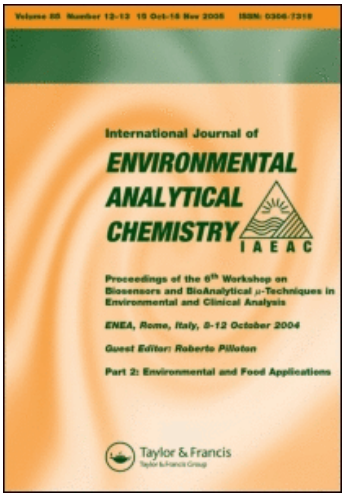

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A new HPIC-UV method to quantify phenolic acids in food and environmental samples

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A new HPIC-UV method to quantify phenolic acids in food and environmental samples

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A simple and rapid HPIC method has been developed for the separation and quantification of nine phenolic acids (PAs): gallic acid, syringic acid, vanillic acid, sinapic acid, ferulic acid, *p*-coumaric acid, protocatechuic acid, caffeic acid and ellagic acid. Separation was carried out on an Dionex Ion-Pac AS-11 (250 mm × 4 mm I.D.) column with a Dionex Ion-Pac AG-11 (50 mm × 4 mm I.D) guard column. Elution was performed using 1000 mM sodium hydroxide (NaOH) and 500 mM sodium acetate (NaOAc) in a multi step binary gradient at a flow rate of 1 mL min^{-1}. Detection was performed using diode array detector set at 230, 250, 280, and 330 nm. After optimisation of various parameters, the separation of the nine phenolic acids was achieved within 23 minutes with a good resolution. Peak areas for each compound showed good linearity ($R2 > 0.999$) in a relatively wide concentration range. Detection limits were in the range of 10–530 μg L^{-1} at a signal-to-noise ratio 3 : 1 and the amount of phenolic acids determined were in the range 0.20–10.0 ng when 20 μl of sample was injected. The developed procedure was successfully applied for the determination of these compounds in food (green tea, tomato juice and wine samples) and environmental samples (soil, surface water, organic fertiliser, organic waste) with minimal sample preparation. Beside good performances (separation, resolution, sensitivity and linearity), the new method is very fast and not expensive which makes it interesting for both scientific research and routine analysis of food and environmental samples.

Keywords: phenolic acids; ion chromatography; UV detection; environmental samples

1. Introduction

The separation and detection of phenolic acids (PAs) is a challenging and vital task owing to the importance of these compounds which are found in substantial levels in commonly consumed fruits, vegetables, herbal products and beverages [1,2]. In view of their anti-oxidative properties, they are said to be potentially protective compounds against cancer and heart disease [3–5]. The family of PAs is also widespread in plants [6]. They are mainly derived from hydroxybenzoic acids and hydroxycinnamic acids, which in turn originate naturally from the cell walls of plants. Various phenolic components and compounds are identified in soils and waters as degradation products of plant material which enter the soil through leaves, roots and bark in a solid or dissolved form [7,8]. Another source of soil

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PAs is the organic wastes commonly produced in agriculture, such as olive mill waste water [9].

Currently, liquid chromatography (LC) combined with diode array detection (DAD) is the most used analytical method for the determination of PAs [10]. A reversed-phase high performance liquid chromatography (RP-HPLC) method with DAD detection has been reported for the determination of 13 phenolic acids in traditional Chinese herbal medicines [11], and in plant-derived foods [12]. A simultaneous determination of 21 phenolic compounds along with 10 non-phenolic acids in fruit juices and drinks by HPLC-DAD was reported [13]. The separation was achieved in 80 min with aqueous sulphuric acid and methanol as eluents on a C18 stationary phase. A HPLC-DAD method for the separation of 16 phenolic acids was developed testing six columns and using several mobile phases [14]. Several HPLC-DAD methods were also reported for the determination of phenolic acids in multiple food systems including berries, fruits [15], peat extracts [16] and walnut liqueur [17]. The determination of some phenolic acids using other chromatographic techniques such as gas chromatography (GC) [18,19] GC-MS and LC-MS [20], electrospray ionisation mass spectrometry (ESI-MS) [21], capillary electrophoresis (CE) [22,23], and microchip-CE [24] have also been reported. Although these methods are considered to be precise and sensitive, run times are often excessive and the sample preparation procedure is time-consuming. By contrast, ion chromatography (IC) is said to be advantageous in several aspects which include simple operation, easily obtained inexpensive and environmentally friendly reagents, short analysis time, together with its versatility and sensitivity [25]. Generally, IC has been primarily used to quantify inorganic anions in food and environmental samples. Single column ion chromatography technique has been used to estimate inorganic anions in drainage water and soil samples [26]. More recently, HPIC methods have been developed to quantify low molecular weight organic acids (LMWOAs). Ion chromatographic analysis of organic acids and inorganic anions in grape juices and soil samples was performed [27,28]. HPIC has also been used for the determination of eight synthetic food colourants in drinks on an anion exchange analytical column with UV detection [29,30].

Alternatively, the high molecular weights and aromaticity of phenolic acids along with typically low levels in environmental samples has up to now, hindered the use of HPIC for the separation and detection of phenolic acids. However, most new HPIC systems are made of polyetheretherketone (PEEK) which enables the use of aqueous and most organic solvents. Also HPIC systems can now be coupled with UV detection. These facts allow for HPIC to be considered a promising technique for the analysis of phenolic acids. Our aim was to further develop the previously mentioned chromatography methods [27,28], developed for the determination of LMWOAs, and to apply it to detect phenolic acids in food and soil systems. Ultimately our goal was to obtain a very simple, rapid HPIC method to enable the separation and detection of phenolic acids in an environmentally friendly way. Also, with this study we wanted to demonstrate that HPIC is an alternative to other chromatography methods for the determination of PAs in food and environmental samples.

2. Experimental

2.1 *Reagents and materials*

All reagents were of HPLC grade unless otherwise specified. Gallic acid, vanillic acid, *p*-coumaric acid, protocatechuic acid, ferulic acid, syringic acid, sinapic acid, caffeic acid

and ellagic acid were purchased from Sigma (Paris, France) and used without further purification. The individual standard stock solutions (200 mg L^{-1}) were prepared in 50% (v/v) ethanol and water. Double deionised water with conductivity of 18.2 MΩ was obtained by using Milli-Q system (Millipore, Bedford, MA, USA). All the solutions and eluents were filtered through a 0.45-μm cellulose acetate membrane filter paper (Whatmann, USA) before the analysis. Also, the eluents were degassed before use. Standard stock, working solutions were stored at 40°C in the dark and used within 2 months after their preparation.

2.2 *Apparatus*

Chromatographic equipment consisted of a Dionex (Sunnyvale, CA, USA) ICS 3000 HPIC system, comprising a Dionex GP 50 gradient pump, Dionex AS 50 thermal auto sampler and a Dionex UVD 170 U UV detector. The separation was carried out on a Dionex Ion-Pac AS-11 (250 mm × 4 mm I.D.) column with a Dionex Ion-Pac AG-11 (50 mm × 4 mm I.D.) as a guard column and a Dionex Ion-Pac ATC-3 (24 mm × 9 mm I.D.) as ion trap. The column is coated with moderately hydrophobic stationary phase and is organic solvent compatible. Also, it remains stable from pH 0 to 14 and for eluents containing 0–100% organic solvents. The column and the auto sampler temperature were set to 40°C and 20°C, respectively. The column is said to be suitable for the determination of organic acids with simple gradient elution using sodium hydroxide solutions. A gradient elution was developed using a mobile phase consisting of 1000 mM NaOH (solution A), 500 mM NaOAc (solution B), and water (Solution C) as follows: (i) isocratic elution 3% A from 0 to 2 min; (ii) linear gradient from 3 to 9% A, from 2 to 9 min; (iii) linear gradient from 9 to 50% A and 0 to 2% B from 9 to 15 min; (iv) gradient from 50 to 40% A and from 2 to 60% B from 15 to 17 min; (v) gradient from 40–0% A and 60 to 3% B with the acquisition off at 0% A, 3% B from 17 to 23 min.

2.3 *Samples manipulation*

2.3.1 *Food samples*

Green tea, tomato juice and wine samples were obtained from the local supermarkets. Ten tea bags (each 2.0 g) were brewed at 90°C in 1000 ml of deionised water for 5 min and cooled to room temperature. Tomato juice was centrifuged at 13445 × g for 10 min and the supernatant was recovered and diluted twice with water. The wine sample was simply filtered and diluted five times with water. All solutions were filtered through 0.45-μm cellulose acetate filters prior to HPIC analysis.

2.3.2 *Environmental samples*

Samples from various origins were selected to reflect the diversity of environmental samples: a soil extract, a surface water, an organic fertiliser and an organic waste were examined. The soil sample was a Fulvic Hypercalcaric Cambisol (34 g kg^{-1} organic matter; pH 8.04; sand, silt, clay respectively 483, 401, 116 g kg^{-1}) collected from the top 30 cm of an agricultural experimental site of INRA Research Centre near Avignon,

France. Prior to analysis it was air dried ground and sieved (<2 mm). The soil material used contained 48.3% clay, 40.1% silt and 11.6% sand with 3.4% organic matter and had a pH of 8.04. An aliquot of soil sample (100 g) was mixed with 200 ml of Milli-Q water and placed in a mechanical shaker at a speed of 35 rpm for 1 h. The suspension was then centrifuged at a speed of 7500 rpm for 20 min. The supernatant was filtered through a 0.45 μm cellulose acetate filter and preserved in amber glass bottles at 4°C. Maple wood chips were mixed with deionised water in an amber glass jar and mechanically shaken at 200 rpm for 1 h. The solution was then centrifuged at 10000 rpm for 20 min and filtered through a 0.45 μm cellulose acetate filter paper (Whatman, USA). Water samples from the Durance River were collected close to the INRA site in Avignon and were pooled together and filtered in the laboratory. The organic liquid fertiliser (Scutts, Ecully, France) was made of a mixture of hydrolysed extracts of beet sugar and cattle manure. The sample was diluted with deionised water and filtrated as previously described. The above samples were selected as representatives of the different matrix commonly found in the environment.

3. Results and discussion

3.1 *Chromatographic conditions*

The method was built based on the use of sodium hydroxide and sodium acetate for the gradient elution protocol in order to minimise the background drift. These two eluents were selected to act both on the ionic and aromatic properties of PAs. In order to reach optimum peak resolution in short analysis time, the major factors that affect the signal, like column temperature, flow rate, injection volume and wavelength, were studied. As a result of our findings the following chromatographic conditions were selected: column temperature of 40°C, flow rate of 1 mL min^{-1}, injection volume of 20 μL. The UV detection of phenolic acids were carried out at wavelengths 230, 250, 280, 330 nm. The specific wavelengths for the phenolic acids were as follow: 250 nm for gallic (GaA), and for syringic acid (SyA), sinapic acid (SiA), ferulic acid (FeA), protocatechuic acid (PrA), ellagic acid (ElA), 280 nm for vanillic acid (VaA), 330 nm for caffeic (CaA), *p*-coumaric (*p*-CoA) and ferulic acids. Under these optimised conditions, satisfactory separation was achieved together with good resolution (Figure 1) in 23 min. In order to obtain better resolution of PAs peaks, the strength of both eluents was increased instead of the merging of peaks and the poor resolution between the PrA and CaA. The small peak near caffeic acid at 250 nm is gallic acid, the identity of which was confirmed by recording the chromatogram at 250 nm for gallic acid only. The peaks do not interfere with caffeic acid determination because its detection is carried out at 330 nm and gallic acid does not absorb at this wavelength. The separation of PAs was achieved within a short period of time (23 min). This is remarkable when compared to other separation methods, which usually take between 30–80 min [8,11,12]. The within-day repeatability ($n = 5$) and between-day precision ($n = 3$) of retention times were within 1.5% of the relative standard deviation (RSD).

The repeatability ($n = 5$) and between-day precision ($n = 3$) of peak area were within 5% RSD. The detection limits obtained with this method are comparable to those obtained with the HPLC, LC-MS and GC-MS methods [20], despite its much lower cost of analysis.

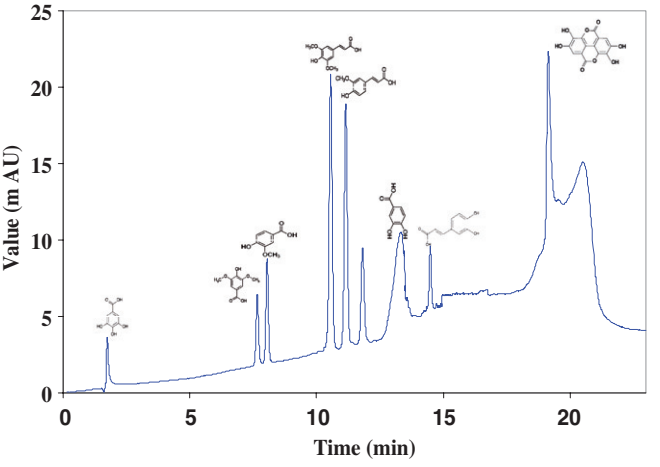

Figure 1. HPIC separation of 9 phenolic acid standards. Separation conditions are as follows: Dionex AS-11 analytical column (250 × 4 mm), AG-11 (50 × 4 mm) guard column, flow rate 1 mL min^{-1}, injection volume 20 μL, column temperature 40°C; detection wavelength 250 nm; mobile phase consists of 1000 mM NaOH, 500 mM NaOAc, water and the elution as follow: isocratic elution 3% A, 0–2 min; linear gradient from 3–9 % A, 2–9 min; linear gradient 9–50% A, 0–2% B, 9–15 min; gradient 50–40% A, 2–60% B, 15–17 min; gradient 40–0% A, 60–3% B and the acquisition off at 0% A, 3% B and 97 % C from 17–23 min. See Table 1 for peak identification.

Table 1. Peak identification, detection wavelengths, retention times and calibration results obtained for the nine phenolic acids.

S. No.	Compound	Detection wavelength (nm)	Retention time (min)	LOD (mg L^{-1})	LOQ (mg L^{-1})	R^2
1	Gallic acid (GaA)	250	1.74	0.500 (10.00)*	1.530 (30.60)	0.9997
2	Syringic acid (SyA)	280	7.79	0.010 (0.200)	0.032 (0.640)	0.9998
3	Vanillic acid (VaA)	280	8.12	0.010 (0.200)	0.030 (0.600)	0.9998
4	Sinapic acid (SiA)	280	10.59	0.015 (0.300)	0.050 (1.000)	0.9991
5	Ferulic acid (FeA)	330	11.42	0.010 (0.200)	0.025 (0.500)	0.9998
6	Coumaric acid (CoA)	330	11.75	0.020 (0.400)	0.035 (0.700)	0.9984
7	Protocatechuic acid (PrA)	280	13.43	0.250 (5.000)	0.500 (10.00)	0.9998
8	Caffeic acid (CaA)	330	14.49	0.025 (0.500)	0.055 (1.100)	0.9992
9	Ellagic acid (ElA)	280	19.18	0.020 (0.400)	0.050 (1.000)	0.9999

Note: *In brackets the amount of phenolic acids (ng) are calculated when the sample was injected using a 20 μL loop.

3.2 *Calibration curves and limit of detection*

Calibration curves were made by diluting the 9-PAs containing stock solution with Milli-Q water. Under the optimised experimental conditions, all nine phenolic acids showed good linearity ($R^2 > 0.999$) between the analyte concentration and peak area. The limit of detection (LOD) and limit of quantification (LOQ) were calculated on a signal-to-noise ratio (S/N) of 3 : 1 and 10 : 1, respectively (Table 1). Under the experimental conditions used the lowest detectable amounts for the analytes of interest based on 20 mL injection varied

Table 2. Recovery values of spiked phenolic acids obtained from soil samples.

S. No	Compound	Amount added ($mg\,L^{-1}$)	Average amount found ($mg\,L^{-1}$) ± SD	Average recovery (%)
1	Gallic acid (GaA)	5	4.82 ± 0.05	96.5
		10	9.81 ± 0.11	98.1
2	Syringic acid (SyA)	5	4.83 ± 0.11	96.6
		10	9.94 ± 0.10	99.4
3	Vanillic acid (VaA)	5	4.90 ± 0.07	98.0
		10	9.76 ± 0.14	97.6
4	Sinapic acid (SiA)	5	4.60 ± 0.05	92.0
		10	9.86 ± 0.13	98.6
5	Ferulic acid (FeA)	5	4.87 ± 0.07	97.4
		10	9.86 ± 0.12	98.6
6	Coumaric acid (CoA)	5	4.84 ± 0.06	96.8
		10	10.30 ± 0.36	103.0
7	Protocatechuic acid (PrA)	5	4.92 ± 0.08	98.4
		10	9.74 ± 0.15	97.4
8	Caffeic acid (CaA)	5	4.83 ± 0.10	96.6
		10	9.90 ± 0.11	99.0
9	Ellagic acid (ElA)	5	4.96 ± 0.16	99.2
		10	9.85 ± 0.12	98.5

from 0.20 to 10.60 ng. The accuracy of the method was tested by spiking the suitable amount of standard solution of each compound to the soil samples with known concentrations. Spiked samples were extracted by the procedure described in Section 2.3.2. The recoveries were in the range between 92 to 103% with RSD in the range of 1.1 to 3.4% (Table 2) showing good precision and accuracy for this method. The identification of the compounds in real samples was achieved by comparing the retention times of peaks as well as by addition of standards. Analytical quantification of the acids was carried out based on peak area.

3.3 *Determination of phenolic acids in food samples*

The validity of the method was tested by determination of phenolic acid content in the food samples. Amounts of phenolic acids varied significantly according to the type of food material. Figures 2a–d show the identified compounds in tea, wine and tomato juice samples; and the related concentrations are presented in Table 3. In order to get better separation results for quantification of phenolic acids in wine and tomato juice samples, we diluted these samples two and five times with water, respectively. Under optimised conditions, the quantification of each sample was run three times and the mean value and standard deviation (SD) were calculated and are presented in the Table 3. In all samples, gallic acid was detected, however it was not quantified due to interference from other peaks having very similar though not the same retention time. Although in previous papers seven phenolic acids were determined in wine samples [15,31], we only found six of them. The phenolic acid content in wine samples mainly varied with different environmental conditions like production zone, climate, harvest time and method of extraction. The amounts of syringic ($3.430\,mg\,L^{-1}$), vanillic ($1.712\,mg\,L^{-1}$), ferulic ($0.885\,mg\,L^{-1}$),

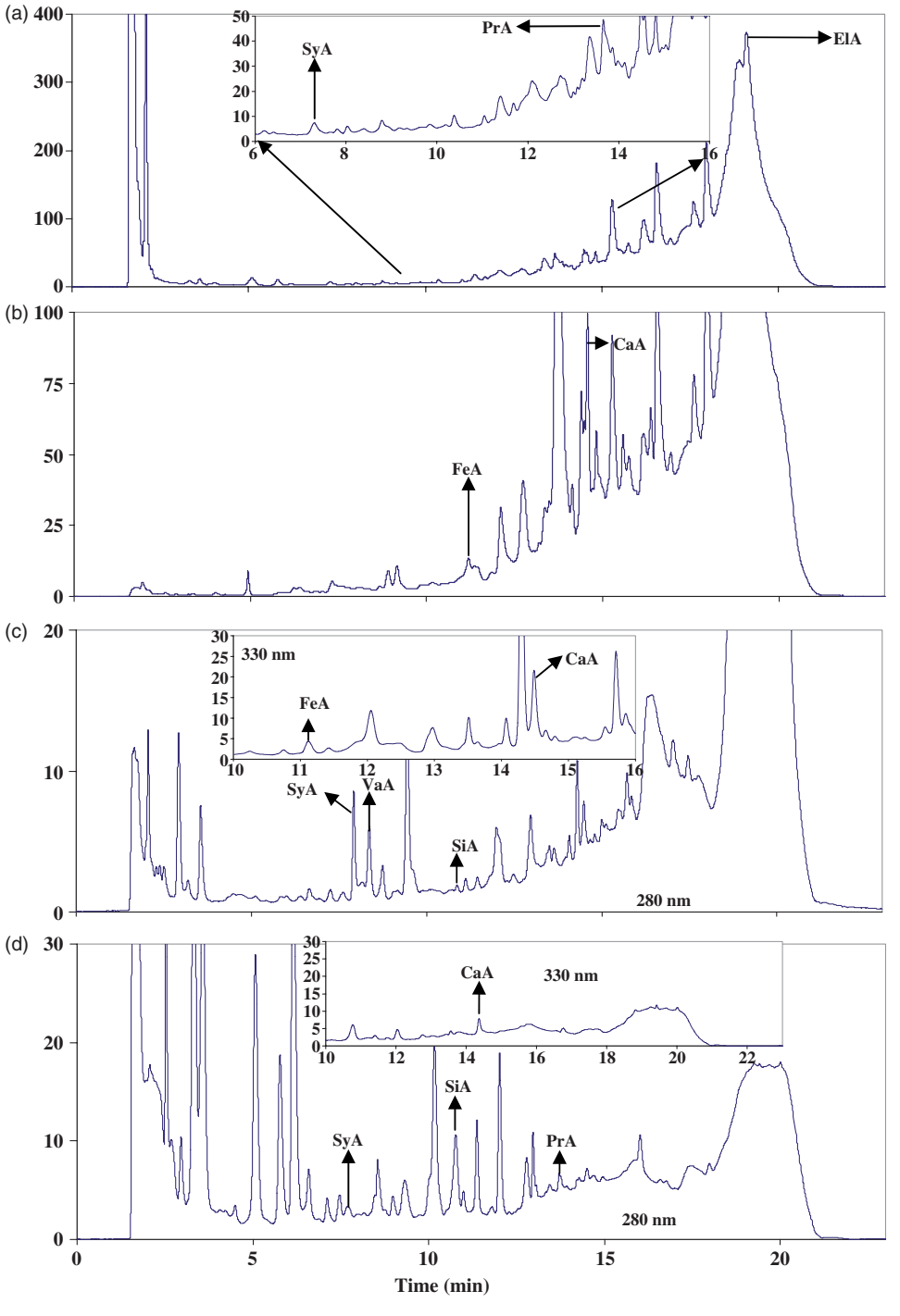

Figure 2. HPIC chromatograms obtained from food samples: tea sample, 250 nm (A), 330 nm (B); wine sample (C), and tomato juice samples (D), separation conditions are the same as for Figure 1.

Table 3. Quantities of free phenolic acids (±SD) in food samples.

Sample	GaA	SyA	VaA	SiA	FeA	CoA	PrA	CaA	ElA
Tea (mg/Kg)	NQ	8.9 ± 0.03	ND	ND	15.0 ± 0.010	ND	0.40 ± 0.03	931.6 ± 0.30	346 ± 1.04
Wine (mg L^{-1})	NQ	3.40 ± 0.02	1.71 ± 0.016	0.87 ± 0.006	0.88 ± 0.013	ND	ND	6.0 ± 0.064	ND
Tomato juice (mg L^{-1})	NQ	0.35 ± 0.01	ND	12.6 ± 0.033	ND	ND	0.60 ± 0.04	5.51 ± 0.05	ND

Notes: GaA: Gallic acid; SyA: Syringic acid; VaA: Vanillic acid; SiA: Sinapic acid; FeA: Ferulic acid; CoA: Coumaric acid; PrA: Protocateohuic acid; CaA: Caffeic acid; ElA: Ellagic acid.
ND: Not detectable.
NQ: Not quantifiable.

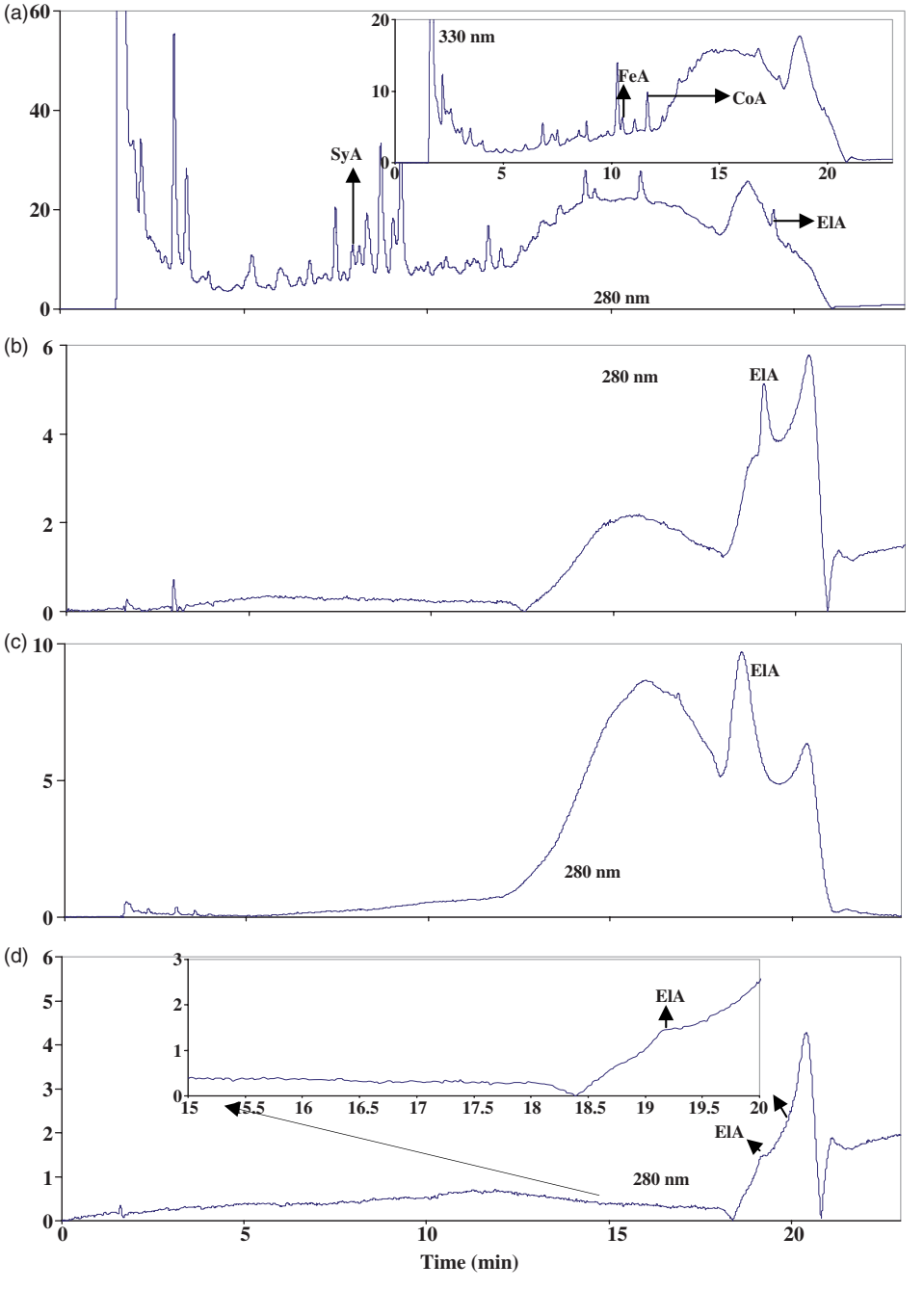

Figure 3. HPIC chromatograms obtained from environmental samples; organic liquid fertiliser (A), maple wood chips extract (B), soil extract (C) and river water (D). Separation conditions are the same as in Figure 1.

Table 4. Quantities of free phenolic acids (±SD) in environmental samples.

Sample	GaA	SyA	VaA	SiA	FeA	CoA	PrA	CaA	ElA
Organic fertiliser ($mg\,L^{-1}$)	ND	0.57 ± 0.051	ND	ND	0.10 ± 0.019	0.25 ± 0.026	ND	ND	0.36 ± 0.10
Maple wood chips (mg/100 g)	ND	ND	ND	ND	ND	ND	ND	ND	1.61 ± 0.51
Soil extract (mg/100 g)	ND	ND	ND	ND	ND	ND	ND	ND	1.90 ± 0.21
River water sample ($mg\,L^{-1}$)	ND	ND	ND	ND	ND	ND	ND	ND	0.065 ± 0.03

Notes: GaA: Gallic acid; SyA: Syringic acid; VaA: Vanillic acid; SiA: Sinapic acid; FeA: Ferulic acid; CoA: Coumaric acid; PrA: Protocateohuic acid; CaA: Caffeic acid; ElA: Ellagic acid. ND: Not detectable.

and caffeic ($6.0\,mg\,L^{-1}$) acids found in the wine sample are in close agreement with literature reported values [15,31]. With our method we also detected low amounts of sinapic acid ($0.87\,mg\,L^{-1}$) in wine but we did not detect coumaric acid. As expected in the tea sample we found high amounts of caffeic acid ($931\,mg\,kg^{-1}$), ellagic acid ($346\,mg\,kg^{-1}$) and small quantities of syringic acid ($8.9\,mg\,kg^{-1}$) and ferulic acid ($15.0\,mg\,kg^{-1}$). However, these amounts were higher than literature reported values [15] probably due to the extraction procedures used. The amounts of sinapic acid ($12.6\,mg\,L^{-1}$) and caffeic acid ($5.51\,mg\,L^{-1}$), we detected were higher in comparison to other phenolic acids in juice samples.

3.4 *Determination of phenolic acids in environmental samples*

The applicability of the method to environmental samples was evaluated by determining the phenolic acid contents in river water, organic fertiliser and aqueous extracts of soil and wood chips. All samples were analysed three times in order to obtain accurate results, and estimated accurately standard deviation was calculated. Separation of PAs in these complex samples was satisfactory (Figure 3a–d). In the soil extract sample (Figure 3d) the small variation in the ellagic acid retention time is due to matrix interferences. In the organic liquid fertiliser the amount of the four detected phenolic acids (syringic, ferulic, *p*-coumaric, and ellagic acids) varied from $0.10\,mg\,L^{-1}$ to $0.57\,mg\,L^{-1}$ (Table 4). In all the environmental samples and in the food sample (tea) we found ellagic acid, higher molecular weight PA. This corresponds to more mature (double aromatic ring) organic material than the fresh samples (i.e. organic fertiliser). This may be due to the fact that ellagic acid is more resistant to biodegradation (two aromatic rings) and is not easily leached by rain and other environmental conditions. Also, ellagic acid was found in higher amounts in the soil samples than in the wood chips. The amount of ellagic acid ($0.065\,mg\,L^{-1}$) found in the river water sample was much lower than that of the soil extract. This is in agreement with the much lower organic matter content of water samples compared to surface soils, and with the low aqueous solubility of ellagic acid in natural conditions.

4. Conclusions

This newly developed HPIC method proved to be suitable for the determination of phenolic acids in food and environmental samples. This method allows the separation of

PAs in a short separation time, and requires simple, inexpensive and environmentally friendly reagents. The detection limits are comparable with the LC-MS and GC-MS methods. No preliminary extraction is needed and no organic solvents are used in this method. The much lower cost of the HPIC instrumentation with UV detection when compared with instruments like LC, GC with MS detection is noteworthy.

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