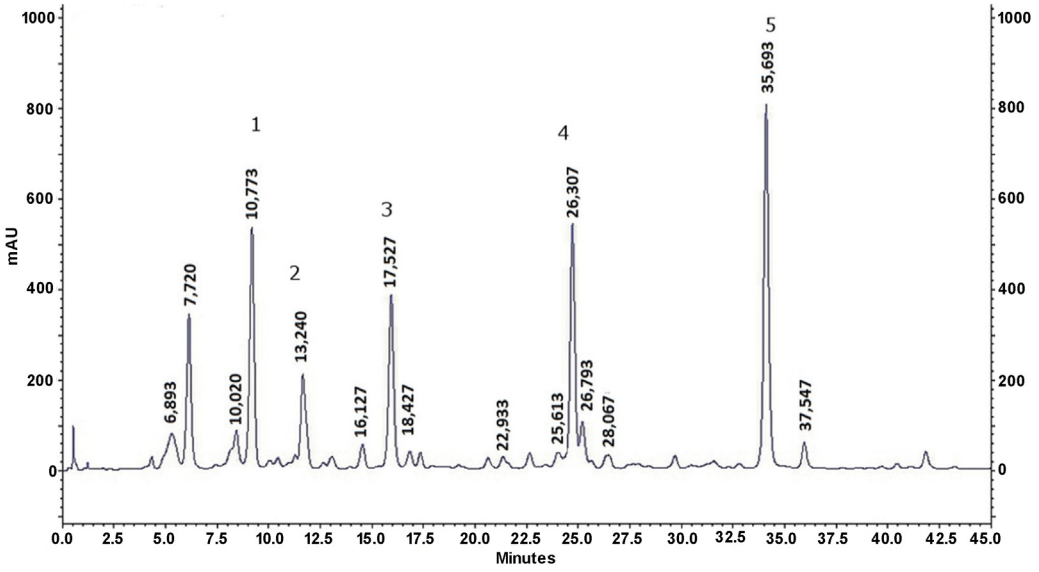

Fig. 1. HPLC chromatograms of the extract of *Equisetum* herb obtained using USAE + SPE methods. 1 – chlorogenic acid, 2 – caffeic acid, 3 – ferulic acid, 4 – isoquercetrin, 5 – 5-glucoside luteolin.

Table 2
Linear relationship between peak area and concentration of polyphenol ($n = 3$).

Compound	Regression equation	R^2	LOQ[a] ($\mu g\,mL^{-1}$)	LOD[b] ($\mu g\,mL^{-1}$)	Linear range ($\mu g\,mL^{-1}$)
Chlorogenic acid	$y = 26{,}416x + 1.065$	0.9990	2.86	8.21	10–100
Caffeic acid	$y = 14{,}370x + 0.2803$	0.9993	0.76	2.22	10–100
Ferulic acid	$y = 57{,}689x + 0.558$	0.9999	0.74	2.61	10–100
Isoquercetrin	$y = 102{,}982x + 0.754$	0.9995	1.21	3.74	10–100
5-Glucoside luteolin	$y = 14{,}536x + 0.312$	0.9994	0.99	3.17	10–100

[a] LOD – limit of detection.
[b] LOQ – limit of quantification.

curves for all standards were linear over the concentration range 10–100 $\mu g\,mL^{-1}$. All the examined compounds showed good linearity. The correlation coefficients of all calibration curves were R^2 >0.9990. Parameters of calibration curves together with LOD, and LOQ values are presented in Table 2.

The relative standard deviation (RSD%), as a measure of repeatability, was from 0.1040% (ASE of isoquercetrin with methanol) to 5.8835% (extraction of caffeic acid in Soxhlet apparatus with 80% aqueous solution of methanol). These values are in good agreement with requirements for a developed method. The intra- and inter-day precision RSD values were less than 2.9% for all compounds, which showed good reproducibility of the developed method.

The recoveries of the SPE, and MSPD method were in the range of 95.7% (for chlorogenic acid) to 102.9% (for isoquercetrin), and of 94.8% (for chlorogenic acid) to 98.5% (for isoquercetrin), respectively. The obtained values are similar to the recoveries reported by other authors using SPE, and MSPD procedures (Dopico-Garcia et al., 2007; Visnevschi-Necrasov et al., 2009; Žiaková et al., 2003). Recoveries for SPE (preceded by USAE), and MSPD methods are presented in Table 3. Considering the results of the recovery test, both – SPE, and MSPD methods are deemed to be accurate.

Table 3
Values of recoveries for each compounds used for extracts' fortification calculated in both SPE (preceded for USAE) and MSPD method ($n = 3$).

Compound	SPE[a] (%)	MSPD[b] (%)
Chlorogenic acid	95.70	94.80
Caffeic acid	98.33	95.90
Ferulic acid	97.30	96.20
Isoquercetrin	102.90	98.50
5-Glucoside luteolin	98.20	97.40

[a] SPE – solid phase extraction.
[b] MSPD – matrix solid-phase dispersion.

4. Conclusions

In this study, we investigated the application of different solid–liquid extraction methods followed by SPE, and matrix solid-phase dispersion for the isolation of selected phenolic acids, and flavonoids from *E. arvense* L. herb. The most effective technique for isolation of analyzed compounds was ultrasound assisted extraction at 60 °C in three cycles for 30 min, with 80% aqueous solution of methanol. Other extraction methods used in experiment gives definitely less yield of polyphenols. Satisfactory yields for these compounds cannot be obtained also by the use of MSPD.

USAE proved to be an effective, and precise technique. This technique (followed by SPE) exhibited appropriate extraction efficiency, reproducibility, and recovery. All of these results clearly infer, that USAE could be useful to extract phenolic compounds from plant material.

References

Abhilash, P.C., Jamil, S., Singh, N., 2007. Matrix solid-phase dispersion extraction versus solid-phase extraction in the analysis of combined residues of hexachlorocyclohexane isomers in plant matrices. J. Chromatogr. A 1176, 43–47.
Bajerová, P., Adam, M., Bajer, T., Ventura, K., 2014. Comparison of various techniques for the extraction and determination of antioxidants in plants. J. Sep. Sci. 37, 835–844.
Barker, S.A., 2000. Applications of matrix solid-phase dispersion in food analysis. J. Chromatogr. A 880, 63–68.
Barker, S.A., 2007. Matrix solid phase dispersion (MSPD). J. Biochem. Biophys. Methods 70, 151–162.

Chen, Y., Guo, Z., Wang, X., Qiu, C., 2008. Sample preparation. J. Chromatogr. A 1184, 191–219.
Capriotti, A.L., Cavaliere, C., Giansanti, P., Gubbiotti, R., Samperi, R., Laganà, A., 2010. Recent developments in matrix solid-phase dispersion extraction. J. Chromatogr. A 1217, 2521–2532.
Dai, J., Mumper, R.J., 2010. Plant phenolics: extraction, analysis and their antioxidant and anticancer properties. Molecules 15, 7313–7352.
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.
Dawidowicz, A.L., Rado, E., 2010. Matrix solid-phase dispersion (MSPD) in chromatographic analysis of essential oils in herbs. J. Pharm. Biomed. Anal. 52, 79–85.
Dawidowicz, A.L., Wianowska, D., Rado, E., 2011. Matrix solid-phase dispersion with sand in chromatographic analysis of essential oils in herbs. Phytochem. Anal. 22, 51–58.
Dopico-Garcia, M.S., Valentao, P., Jagodzinska, A., Klepczynska, J., Guerra, L., Andrade, P.B., Seabra, R.M., 2007. Solid-phase extraction versus matrix solid-phase dispersion: application to white grapes. Talanta 74, 20–31.
Dos Santos, J.G., Blanco, M.M., Do Monte, F.H.M., Russi, M., Lanziotti, V.M.N.B., Leal, L.K.A.M., Cunha, G.M., 2005. Sedative and anticonvulsant effects of hydroalcoholic extract of *Equisetum arvense*. Fitoterapia 76, 508–513.
Fernandez-Agullo, A., Pereira, E., Freire, M.S., Valentao, P., Andrade, P.B., Gonzalez-Alvarez, J., Pereira, J.A., 2013. Influence of solvent on the antioxidant and antimicrobial properties of walnut (*Juglans regia* L.) green husk extracts. Ind. Crops Prod. 42, 126–132.
Garcia, D., Ramos, A.J., Sanchis, V., Marín, S., 2012. Effect of *Equisetum arvense* and *Stevia rebaudiana* extracts on growth and mycotoxin production by *Aspergillus flavus* and *Fusarium verticillioides* in maize seeds as affected by water activity. Int. J. Food Microbiol. 153, 21–27.
Garcia, D., Ramos, A.J., Sanchis, V., Marin, S., 2013. Equisetum arvense hydroalcoholic extract: phenolic composition and antifungal and antimycotoxigenic effect against *Aspergillus flavus* and *Fusarium verticillioides* in stored maize. J. Sci. Food Agric. 93, 2248–2253.
Garcia-Lopez, M., Canosa, P., Rodriguez, I., 2008. Trends and recent applications of matrix solid-phase dispersion. Anal. Bioanal. Chem. 391, 963–974.
Karabegović, I.T., Stojičević, S.S., Veličković, D.T., Todorović, Z.B., Nikolić, N., Lazić, M.L., 2014. The effect of different extraction techniques on the composition and antioxidant activity of cherry laurel (*Prunus laurocerasus*) leaf and fruit extracts. Ind. Crops Prod. 54, 142–148.
Kohlmunzer, S., 2003. Pharmacognosy. PZWL, Warsaw, pp. 150–196.
Kristenson, M.E., Ramous, L., Brinkman, U., 2006. Recent advances in matrix solid-phase dispersion. Trends Anal. Chem. 25, 96–111.
Li, S., Li, S.-K., Gan, R.-Y., Song, F.-L., Kuang, L., Li, H.B., 2013. Antioxidant capacities and total phenolic contents of infusions from 223 medicinal plants. Ind. Crops Prod. 51, 289–298.
Majd, M.H., Rajaei, A., Bashi, D.S., Mortazavi, S.A., Bolourian, S., 2014. Optimization of ultrasonic-assisted extraction of phenolic compounds from bovine pennyroyal (*Phlomidoschema parviflorum*) leaves using response surface methodology. Ind. Crops Prod. 57, 195–202.
Melecchi, M.I.S., Peres, V.F., Dariva, C., Zini, C.A., Abad, F.C., Martinez, M.M., 2006. Optimization of the sonication extraction method of *Hibiscus tiliaceus* L. flowers. Ultrason. Sonochem. 13, 242–250.
Muñiz-Márquez, D.B., Martínez-Ávila, G.C., Wong-Paz, J.E., Belmares-Cerda, R., Rodríguez-Herrera, R., Aguilar, C., 2013. Ultrasound-assisted extraction of phenolic compounds from *Laurus nobilis* L. and their antioxidant activity. Ultrason. Sonochem. 20, 1149–1154.
Nagai, T., Myoda, T., Nagashima, T., 2005. Antioxidative activities of water extract and ethanol extract from field horsetail (tsukushi) *Equisetum arvense* L. Food Chem. 91, 389–394.
Nour, V., Trandafir, I., Cosmulescu, S., 2014. Antioxidant capacity, phenolic compounds and minerals content of blackcurrant (*Ribes nigrum* L.) leaves as influenced by harvesting date and extraction method. Ind. Crops Prod. 53, 133–139.
Oniszczuk, A., Waksmundzka-Hajnos, M., Skalicka, K., Głowniak, K., 2013. Comparison of matrix-solid phase dispersion and liquid–solid extraction connected with solid-phase extraction in the quantification of selected furanocoumarins from fruits of *Heracleum leskowii* by high performance liquid chromatography. Ind. Crops Prod. 50, 131–136.
Visnevschi-Necrasov, T., Cunha, C., Nunes, S., Oliveira, E.M.B.P.P., 2009. Optimization of matrix solid-phase dispersion extraction method for the analysis of isoflavones in *Trifolium pratense*. J. Chromatogr. A 1216, 3720–3724.
Vongsak, B., Sithisarn, P., Mangmool, S., Thongpraditchote, S., Wongkrajang, Y., Gritsanapan, W., 2013. Maximizing total phenolics, total flavonoids contents and antioxidant activity of *Moringa oleifera* leaf extract by the appropriate extraction method. Ind. Crops Prod. 44, 566–571.
Waksmundzka-Hajnos, M., Wianowska, D., Oniszczuk, A., Dawidowicz, A.L., 2008. Effect of sample-preparation methods on the quantification of selected flavonoids in plant materials by high performance liquid chromatography. Acta Chromatogr. 20, 475–488.
Wang, X., Wu, Y., Chen, G., Yue, W., Liang, Q., Wu, Q., 2013. Optimisation of ultrasound assisted extraction of phenolic compounds from *Sparganii rhizoma* with response surface methodology. Ultrason. Sonochem. 20, 846–854.
Žiaková, A., Brandšteterová, E., Blahová, E., 2003. Matrix solid-phase dispersion for the liquid chromatographic determination of phenolic acids in *Melissa officinalis*. J. Chromatogr. A 983, 271–275.