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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.

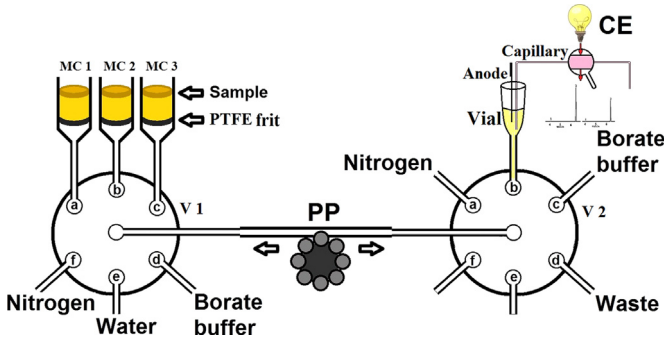

Fig. 1. The suggested MCSWIA setup for determination of ascorbic acid in medicinal plants and food samples by capillary zone electrophoresis ultraviolet detection. MC, mixing chamber; PP, peristaltic pump; V1, valve 1; V2, valve 2; and CE, capillary electrophoresis.

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.