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On-line coupled dynamic sonication-assisted extraction–liquid chromatography for the determination of phenolic acids in *Lamiaceae* herbs

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ABSTRACT

A fast and efficient on-line coupled dynamic sonication-assisted extraction–liquid chromatography (DSAE–LC) method was developed for the determination of phenolic acids in basil, oregano, rosemary, sage, spearmint and thyme. The extraction and chromatography were coupled via a solid-phase trap filled with strong anion exchange material. The relative standard deviations (RSDs) for the retention times were less than 0.4% and those for the peak heights less than 3% except for gallic acid (RSD 1.2% for the retention times and 11% for the peak heights). Limits of detection were below ~3 ng.

1. Introduction

The polyphenol content of herbs of the *Lamiaceae* family has been widely studied. In most of these studies, the polyphenols have been extracted from the matrix by conventional solvent extraction. The polarities of the polyphenols range from polar to nonpolar and thus a wide range of solvents have been used. These include water/hot water [1–8], methanol [2,8–15], ethanol [2,6,8], acetone [2,16,17], ethyl acetate [2] and hexane. In addition, herbal samples have been extracted with novel methods such as pressurised hot water extraction (PHWE) [6,8,17], solid-phase extraction (SPE) with molecularly imprinted polymer [14], matrix solid-phase dispersion [14] and supercritical fluid extraction (SFE) [6,14,18–20].

There is a growing interest in efficient and environmentally friendly extraction methods. The desirable features of "green" extraction methods are small solvent consumption, short extraction time and high extraction yield. The extraction speed and yield can be improved by applying heat or ultrasound or other auxiliary energy during the extraction. The power of ultrasound rests on the cavitation phenomenon. The cavitation bubbles, which are formed and compressed when ultrasound is applied, finally collapse and high local temperatures and pressures are formed as a result. These enhance the penetration of solvent into the sample matrix, improve the contact between solid and liquid phase surfaces and accelerate the mass transfer [21,22]. Ultrasound has been used in both static and dynamic modes in extracting metals [23–26], biophenols [8,27–32], pollutants [33], *trans*-fatty acids [34] and pesticides [35].

Another clear trend in methods development is towards on-line systems that integrate the sample preparation, separation and detection. On-line refers to a coupling via a transfer line, and with on-line coupled systems the whole analysis is performed in a closed unit. The primary benefit of an on-line system is higher sensitivity. In addition, the sample will be concentrated, the whole sample will be analysed, manual work is minimised and solvent consumption is decreased [36,37]. Extraction methods coupled on-line to liquid chromatography (LC) include SFE [38–40], dynamic microwave-assisted extraction [41], continuous-flow liquid membrane extraction [42], subcritical water extraction [43] and SPE [44,45].

In this work, we coupled a fast and effective dynamic sonication-assisted ethanol extraction unit via a solid-phase trap on-line to a liquid chromatograph. The on-line system was used in extracting phenolic acids from six herbs of the *Lamiaceae* family. The results are compared with those of earlier studies.

2. Experimental

2.1. Chemicals and samples

The solvents were methanol (Chromanorm for HPLC, VWR International, Fontenay-sous-Bois, France), ethanol (min. 99.5%, w/w, Altia, Rajamäki, Finland), acetonitrile (HPLC far UV grade, Lab-

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Scan, Analytical Sciences, Dublin, Ireland) and acetic acid (99–100% glacial, J.T. Baker, Deventer, The Netherlands). Orthophosphoric acid (85%), trifluoroacetic acid and citric acid (PA) were from Merck (Darmstadt, Germany). The phenolic acids (caffeic, chlorogenic, ferulic, gallic, *p*-coumaric, syringic and vanillic acids) were from Sigma–Aldrich (Steinheim, Germany). The dried herbs were purchased from a local supermarket and milled into fine powder in a laboratory-scale mill (IKA Labortechnik, Janke&Kunkel, Staufen, Germany). The herbs included basil (*Ocimum basilicum* L.), oregano (*Origanum vulgare* L.), rosemary (*Rosmarinus officinalis* L.), sage (*Salvia officinalis* L.), spearmint (*Mentha spicata* L.) and thyme (*Thymus vulgaris*). Distilled water was deionised with a Milli-Q system (Millipore, Molsheim, France).

2.2. Off-line extraction procedures

2.2.1. Dynamic sonication-assisted extraction (DSAE) with ethanol

The DSAE system consisted of one Jasco PU-980 pump (Tokyo, Japan), one extraction vessel (30 mm × 5 mm I.D., Krotek, Tampere, Finland) made of polyether ether ketone (PEEK) and an ultrasound bath (Bransonic Model 3510E-MTH, output 42 kHz, Branson Ultrasonics, Danbury, CT, USA). All connections were made with PEEK capillaries (1.6 mm O.D., 0.5 mm I.D.). The extraction procedure was according to the procedure optimised earlier [46]. The amount of herb was 4–6 mg and final extraction parameters were 60% ethanol, flow rate 0.25 ml/min, temperature 45 °C and extraction time 15 min.

2.2.2. Solid-phase extraction

The preliminary tests of solid-phase materials were done with commercial cartridges, and the tested materials were polymer based hydrophilic–lipophilic balance (HLB) and mixed-mode anion exchange and reversed-phase (MAX) sorbents (Oasis, Waters, Milford, MA, USA) and silica-based materials cyclohexyl (CH) and strong anion exchange (SAX) sorbents (Isolute, IST, Mid Glamorgan, UK). For on-line coupling a small column (30 mm × 2.1 mm I.D.) was packed in the laboratory with SAX bulk material (Isolute, IST). Before SAX material was used for the first time, it was treated with methanol, 100 mM acetic acid and 10 mM acetic acid. Different proportions of acids (orthophosphoric, acetic, citric, trifluoroacetic and formic) and organic modifiers (methanol and acetonitrile) were tested to desorb the trapped analytes.

2.3. Coupling of extraction and liquid chromatography on-line

The constructed on-line coupled DSAE–LC apparatus is presented in Fig. 1. The analytical procedure was the following:

Step 1: Conditioning of the solid-phase trap: Methanol 2 min, 2 ml/min and 10 mM acetic acid 5 min, 1 ml/min.
Step 2: Dynamic sonication-assisted extraction and solid-phase trapping: The conditions for the DSAE extraction were 60% ethanol, 15 min, 0.25 ml/min, water bath 45 °C. The extract from the DSAE was diluted with water (1:1, v/v) fed by an extra pump connected with a T-piece and then directed through the solid-phase trap.
Step 3: Elution and analysis: The loop (volume 500 μl) was filled with acidic solution for the desorption of the trapped analytes. The LC analysis was turned on and valve number one was changed to second position. The eluent from the HPLC 1050 system was redirected through the loop and solid-phase trap to the analysing column.

After 2 min, valve number one was turned back to its original position and a new analysis was started from step 1.

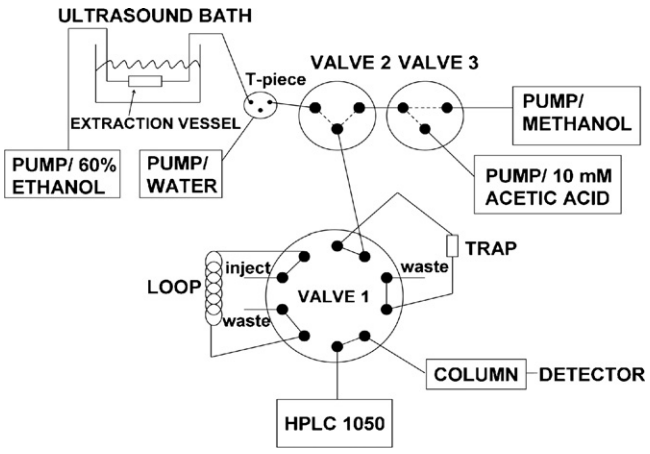

Fig. 1. Setup of the constructed DSAE–LC system.

The HPLC system consisted of a Hewlett-Packard (Waldbronn, Germany) 1050 system with an ultraviolet detection system. Data were collected and analysed with a Hewlett-Packard computing system. The analytical column was XBridge C18 (75 mm × 4.6 mm I.D., 2.5 μm, 100 Å, Waters). The final analytical separation was achieved at a flow rate of 1.0 ml/min with the following gradient program: 0 min 5% B, 2 min 5% B, 6 min 25% B, 13 min 40% B, 26 min 40% B. Eluent A was 0.5% acetic acid (v/v) in water and eluent B was methanol. The monitoring wavelength was 280 nm.

2.4. Measurements of recovery, breakthrough and memory effects

Recoveries of the phenolic acids were determined by first extracting and analysing the standard solution of the acids (10 μg/ml) with the on-line system. Then the same standard solution was analysed off-line by HPLC and the peak areas were compared.

The breakthrough for the standards was measured in off-line and on-line modes. In off-line mode the solution that eluted through the SPE trap was collected to a vial and then concentrated and analysed by HPLC. In on-line mode, the standard solution was injected to the elution loop and then injected along with 30% ethanol to the SPE trap and further eluted to the HPLC column.

The memory effects of the trap were checked by repeating the desorption procedure.

2.5. Confirmation of compound identification by LC–time-of-flight mass spectrometry (TOF-MS)

To ensure the compound identification, herb extracts were also analysed by LC–TOF-MS (Bruker Daltonics, Germany). A MicroTOF mass spectrometer was connected to the LC via an electrospray ion (ESI) source operated in negative mode. The detected mass range was 100–700 *m*/*z*. Other parameters were nebulizer 0.8 bar, dry gas 7.0 l/min, dry temperature 200 °C and acquisition frequency 0.5 Hz.

3. Results and discussion

The work proceeded in four steps: optimisation of the solid-phase trapping, construction and optimisation of the on-line system, validation of quality parameters and the analysis of samples. The DSAE parameters had been optimised previously for the off-line procedure.

Table 1
The peak widths, symmetry and resolution of the off-line and on-line measurements.

	Compound	Peak width off-line (min)	Peak width on-line (min)	Symmetry off-line	Symmetry on-line	Resolution off-line	Resolution on-line
1	Gallic acid	0.13	0.16	0.71	0.9		
2	Chlorogenic acid	0.14	0.17	0.78	0.86	36.5	35.1
3	Vanillic acid	0.14	0.17	0.9	1.02	3.4	2.4
4	Caffeic acid	0.16	0.19	0.84	0.89	1.3	1
5	Syringic acid	0.16	0.19	0.94	0.94	3.2	3
6	*p*-Coumaric acid	0.19	0.24	0.86	0.95	9.6	7.4
7	Ferulic acid	0.18	0.23	0.87	0.93	4.3	3.6

3.1. Optimisation of solid-phase trapping conditions in off-line mode

The preliminary tests of the solid-phase material for the trap were done with commercial cartridges. Both sorbent materials from Oasis (HLB and MAX) retained the analytes well. The difference between the materials is that, for the HLB sorbent, the pH of the solution has to be acidic to avoid the breakthrough of gallic and chlorogenic acids. The major problem with these polymer based sorbents is the strong retention of the analytes, which requires the use of a large amount of organic solvent for the elution. In an on-line coupled system, the subsequent chromatographic step must always be kept in mind, and a solvent of low elution strength is required in the reversed-phase liquid chromatography (RPLC) separation. This, in turn, means that the amount of organic solvent should be small so that the fraction transferred from the trap can be focused into a narrow zone at the beginning of the RPLC column. Thus, the polymeric SPE materials were not used in further experiments. The Isolute CH sorbent was also rejected because of the partial breakthrough of gallic acid. The Isolute SAX sorbent gave the most promising results in off-line extraction experiments and accordingly, a small column was packed with bulk SAX material and used in the on-line experiments.

3.2. Construction and optimisation of on-line coupled system

The DSAE extraction was performed with 60% ethanol with a flow rate of 0.25 ml/min. It was necessary to dilute the ethanol extract with water to half before the SPE trap to ensure efficient retention of the analytes. Conditioning of the trapping material was also found to be important to the repeatability of the results. The baseline and recoveries were not stable when the trap was conditioned with methanol and water. The stability and repeatability were significantly improved when water was replaced with 10 mM acetic acid.

The elution of the analytes was examined with use of different proportions of acidic solutions 0.2 M orthophosphoric/citric acid, or 1–5% (v/v) acetic/trifluoroacetic/formic acid and different amount of organic modifiers (methanol or acetonitrile). The amount of organic solvent was kept below 20% to ensure effective refocusing at the beginning of the RPLC column during the elution. The best results were obtained with 0.2 M orthophosphoric and citric acids and these were further studied. However, citric acid gave two peaks in chromatogram and at the same retention time two of the studied analytes co-eluted and thus, the 0.2 M orthophosphoric acid was chosen as final solvent for the elution. The pH of the solution was adjusted to 2.5 to avoid the dissolution of silica.

The volume of the eluent was tested in the range 130–1000 μl, and a volume of 500 μl was found to be the most suitable. Methanol and acetonitrile (2–20%, v/v) were tested as organic modifier. Although the addition of organic modifier had no significant effect on the recovery, the peaks became broader and, thus, 0.2 M orthophosphoric acid at pH 2.5 was used as such for the elution. No significant band broadening was noticed owing to relatively large volume of the extract (500 μl). The performance of the on-line system in comparison with off-line system is shown in Table 1. As can be seen, with direct injection of analytes the peak widths were slightly narrower than in the on-line system, but on the other hand, the symmetry values of the peaks were better with the on-line system. The resolution was not significantly changed either. These results showing that no significant band broadening took place during large volume transfer of the extract. The chromatograms of standard solution (10 μg/ml) obtained with the on-line system and with direct injection to the HPLC 1050 system are presented in Fig. 2.

3.3. Recovery, breakthrough and memory effects of solid-phase trap in on-line mode

The recovery of the analytes varied from 90% to 106%. The recovery of the first eluting compounds (gallic and chlorogenic acids) was 90% and the recovery of the last two eluting compounds (*p*-coumaric and ferulic acids) was over 100% (102% and 106%, respectively).

No peaks were detected in either breakthrough experiments indicating that the trap material retained the analytes as well in on-line as in off-line mode.

The sorbent material was conditioned the same way before each analysis, and no carry over of the analytes was detected after the

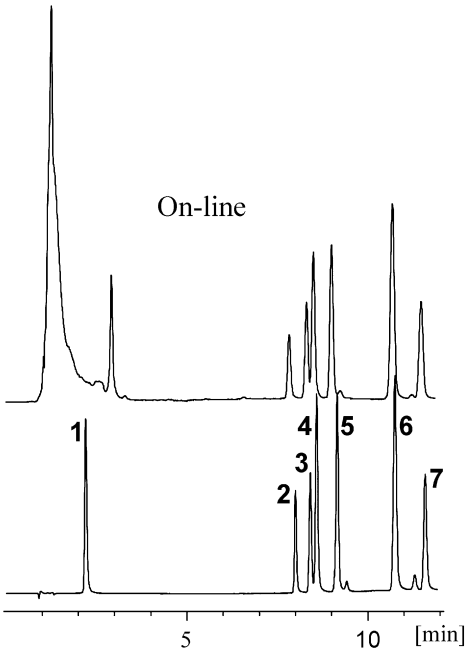

Fig. 2. Chromatograms of the standard solution (10 μg/ml). Upper: on-line DSAE–LC; lower: HPLC (without DSAE). Detection at wavelength 280 nm. Peaks: (1) gallic, (2) chlorogenic, (3) vanillic, (4) caffeic, (5) syringic, (6) *p*-coumaric and (7) ferulic acids. Gradient: 0 min 5% B, 2 min 5% B, 6 min 25% B, 13 min 40% B. Eluent A 0.5% acetic acid (v/v) in water and eluent B methanol. Flow rate 1.0 ml/min.

Table 2
Accuracy, limits of detection, linearity and relative standard deviations of retention times, peak heights and areas.

	Compound	Accuracy (%)*	LOD (ng)	Linearity (ng)	Linearity R^2		RSD (%)		
					Height	Area	Time, $n=10$	Height, $n=3$	Area, $n=3$
1	Gallic acid	14	4	35–1970	0.995	0.996	1.2	11	8
2	Chlorogenic acid	7	5	70–1700	0.996	0.996	0.3	4	3
3	Vanillic acid	10	4	60–1450	0.995	0.994	0.3	2	2
4	Caffeic acid	9	2	30–2570	0.999	0.999	0.3	1	2
5	Syringic acid	8	2	30–1450	0.998	0.998	0.3	1	2
6	*p*-Coumaric acid	4	2	25–1260	0.997	0.996	0.3	3	3
7	Ferulic acid	8	3	35–1904	0.999	0.999	0.3	2	3

* Based on peak height.

Table 3
Quantitative results for herb extracts (μg/g dry weight) obtained by on-line coupled DSAE–LC.

	Compound	Basil	Oregano	Rosemary	Sage	Spearmint	Thyme
1	Gallic acid	4	3	10	6	9	6
2	Chlorogenic acid	17	176	5	172	18	30
3	Vanillic acid	16	8	119	<4	<4	12
4	Caffeic acid	153	92	154	257	285	299
5	Syringic acid	32	38	19	3	3	62
6	*p*-Coumaric acid	12	41	35	17	17	14
7	Ferulic acid	5	<2	6	48	13	<2

conditioning procedure. In addition, the trap material was changed after about 10 analyses.

3.4. Validation of quality parameters

After optimisation of the on-line DSAE–RPLC system, linearity, limits of detection (LODs) and accuracy of the system was studied. The results are summarised in Table 2. The calibration curves were constructed from peak heights at six concentration levels (6–2600 ng). The calibration curves were linear with correlation coefficients higher that 0.995. The relative standard deviation (RSD) of the retention times was highest for gallic acid (1.2% $n=10$). For all other compounds RSD values were below 0.4% ($n=10$). Likewise for the peak heights, the RSD value was highest for gallic acid, 11% ($n=3$, 197 ng), and for the other compounds below 3%. For peak areas, RSD values were slightly lower for standards (<8%), however, for real samples peak heights gave clearly better repeatability. Thus, peak heights were used in quantitative analysis. The RSD values of peak heights for real samples varied between 5% and 15%. The values are higher for gallic acid, because gallic acid is the first compound to elute and the change in the valve position and the eluent composition affect it the most.

The LODs (defined as three times the baseline noise) were below 5 ng, corresponding to 0.03 μg/ml. The accuracy for the gallic acid was 14% and for other analytes below 10%. The value was counted for the standard solution because blank samples were not available.

3.5. Analysis of herb extracts

The optimised on-line coupled DSAE–LC system was applied to the analysis of herbs. As an example, three chromatograms in Fig. 3 show the differences in off-line and on-line analyses of sage. The chromatogram in Fig. 3A is for an off-line extraction (100 mg of sage extracted and diluted to 10 ml), and that in Fig. 3B for an on-line extraction (5 mg), where the extract was collected after the trap and introduced manually to the LC system. The extract was concentrated ~200 μl. These two extracts were analysed as described in Section 2.4. Fig. 3C shows the chromatogram obtained with the on-line system. From the intensities of the peaks it is clear that the sample is substantially concentrated in the on-line system and a smaller amount of sample is sufficient for the analysis. Note that the scale in Fig. 3C differs from that in Fig. 3A and B. Note, too, that gallic and syringic acids are found with the on-line system (Fig. 3B and C, peaks 1 and 5) but not with the off-line extraction. The use of anion exchange material for trapping improves the baseline and some of the partly co-eluting peaks in the elution time 7–12 min elute in on-line system as well separated peaks.

The quantitative results are presented in Table 3. In earlier studies [46,47] we analysed the same herbs by LC–MS, LC–UV and

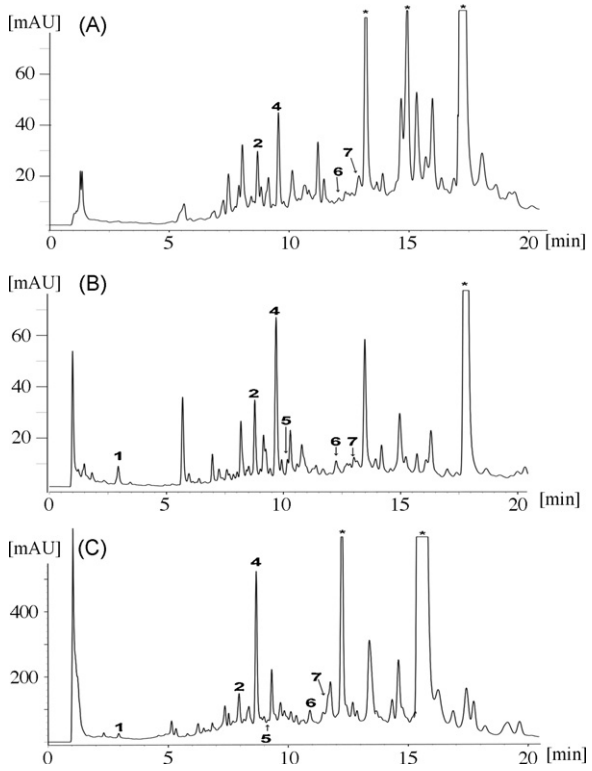

Fig. 3. Chromatograms of sage samples extracted by DSAE. (A) Extraction done off-line (100 mg, total solvent volume 10 ml), (B) extraction through the SAX trap, extract collected after the trap (5 mg, total solvent volume ~200 μl) and (C) analysis with the on-line system. Peaks: (1) gallic, (2) chlorogenic, (4) caffeic, (5) syringic, (6) *p*-coumaric and (7) ferulic acids. The peaks marked with an asterisk have been cut off. For other conditions see Section 2.

comprehensive two-dimensional liquid chromatography (LC × LC) using off-line extraction with DSAE. In general, with our present on-line extraction, the chromatogram of the extract was cleaner, target compounds were more concentrated and the sensitivity was better for most of the compounds. In addition to these compounds, rosmarinic acid is present in the samples in high concentrations (3080–9960 μg/g dry weight). Rosmarinic acid was not included to this study, because it would require a separate analysis with a clearly smaller amount of sample due to its high concentration.

Comparison of the present and earlier results showed them to be mostly at the same level. Herbs are a difficult matrix, however, and in the earlier quantitation made by LC–UV some of the analytes probably co-eluted with matrix compounds. Thus, the quantitation was not considered entirely reliable. In particular, vanillic, syringic, *p*-coumaric and ferulic acids suffered from insufficient separation from the matrix compounds. In the present study, the use of strong anion exchange material in the trap made the matrix easier to handle and reliability was increased. The separation was improved and some of the co-eluting peaks were separated. In part this explains the decreased amounts of vanillic, syringic, *p*-coumaric and ferulic acids found here.

The results of the present and earlier methods agreed best for sage. The amount of caffeic acid was less when MS detection was used. The greatest differences were found for rosemary. Compared with methods with MS detection, the concentrations of vanillic and caffeic acids were higher and the concentration of chlorogenic acid was lower.

4. Conclusions

The on-line coupled dynamic sonication-assisted extraction–liquid chromatography system that was developed provided a fast and reliable method for the quantitation of phenolic acids in herbs. The extra sample clean-up step involving trapping the analytes to strong anion exchange material decreased interference from the matrix and improved the separation, allowing UV detection. With on-line coupling the amount of sample could be smaller and the sensitivity was increased. Moreover, the whole analysis took only 30 min, including extraction, clean-up and analysis. The analysis time was about half that required for conventional off-line analysis. The on-line system can be applied for the analysis of acidic compounds in other herbal samples as well as other sample matrices. For different type of matrices, some modifications of DSAE conditions may be required.

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