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Multicommutated stepwise injection determination of ascorbic acid in medicinal plants and food samples by capillary zone electrophoresis ultraviolet detection

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ABSTRACT

An automation of the extraction of analytes from solid samples into the aqueous phase based on multicommutated stepwise injection analysis concept has been suggested. The feasibility of the approach has been demonstrated by determination of ascorbic acid as model analyte. The method includes automated extraction of ascorbic acid from solid sample into borate buffer solution pH 8 in mixing chamber during vigorous mixing by nitrogen stream, and subsequent detection by capillary zone electrophoresis at 254 nm. The method has a linear range of 0.1–5.0 mg g^{-1} for ascorbic acid with the LOD of 0.03 mg g^{-1}. The sample throughput was 7 h^{-1}. This method was applied for determination of ascorbic acid in various medicinal plants and food samples.

1. Introduction

Direct analysis of solid samples is difficult since the most of analytical techniques require the samples to be in the liquid phase. Therefore, the analytical procedure usually includes sample pre-treatment steps focused on the dissolution of sample or extraction of the analyte into liquid phase. These steps are tedious and laborious since they are often manually performed. Therefore currently, automation of solid sample pre-treatment is a challenging task for analytical chemists [1,2]. Automation and miniaturization go hand in hand with the requirements of green analytical chemistry [3–7]. From this viewpoint, the flow methods have great potential.

Various flow injection (FIA) [8–10] and sequential injection (SIA) methods [11–16] have been reported for an automation of the extraction of the analytes from solid samples. For example, FIA and SIA systems allow automation of dissolution testing of solid pharmaceuticals [9,10,13,16], on-line fractionation and automatic determination of inorganic phosphorus in environmental solid samples [17,18], on-line electrolytic dissolution of alloys [19,20]. FIA, which exploits the continuous flow of reagents, offers a high sample throughput; however, it consumes relatively large volumes of reagents and produces a great amount of waste. In contrast, SIA, which can be considered as the second generation of FIA, operates with only microliter volumes of both samples and reagents. In general, in SIA the sample and reagent zones are aspirated into a holding coil and forwarded to the detector. The reaction product is formed as a consequence of dispersion of the zones. Various FIA [21–23] and SIA [24,25] methods have been reported for the determination of ascorbic acid in a fruit juices, pharmaceuticals and food products. Some of them are represented in Table 1. However, to the best of our knowledge no reports have been devoted to the fully automated determination of ascorbic acid in plants.

The flow-batch analysis (FB) [27], stepwise injection analysis (SWIA) [26,28–30] and multicommutated stepwise injection analysis (MCSWIA) [31] are one of the universal solutions for the automation of analytical reactions in which the equilibration in the reaction is reached but dispersion of the reactants is prevented. The MCSWIA and FB manifolds include mixing chambers. In the FB manifold, the solutions are mixed up in the mixing chamber by a magnetic stirrer liner, and in the MCSWIA manifold it is done by a gas stream (air or inert gas). Including into the FB manifold magnetic stirrer significantly

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Table 1
Comparison of the suggested method with previously reported flow methods for determination of ascorbic acid.

Technique	Flow method	Extraction medium	Automated extraction or dissolution	Centrifugation	Throughput (per h)	Sample	Linear range	LOD	Reference
UV–vis	FIA	–	No	3000 × g For 20 min	40	Rat's tissues	0.5–20 ppm	0.2 ppm	[21]
UV–vis	FIA	0.1 M acetic acid	No	–	180	Pharmaceuticals	0.08–10 μM	24 nM	[35]
UV–vis	FIA	Deionized water	No	–	30	Soft drinks, preserved fruit juices and pharmaceuticals	1–25 μg mL^{-1}	0.5 μg mL^{-1}	[22]
Chemiluminescence	FIA	H_2O_2, KIO_4, EDTA	No			Vitamin C tablets	1.0×10^{-7}–1.0×10^{-5} M	6.0×10^{-8} M	[39]
Conductometry	FIA	Water	No	–	90	Vitamin C tablets	Up to 8000 ppm	–	[38]
CV	FIA	–	No	–	–	Orange juice	0.5–100 μM	28.7 nM	[36]
UV–vis	SIA	Deionized water	No	–	60	Vitamin C tablets	Up to 1200 mg L^{-1}	–	[24]
UV–vis	SIA	–	No	3500 × g for 4 min	15	Pharmaceuticals and fruit juices	6×10^{-6}–5×10^{-4} M	2×10^{-6} M	[25]
UV–vis	SIA	Distilled water	No	–		Pharmaceuticals and food samples	Up to 120 μg mL^{-1}	–	[37]
UV–vis	SWIA	Water	No	–	12	Pharmaceuticals	0.05–0.3 g L^{-1}	0.02 g L^{-1}	[26]
CE-UV	MCSWIA	Borate buffer	Yes	–	7	Medicinal plants and food samples	0.1–5.0 mg g^{-1}	0.03 mg g^{-1}	This work

CV, cyclic voltammetry; AA, ascorbic acid.

complicates its design. The combination of the mixing chamber with the path length flow cell of spectrophotometric detector limits the variation of the sample volume and the optical path length, as well as the use of several detectors in the flow manifold. Commutation of two solenoid valves, peristaltic pump and several mixing chambers to the MCSWIA setup provides the possibility to carry out the automation of the analyte extraction from the solid samples and it subsequent detection by capillary zone electrophoresis.

Based on the above, the aim of this work was to develop an automated procedure based on MCSWIA concept for the automation of the solid sample analysis. To demonstrate the efficiency of the proposed approach, the determination of ascorbic acid in medicinal plants and food samples by capillary zone electrophoresis ultraviolet detection was performed.

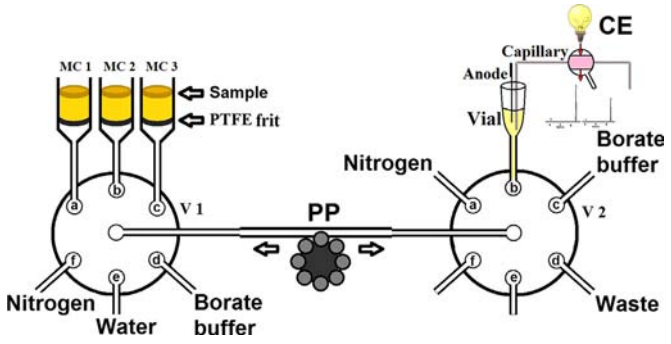

Fig. 1. The suggested MCSWIA setup for determination of ascorbic acid in medicinal plants and food samples by capillary zone electrophoresis ultraviolet detection. MC, mixing chamber; PP, peristaltic pump; V1, valve 1; V2, valve 2; and CE, capillary electrophoresis.

2. Experimental

2.1. Reagents and solutions

Analytical grade chemicals and Milli-Q water (Millipore, MA, USA; 18 MΩ cm^{-1}) were used throughout the work. Ascorbic acid, EDTA, HCl, NaOH, and sodium tetraborate were purchased from Sigma-Aldrich (St. Louis, MO, USA). The 0.28 mmol L^{-1} stock solution of ascorbic acid was prepared daily by dissolving it in the borate buffer solution, and stored in a cool dark place. The working solutions of ascorbic acid in the range from 0.01 to 0.28 mmol L^{-1} were prepared by dilution of stock solution with borate buffer solution prior to use.

The borate buffer solution with pH 8 was prepared by mixing 50 mL of 0.05 mol L^{-1} sodium tetraborate, 25 mL of 0.2 mol L^{-1} HCl and 25 mL of 0.4 mol L^{-1} EDTA. EDTA was added in the borate buffer to bind metal ions present in the obtained extracts and to avoid oxidation of ascorbic acid. The pH was adjusted to 8 by addition of 1 mol L^{-1} NaOH solution. The borate buffer solution was used as the extraction medium. The 0.35 mmol L^{-1} solution of sodium 2,6-dichlorophenol-indophenolate (2,6-DPIP) was prepared by dissolving appropriate amount of reagent in water.

2.2. Apparatus

2.2.1. MCSWIA setup

The multicommutated stepwise injection setup (Fig. 1) is based on a PIAKON-30-1 flow analyzer (Rosanalit, Saint Petersburg, Russia). The suggested MCSWIA setup consist of two solenoid valves (Cole-Parmer Inc., USA), peristaltic pump MasterFlex L/S (Cole-Parmer Inc., USA) ensuring the reverse flow and operating in flow rate range from 0.5 to 5 mL min^{-1}, three homemade disposable mixing chambers (MCs), and communication tubes (PTFE, 0.5 mm i.d.).

Valve 1 is connected with MCs; the number of MCs is limited only by free of valve channels. The second valve is used for sequential injection of borate buffer solution and gas and commutation of the system with CE unit. The automatic setup was operated automatically by means of a computer with an in-house developed software.

The manifold is at-line connected to CE unit Capel 103 PT (Lumex, Saint-Petersburg, Russia) which is comprised of a ± 20 kV high-voltage supply, variable-wavelength detector and a 75 μm i.d. fused-silica capillary tube with 60 cm total length. The capillary was conditioned daily before use for 30 min with 0.1 mol L^{-1} NaOH and 10 min with water.

For efficient extraction of analytes from solid samples into aqueous phase, the homemade mixing chambers (MCs) were constructed from polypropylene syringe barrels (50 mm in height and 5 mm i.d.) with porous PTFE frit pressed into a funnel-shaped bottom. PTFE frit serves for formation a large number of nitrogen bubbles during the mixing of the sample, and also for filtering of the extract before being introduced into the MCSWIA setup. To obtain the PTFE frit, a PTFE powder (fluoroplast-4) was sintered at 380 °C for 3 h in metal form ($20 \times 50 \times 50$ mm^3), and then a PTFE plate was crushed in a blender. Various fractions of PTFE powder were selected with sieves, which were re-sintered in metal form with holes (diameter – 5 mm, height – 7 mm) at 380 °C for 1.5 h. Effect of the fractions of PTFE powder on the reproducibility of the analytical signal has been investigated. Based on the obtained results a PTFE frit, obtained from fraction 0.45–0.9 mm, was chosen for further experiments.

2.2.2. Batch experiments

A SHIMADZU UVmini-1240 spectrophotometer (Shimadzu Scientific Instruments, Japan) equipped with matched quartz cell with (l=10 mm) was employed for batch spectrophotometric measurements. A I-500 potentiostat (Akvilon, Russia) with glass and silver chloride electrodes was used for measuring the pH.

2.3. Real sample preparation

The medicinal plants *Ribes nigrum* (leaves) and *Sorbus aucuparia* (fruits), sweet pepper, kiwi, apple, and applesauce were purchased in a local market in Saint Petersburg (Russia).

The medicinal plants were stored at room temperature in the dark and under humidity – proof conditions. Before analysis, the plant samples were kept in a hot-air oven at 80 °C for 1 h to obtain a dry mass, which was subsequently milled. Food samples previously refrigerated for 1 day at 6 °C were milled. The plants and food samples were immediately analyzed according to the developed procedure described in Section 2.4 and reference method (Section 2.5).

2.4. Procedure for the MCSWIA-CE-UV determination

Initially, 0.01 g of sample was accurately weighed and placed into each disposable MC. Each MC was connected to the solenoid valve 1. Afterwards, 1 mL of borate buffer solution with pH 8 was delivered through the valve 1 (port a) into MC1 by movement of the peristaltic pump. The extraction of ascorbic acid from the plants and food samples into the borate buffer solution took place under mixing at 25 °C by a nitrogen flow (valve 2, port a) at a rate of 5 mL min^{-1} for 7 min. Afterwards, 0.2 mL of aqueous extract from the MC1, 0.2 mL of borate buffer (valve 1, port d) and a nitrogen flow (valve 1, port f) were sequentially delivered by movement of the peristaltic pump into the polypropylene vial (valve 2, port b), from which electrokinetic injection was performed. The vial of a CE unit was connected to the valve 2 by PTFE tube in the bottom part. Separation was carried out in the borate buffer, at +20 kV, 20 °C and normal polarity. The detection wavelength was 254 nm.

Simultaneously with this detection step, the extraction in the second MC2 was carried out according to the above-described sequences after cleaning of the tubes with water (valve 1, port e) to prevent any cross-contamination. Then the procedure was repeated for the third sample. The MCs were replaced after each determination by a new set. The key steps of the entire procedure are displayed in Table 2.

2.5. Procedure for the spectrophotometric determination

The 0.02 g of the sample was placed into a polypropylene conical tube with a volume of 1.5 mL and 1 mL of water was added. The tube was sealed and heated in an ultrasonic bath at 40 °C for 15 min. The solution was then centrifuged at 5000 rpm for 5 min. The aqueous phase was separated and then diluted by water for required number of times. To the 0.5 mL aliquot obtained by this way, 0.1 mL of 0.01 mol L^{-1} HCl and 0.5 mL of 0.35 mmol L^{-1} 2,6-DPIP were added, and the absorbance was measured at 515 nm wavelength. A blank solution was prepared in the same way but without the addition of 2,6-DPIP reagent [32].

3. Results and discussion

3.1. Preliminary investigations

The background electrolyte (BGE) affects the migration time and the separation of analytes. Since ascorbic acid is weak acid, a weak basic buffer system is preferred to have a suitable migration time. Considering that tetraborate ion and the compound containing hydroxide groups can form a chelate bond which can increase the negative charge and the resolution of the determination [33]. Ascorbic acid was detected in 6 min with a stable baseline in borate buffer at pH 8, and there was also good peak sharpness and symmetry. Therefore, sodium tetraborate was chosen as the BGE in this experiment. The effect of electrolyte concentration was also studied, and the best results were obtained at 25 mmol L^{-1} of borate buffer, which was chosen for further experiments.

The effect of injection time on analytical signal has been investigated by injection of 0.05 mmol L^{-1} AA standard solution in the CE unit for 2, 4, 6, 8 and 10 s (0.5 psi). When the injection time was greater than 4 s, the sensitivity did not change significantly while the peak shapes became inferior because of the band broadening. As a result, an injection time of 4 s was selected.

3.2. Sample pretreatment optimization

The variables which can affect the extraction efficiency of ascorbic acid from plants and food samples, like sample weight, extraction time, volume of extractant, were studied using univariate optimization method, when only one variable is changed and all others are kept constant. The extraction efficiencies were calculated based on the results of two consecutive MCSWIA extractions of same sample and CE-UV detection. The extraction was carried out at 25 °C, since the oxidation rate of ascorbic acid increases with the temperature increase.

When studying the effect of sample weight, a volume of extractant and extraction time were adjusted at 1 mL and 10 min, respectively. The weight of sweet pepper, *Ribes nigrum* leaves, and applesauce in the range from 0.005 to 0.02 g were placed in MCs and subjected to the analysis according to the developed procedure described in Section 2.4. Based on the obtained results (Fig. 2A), the most suitable value at 0.01 g was chosen for further experiments.

When studying the influence of extractant volume, the sample weight and extraction time were set at 0.01 g and 10 min, respectively. The volume of extractant volume was varied from 0.5 to 2 mL. While during the study of the effect of extraction time, the sample weight and extractant volume were adjusted at 0.01 g and 1 mL, respectively. Whereas the stirring time varied from 3 to 30 min. Based on the obtained results (Fig. 2B and C), a volume of 1 mL of extractant and 7 min of the extraction time were chosen as the most appropriate for further experiments. These conclusions were made to meet the requirements of green chemistry in reducing the consumption of time, reagents and samples.

Table 2
The sequence of the steps in the optimized control program for the MCSWIA-CE-UV determination of ascorbic acid in medicinal plants and food samples.

Key step	Time (s)	Volume (ml)	Valve 1 position	Valve 2 position	Direction of the flow*	Measurement of the signal**	Operation
1	20	1	a	c	−1	Off	Filling of MC1 with extractant
2	420	–	a	a	−1	Off	Stirring of the extract with nitrogen
3	5	0.2	a	b	1	Off	Supply of the extract into the vial
4	5	0.2	d	b	1	Off	Supply of buffer solution into the vial
5	20	1	f	b	1	Off	Stirring of the mixture into the vial with nitrogen
6	8	0.5	e	d	1	On	Washing of the tubes/electrophoretic separation
7	15	–	f	d	1	On	Conditioning of the tubes/electrophoretic separation
8	20	1	b	c	−1	On	Filling of MC2 with extractant/electrophoretic separation
9	420	–	b	a	−1	On	Stirring of the extract with nitrogen/electrophoretic separation
10	5	–	a	b	−1	Off	Waste of extract from the vial
11	8	0.5	e	d	1	Off	Washing of the tubes and vial
12	15	–	f	b	1	Off	Conditioning of the tubes
13	5	–	a	b	−1	Off	Waste of solution from the vial
	5		f	d	1		
14	5	0.2	b	b	1	Off	Filling of the vial with extract and repetition of steps

* −1, 0, +1 Refer to the clockwise rotation, stopping, and counterclockwise rotation of the pump, respectively.
** On, off refer to measurement of the signal, and no measurement of the signal, respectively.

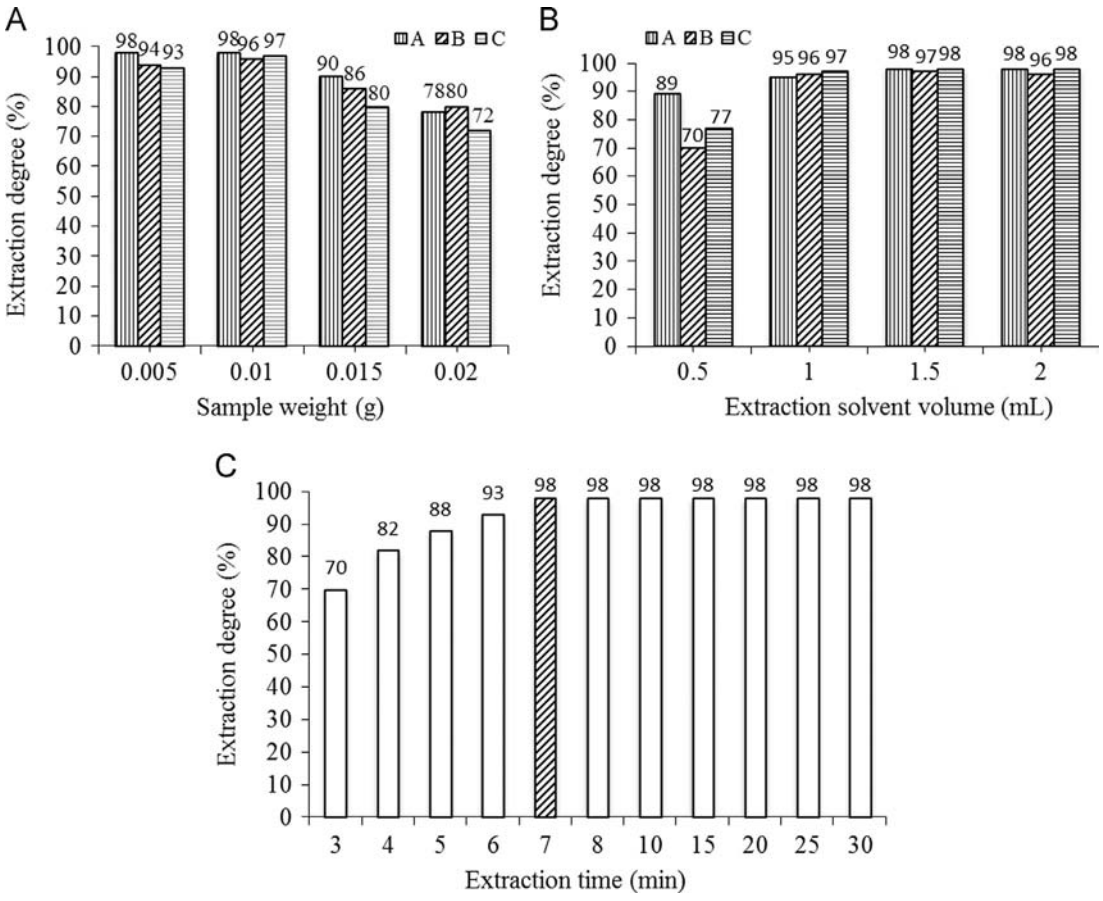

Fig. 2. The effect of (A) sample weight. Nitrogen flow rate, 5 mL min^{-1}; volume of extractant, 1 mL; and mixing time, 10 min. A, sweet pepper; B, *Ribes nigrum* leaves; C, applesauce. (B) Volume of extractant nitrogen flow rate, 5 mL min^{-1}; sample weight, 0.01 g; mixing time, 10 min. A, sweet pepper; B, *Ribes nigrum* leaves; C, applesauce. (C) Exrtaction time nitrogen flow rate, 5 mL min^{-1}; volume of extractant, 1 mL; and sample weight, 0.01 g.

3.3. Interference study

The effect of potentially interfering substances encountered in the tested medicinal plants was investigated using model samples. Model samples which contain 0.05 mmol L^{-1} of ascorbic acid and various amount of the interfering substance were subjected to the analysis according to the suggested MCSWIA-CE-UV procedure. Adequate recovery was taken to be an analytical response with a signal deviation up to ±5%. Interferences were not found for tartaric and folic acids at up to 50-fold excess, for citric, malic, malonic, oxalic, succinic and sorbic acids at up to 100-fold excess, since the peak areas and the migration times remain unchanged. The ratio of ascorbic acid and interferents in real samples are usually less; it can be assumed that the developed procedure

Table 3
Experimental conditions and metrological characteristics of the developed MCSWIA-CE-UV procedure for determination of ascorbic acid.

Parameter	Optimal value
Tetraborate ion concentration in the buffer solution (mmol L^{-1})	25
pH (borate buffer)	8
EDTA concentration (mol L^{-1})	0.1
Applied voltage (kV)	20
Temperature (°C)	+20
Extraction solvent volume (mL)	1
Sample weight (g)	0.01
Extraction time (min)	7
Linear range (mg g^{-1})	0.1–5.0
Detection limit (mg g^{-1})	0.03
Sample throughput (h^{-1})	7

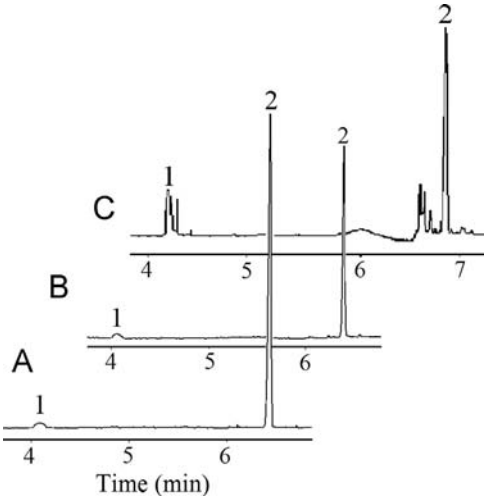

Fig. 3. The electrophoregrams (A) sweet pepper; (B) kiwi; (C) *Sorbus aucuparia* fruits (1, acetone; 2, AA). tetraborate ion concentration, 25 mmol L^{-1}, pH 8; injection time, 4 s; applied voltage, +20 kV; temperature, +20 °C; and detection wavelength, 254 nm.

Table 4
Determination of ascorbic acid in medicinal plants and food samples ($n=5$)[a].

Sample	The found content (mg g^{-1})	
	MCSWIA	Reference method [32]
Ribes nigrum leaves	2.00 ± 0.10	2.20 ± 0.20
Sorbus aucuparia fruits	1.20 ± 0.05	1.40 ± 0.10
Kiwi	1.80 ± 0.01	1.80 ± 0.20
Apple	0.60 ± 0.03	0.60 ± 0.10
Sweet pepper	2.50 ± 0.10	2.70 ± 0.20
Applesauce	1.30 ± 0.07	1.40 ± 0.15

[a] $\bar{x} \pm \frac{ts}{\sqrt{n}}$ ($t=2.776$, $P=0.95$); t, Student coefficient for $n-1$ degrees of freedom.

should be applicable for the determination of ascorbic acid in real plant samples [34]. Interferences were not found for sugars including saccharose and glucose at much greater ratios [interferent]/[ascorbic acid], than those found commonly in medicinal plants. Also the effect of potentially interfering ions, which are the catalysts for ascorbic acid oxidation, especially inorganic ions, was investigated. In case of determination of ascorbic acid, Sn(II) interfered as low as 1-fold excess, Fe(II) – at 2-fold excess, Cu(II), Ni(II), Mn(II) – at 3-fold excess. It is possible to eliminate their interfering effect by the introduction of EDTA as a masking agent in a concentration 0.1 mol L^{-1}.

3.4. Analytical performance

The calibration plot was constructed using a series of working solutions containing the various amounts of ascorbic acid in the range of 0.01–0.28 mmol L^{-1}. Under the optimum experimental conditions, summarized in Table 3, the linearity between the concentration of ascorbic acid, expressed as mg g^{-1} content in medicinal plants and food samples, and the peak area in the range of 0.1–5.0 mg g^{-1} was obtained. The regression equation was $Y=3.079C-0.029$, where Y is the peak area and C is the content of ascorbic acid in plants and food samples in mg g^{-1}, and the correlation coefficient (r^2) was 0.999. The limit of detection (LOD), calculated as three-times the standard deviation (3 s) of the blank test ($n=10$) was assessed as 0.03 mg g^{-1}. A comparison of the proposed method with different flow approaches previously published in the literature for the determination of ascorbic acid is given in Table 1. The suggested procedure showed satisfactory repeatability of the analytical response by evaluation of the relative standard deviation (RSD) from 10 replicate measurements of the content of ascorbic acid in real samples, with a value from 5% to 7%. The system throughput, assessed as the sampling frequency, was found to be 7 h^{-1}.

3.5. Analytical application

To demonstrate the feasibility of the suggested procedure, the determination of ascorbic acid in various medicinal plants and food samples were carried out. The sample was pre-treated prior to analysis according to procedure described in Section 2.3. Acetone was used as the internal standard, and the electropherograms are depicted (Fig. 3). The obtained results by developed MCSWIA-CE-UV procedure (Table 4) show no significant differences between the ascorbic acid concentration obtained by the suggested method and those obtained by reference spectrophotometric method.

4. Conclusions

An automated procedure for analysis of the solid samples has been developed. The manifold is based on multicommutated stepwise injection analysis concept. The method includes automated extraction of the analyte into an aqueous phase in the mixing chamber and it subsequent detection by capillary zone electrophoresis. The vigorous stirring of the solution is ensured by passing of nitrogen stream through the PTFE frit. The applicability of the method was demonstrated, as the analysis of medicinal plants and food samples and the obtained results were comparable with those of the reference method. Ascorbic acid was used as model analyte because it is an important micronutrient and a major water-soluble antioxidant within the body.

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