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Application of solid phase extraction with the use of silica modified with polyaniline film for pretreatment of samples from plant material before HPLC determination of triterpenic acids

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ABSTRACT

The new sorbent based on silica gel coated with a film of polyaniline (Si-PANI) was obtained in a process of *in situ* polymerization directly on carrier particles and its potential application for pretreatment of plant material samples with the use of solid phase extraction (SPE) was investigated. Parameters such as cartridge conditioning, the volume and concentration of the sample, the type and volume of the elution solvent were optimized and compared with parameters obtained for RP-18 and aminopropyl silica cartridges. The high recovery values above 97% after the SPE procedure with the use of Si-PANI cartridges proves their utility for analysis of triterpenic acids.

The sorbent tested was successfully used for clean-up of extracts from *Salvia officinalis* L., *Syzygium aromaticum* (L.) Merrill., and *Origanum vulgare* L. prior to HPLC-DAD determination of oleanolic, ursolic and betulinic acid.

The efficiency of sample purification was verified by monitoring of chromatograms in the region between 190 nm and 400 nm during the gradient elution. The fewest components or their lowest concentrations were observed for all the investigated samples after the SPE procedures.

1. Introduction

Analysis of bioactive components requires isolation thereof from investigated material. Solvent extraction methods, both classic: maceration (ME); Soxhlet (SE); heat reflux extraction (HRE) and assisted: ultrasonic extraction (UE); microwave-assisted extraction (MAE); or accelerated solvent extraction (ASE) are commonly used for this purpose in the case of plants and herbal preparations [1].

Frequently, biologically active compounds occur in natural products in trace amounts. Moreover, the complex matrix can cause reduction of the HPLC column longevity and decrease the sensitivity of determination, therefore sample pretreatment before the analysis is a further, necessary step of most analytical procedures. Liquid–liquid extraction (LLE) and solid phase extraction (SPE) are usually used for sample preparation; however, LLE is not a good technique for isolation of a large group of polar components. These compounds are partially soluble in water and this yields unsatisfactory recovery values. SPE is recommended owing to its numerous advantages such as low consumption of organic solvents, selectivity, flexibility, simplicity, lack of emulsion formation, reproducibility, and automation [2–4]. It could also be used for direct isolation of target components without solvent-based extraction (MSPD—matrix solid phase dispersion).

The bulk of commercially available SPE sorbents is based on modification of silica [5,6]; however, their main drawbacks include the cost of disposable cartridges and a narrow working pH range from 2 to 8 [7]. Recently, polymer-based SPE cartridges, mainly copolymers of styrene and divinylbenzene, have gained increasing popularity since they are designed to extract a wide spectrum of lipophilic, hydrophilic, acidic, basic, and neutral compounds [1,7–10]. Mixed-mode sorbents containing ion-exchange and alkyl groups are also frequently used in many laboratories. While employing the disposable column is a common practice, new materials for solid phase extraction are still being elaborated and developed [4,11,12].

Conductive polymers (CPs) are a subject of interest for many researchers due to their multiple applications [13–15]. Their physicochemical properties such as hydrophobicity, π-conjugated structure, polar groups, and ion exchange ability suggest the possibilities of application thereof in separation techniques [16–20]. Recently, among CPs special attention is paid to polyaniline (PANI) due to its unique electrical, optical, and chemical properties, high stability

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against temperature and pH variation, easy preparation, and affordability [21–23]. There are some literature data about application of pure polyaniline in the SPE technique; *e.g.*, for extraction of pesticides from aquatic media [24] or fluoroquinolones from honey [25].

In our earlier studies, the new stationary phase based on silica with polyaniline film (Si-PANI) was obtained by *in situ* polymerization of aniline directly on the carrier particles, and it was applied for ion analysis in non-suppressed ion chromatography [26,27]. The aim of the present work was to test the potential ability of the Si-PANI sorbent for clean-up of plant samples by the SPE technique. Triterpenic acids were selected for the research due to their pharmacological importance and widespread presence in the plant kingdom. There are numerous publications about their anti-inflammatory, hepatoprotective, antitumor, and antimicrobial properties [28–30]. These compounds are relatively non-toxic and have been used in cosmetics, health products, and traditional medicine.

2. Experimental

2.1. Materials and reagents

Betulinic (BA) ($\geq$ 98%), oleanolic (OA) ($\geq$ 97%), and ursolic (UA) ($\geq$ 98.5%, Fluka) acid standards were purchased from Sigma-Aldrich (St. Louis, MO, USA). Aniline (for analysis EMSURE), ammonium peroxydisulphate (extra pure), ammonia solution 25% (suprapur), ortho-phosphoric acid 85% (suprapur), and solvents: methanol; acetonitrile (gradient grade for liquid chromatography); acetone; ethyl acetate (grade for liquid chromatography); and diisopropyl ether (for analysis EMSURE) were from Merck (Darmstadt, Germany). Water was deionized and purified by ULTRAPURE Milipore Direct-Q® 3UV-R (Merck). Silica gel Lichrosorb 60 Si (Merck) was used for preparation of the stationary phase. LiChrolut RP-18e 200 mg, 3 mL (Merck) and Speedisk Amino 200 mg, 3 mL (J.T. Baker, Phillipsburg, NY, USA) SPE cartridges were also used.

2.2. Synthesis of the Si-PANI stationary phase and preparation of SPE columns

The stationary phase was prepared by *in situ* polymerization of aniline at a temperature of 0–2 °C, directly on silica particles with the use of ammonium peroxydisulphate as an oxidation agent. The procedure of polyaniline deposition was described in detail in our earlier publication [26].

The quality of covering with the polyaniline film immediately after synthesis and after the series of 10 experiments was confirmed by Raman analysis using a Thermo Scientific DXR confocal Raman Microscope equipped with the Omnic 8 software from Thermo Fisher Scientific USA (Madison, Wisconsin). The excitation laser wavelength was 780 nm. Filters of 780 nm and 400 lines/mm grating were used. A Peltier-cooled CCD detector registered dispersed light with a wavenumber range between 200 and 2000 cm^{-1}. Laser power was set to 10 mW and exposure time to 5 s with 5 exposures per point.

0.2 g of the Si-PANI sorbent was packed into a 3-mL polypropylene column, and the material was retained by two polyethylene frits. The adsorbent was washed from 5 to 10 times to obtain a colorless eluate with small portions (1–2 mL) of acetonitrile and, next, methanol to remove residues of short-chain oligomers of aniline.

2.3. Preparation of standards and samples solutions

Salvia officinalis L. (Synoptis Pharma, Poland), *Syzygium aromaticum* (L.) Merrill. (Prymat, Poland) and *Origanum vulgare* L. (Prymat, Poland) were obtained from the local market.

Stock solutions containing 550 μg/mL of each triterpenic acid were prepared by dissolving the standards in 80 mL of methanol and then, made up to 100 mL of water. Solutions were further diluted with mixture of methanol and water (8:2 v/v) to appropriate concentrations and stored in the dark at 4 °C.

The plant material was pulverized, accurately weighted (2.00 g), and extracted with methanol (2 × 50 mL) in ultrasonic bath (2 × 15 min) at 30 °C. Obtained extracts were filtered. The extracts from *S. aromaticum*, and *O. vulgare* were concentrated by evaporation of the solvent under vacuum. The final volumes were as follows: 100 mL for *S. officinalis*; 20 mL for *S. aromaticum*; and 20 mL for *O. vulgare*. All samples were filtered before analysis through Millex Samplicity Filters 0.20 μm (Merck).

2.4. SPE procedure

The system with a Millipore vacuum pump (Merck, Darmstadt, Germany) was applied for SPE investigations. All experiments were conducted at a constant temperature of 25 ± 1 °C. The flow rate was 1 mL/min. The Si-PANI sorbent was deprotonated before use by passing 2 mL of 2.5% (v/v) ammonia in methanol through the SPE cartridge and next washing with methanol (5 mL) and water (5 mL).

2.4.1. Optimization of SPE conditions

Retention experiments: the cartridges were conditioned with 2 mL of methanol or water, respectively and next 1 mL of the methanol/water solution (80:20 v/v) of the investigated compounds at a concentration of 0.500 mg/mL was applied.

In order to estimate the breakthrough volume and concentration, different volumes from 0.25 to 10 mL at the concentration range of 0.055–0.55 mg/mL of the investigated compounds were applied on the SPE columns.

Washing solutions: 1 mL solution of oleanolic acid at a concentration of 0.275 mg/mL was applied on the SPE cartridges and next 5 mL of solutions with a varied percentage of methanol in water in the range from 0% to 50% were passed through. 1 mL portions of the eluate were collected.

Elution: 1 mL solution of oleanolic acid at a concentration of 0.500 mg/mL was applied on the SPE cartridges. 5 mL of acetone, ethyl acetate, diisopropyl ether, acetonitrile, or methanol were used for elution. The eluates were concentrated to 1 mL.

All eluates were analyzed by the HPLC method.

2.4.2. Clean-up of plant extracts on SI-PANI

The extracts were purified as follows: the cartridges were conditioned of water, and then 1 mL of the sample was applied. 3 mL of the washing solution (methanol and water 20:80 (v/v)) was passed through the adsorbent and next the investigated compounds were eluted with 3 mL of 2.5% ammonia in methanol. The eluates were evaporated to dryness in a stream of N_2, the residues were dissolved in 1 mL of methanol and analyzed with the HPLC method.

2.5. HPLC analysis

The HPLC analysis was conducted using a VWR Hitachi Chromaster 600 chromatograph (Merck) with a pump (5160), an online degasser, a thermostat (5310), an autosampler (5260), and a DAD detector (5430). The analytes were separated on a Discovery (Supelco, Sigma-Aldrich) C18 reversed-phase column (25 cm × 4.0 mm i.d., 5 μm particle size) with using a mobile phase consisting of acetonitrile–water–1% phosphoric acid (90:10:0.5 v/v/v). Elution was performed at a 0.8 mL/min flow rate at 10 °C, and

the injection volume was 20 μl. The triterpenic acids were detected at 200 nm.

The gradient elution of the extracts was performed with the use of a mixture of acetonitrile and water. The content of acetonitrile was constantly increased from 10% to 100% during 60 min.

3. Results and discussion

3.1. Si-PANI stationary phase

The quality of polyaniline film deposition on silica directly after synthesis and after the series of 10 experiments was verified on the basis of microscopic pictures and comparison of the spectrum: pure silica, PANI, and silica modified with PANI obtained from the confocal Raman Microscope. The results indicated a uniform distribution of PANI, both on the surface of the adsorbent and in the pores of the particle. No significant changes of polyaniline film quality were observed after SPE experiments (Fig. 1).

Different forms of polyaniline varying in color and protonation can be formed depending on the acidity of the medium [21]. A base form of polyaniline is necessary to bond the investigated triterpenes on the adsorbent due to their acidic properties. Thus, the obtained sorbent should be conditioned with 2.5% ammonia in a methanol solution before use.

3.2. HPLC conditions

Chromatographic conditions to quantification of triterpenic acids were established on the basis of our earlier study [31,32]. Peaks were identified by comparison of retention times (BA: t_R=7.75 ± 0.10, OA: t_R= 9.11 ± 0.12, UA: t_R=9.59 ± 0.18) and UV spectra with those of the corresponding standards. The purity of the peaks was checked by acquisition of UV spectra at the upslope, apex, and downslope of each peak.

The analyses were performed at 10 °C, since lowering the temperature resulted in better resolution of oleanolic and ursolic acids [32,33].

3.3. Optimization of solid phase extraction

3.3.1. Retention experiments

The percentage of retention for all the retention experiments was calculated on the basis of the difference between the amount applied (100%) and the amount determined in the eluate by the HPLC method.

Initially, the influence of the conditioning solution on sorption of triterpenic acids was examined. As can be seen in Table 1, retention of triterpenic acids on RP-18 strongly depends on the conditioning solution. As the best conditioning solution for all sorbents, water was chosen for further experiment.

The impact of the amount of water in the methanol stock solution on sorption of OA, UA, and BA was also investigated. The solutions at a concentration of 0.550 mg/mL were prepared by dissolving appropriate amounts of triterpenic acids in methanol,

Table 1
Average percentage of investigated triterpenes retention depending on the conditioning solution (n=3).

Conditioning solution	Si-PANI			RP-18			Aminopropyl silica		
	BA (%)	UA (%)	OA (%)	BA (%)	UA (%)	OA (%)	BA (%)	UA (%)	OA (%)
Water	97.41	98.41	97.98	95.25	95.11	95.15	98.99	99.02	99.36
Methanol	98.04	98.42	98.14	82.41	80.11	81.12	98.61	98.56	99.42

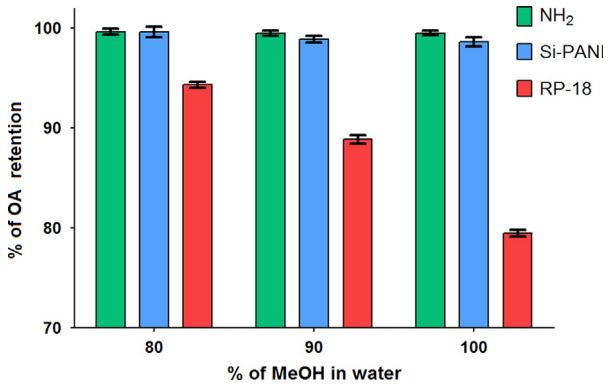

Fig. 2. The percentage of retention for oleanolic acid depending on the content of methanol in water.

Table 2
The percentage of investigated triterpenes bonded on tested cartridges (n=3).

Amount applied [mg]	Si-PANI			RP-18			Aminopropyl silica		
	BA (%)	UA (%)	OA (%)	BA (%)	UA (%)	OA (%)	BA (%)	UA (%)	OA (%)
0.5500	99.91	99.95	99.96	94.76	94.98	94.89	99.89	99.94	99.90
0.4125	99.92	99.88	99.95	93.02	93.12	93.19	99.85	99.90	99.93
0.2750	99.75	99.89	99.82	92.87	92.77	92.65	99.85	99.67	99.81
0.1375	99.85	99.66	99.56	91.42	91.71	91.35	99.64	99.55	99.78
0.0550	99.27	98.91	99.45	80.18	82.01	84.55	99.64	99.44	99.28

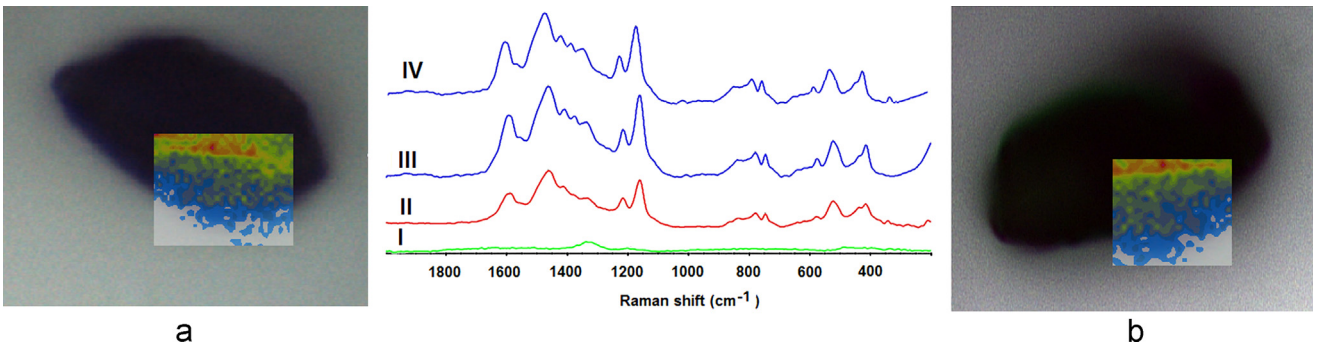

Fig. 1. Video image of Si-PANI particles: (a) directly after synthesis and (b) after 10 SPE experiments; and spectra of silica (I), PANI granules (II), Si-PANI sorbent before (III) and after SPE (IV).

methanol/water 90:10 (v/v), and methanol/water 80:20 (v/v) mixtures. 1 mL of each solution was applied on the SPE cartridges and the eluate was collected. An example of the relationship between the composition of the solvent and retention for oleanolic acid is shown in Fig. 2.

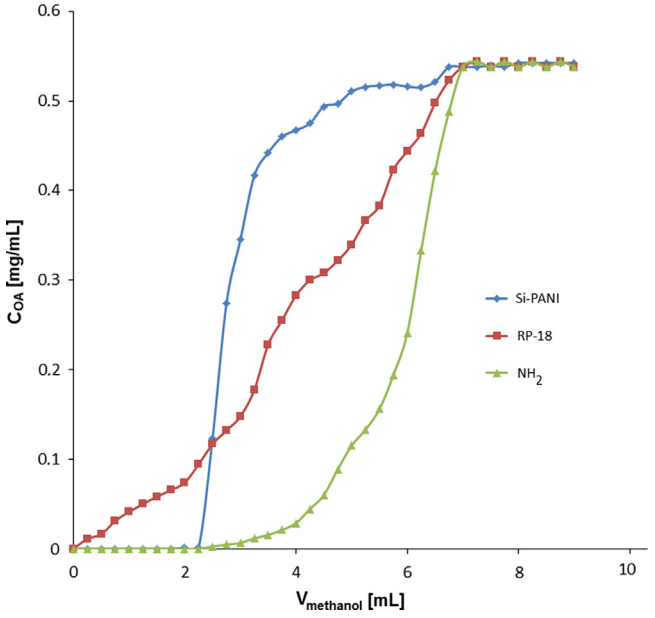

Fig. 3. The relationship between the volume of the standard solution (0.550 mg/mL) applied on cartridges and the concentration of oleanolic acid in the eluate.

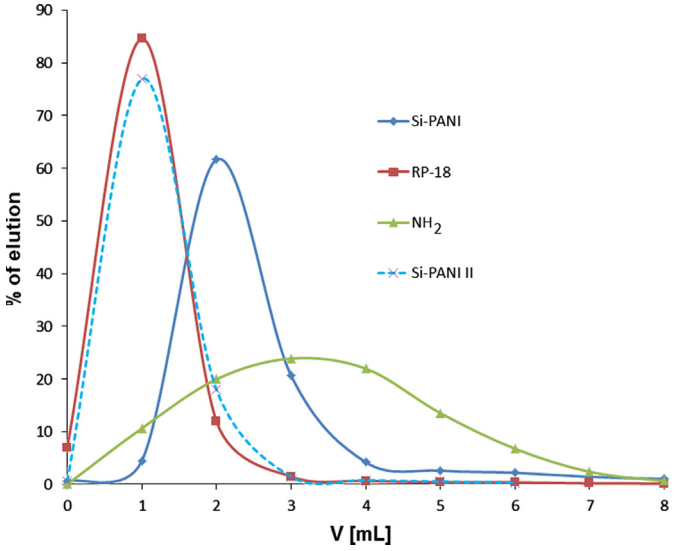

Fig. 4. The relationship between the volume of methanol with ammonia for Si-PANI (dashed line) or the volume of methanol for Si-PANI, RP-18 and aminopropyl adsorbents (solid lines) and the percentage of oleanolic acid elution.

Only in the case of the RP-18 cartridges the water content significantly affected the retention. The addition of 20% water to methanol proved to be optimal for the tested sorbents. In this condition, the average amount of retained compounds was above 95% for all cartridges.

In order to estimate the maximum amount of the investigated triterpenes that could be bonded on the tested cartridges, 1 mL of solutions of triterpenic acid standards at a concentration range from 0.0550 to 0.5500 mg/mL was applied on the SPE columns with different adsorbents. The results obtained are presented in Table 2.

It can be seen that the investigated triterpenes are bonded by the Si-PANI and aminopropyl silica cartridges more strongly than by octadecyl silica.

The slight differences in the chemical structures of the tested compounds did not affect sorption, hence oleanolic acid was chosen for further investigations. Preparation of a solution of this compound at a higher concentration was impossible due to its limited solubility in the methanol/water mixture 80:20 (v/v); therefore, in the second part of the sorption experiment, a 0.550 mg/mL standard solution of oleanolic acid was constantly passed through the cartridges. 0.25 mL portions of the eluate were collected and analyzed. The relationship between the volume applied and the concentration of OA in the eluate is presented in Fig. 3.

As can be noticed, only 2.25 mL of the tested solution could be applied on Si-PANI and aminopropyl silica to avoid a simultaneous retention/elution process that caused waste of the target compound. However, for aminopropyl silica in a range of 2.25–2.75 mL, the loss of the investigated triterpene was relatively low (0.8%) compared to that of Si-PANI (49.8%). The weak strength bond on RP-18 resulted in about 4–5% wastage after passing 0.5 mL of the OA solution through the cartridge.

3.3.2. *Washing solution*

The main role of the washing solution is reduction of non-specific sorption of the target compound and removal of a non-bonded analyte. Moreover, the washing solution can simplify the matrix *e.g.*, using water for clean-up can eliminate polar compounds such as sugars or certain glycosides derivatives. However, the washing solution should not elute the investigated substances from the adsorbent. On the basis of our experiments, 20% methanol in water was selected as a washing solution. 3 mL of this mixture did not elute the target component. The elution process started above this volume. The amount of the eluted compound was about 0.3% and 0.8% for 4 mL and 5 mL, respectively. The higher methanol content in the washing solution resulted in a significant increase in target compound elution.

3.3.3. *Optimization of the type and volume of the elution solvent*

Several solvents such as acetone, ethyl acetate, diisopropyl ether, acetonitrile, and methanol were tested in order to determine the elution strength. Diisopropyl ether, which eluted 3.0–3.4% of triterpenic acid, had the lowest elution strength; ethyl acetate eluted 42.0–42.5%; the best results were achieved

Table 3
Average of recovery value (%) for triterpenic acids ($n=5$).

Concentration [mg/mL]	Si-PANI			RP-18			Aminopropyl silica		
	BA (%)	UA (%)	OA (%)	BA (%)	UA (%)	OA (%)	BA (%)	UA (%)	OA (%)
0.550	97.33	98.22	98.12	93.44	93.41	93.01	98.87	99.25	99.65
0.055	98.56	97.99	98.02	92.21	92.54	92.87	98.58	98.45	99.02

Table 4
Validation parameters for determination of triterpenic acids ($n=5$).

Parameters	Oleanolic acid	Ursolic acid	Betulinic acid
Concentration range (mg/mL)	0.05–1.00	0.005–1.00	0.002–0.10
Correlation coefficient (r)	0.9994	0.9999	0.9997
Linear regression equation	$y=80{,}019{,}373x-58522$	$y=124{,}613{,}873x-18{,}314$	$y=102{,}640{,}810-28{,}487$
RSD values of peak area (%)	0.71–1.21	0.63–1.03	0.08–0.64
LOD (μg/mL)	0.14	0.15	0.11
LOQ (μg/mL)	0.45	0.47	0.33

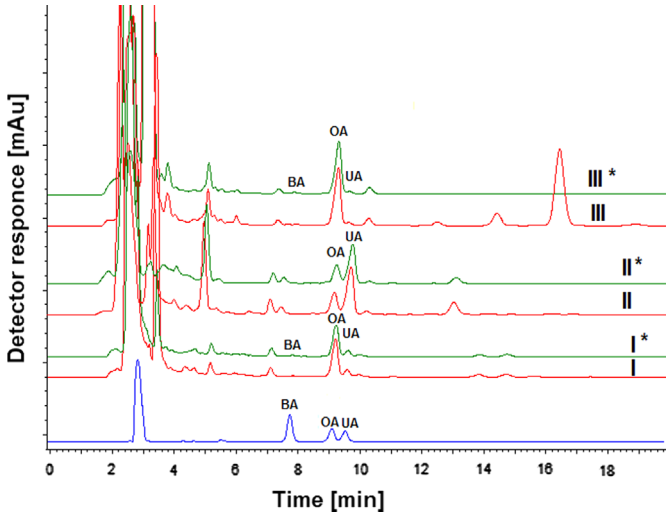

Fig. 5. Chromatograms of extracts before and after SPE purification*. Samples: (I) *Syzygium aromaticum*; (II) *Salvia officinalis*; and (III) *Origanum vulgare*.

for acetonitrile and methanol which eluted 98.1–98.5% and 98.5–98.7% of the analyte, respectively. Thus, methanol was used for determination of the volume of the solvent for elution of triterpenic acids from the examined cartridges.

As shown in our earlier investigations, triterpenic acids are bonded the most weakly on RP-18, thus only 3 mL of methanol was required for elution of 98% of the compound retained on the cartridge. The highest volume of the solvent was used for elution from aminopropyl silica (7 mL). The result obtained indicates higher bond strength between OA and this sorbent, compared to RP-18 and Si-PANI. The acidic properties of the tested compound suggest that addition of base to the mobile phase could influence elution thereof. Covering silica with polymers improves its stability in a wide pH range [27,34,35]. Thus, methanol and 2.5% ammonia in methanol were used for the elution test on Si-PANI. Ammonia in methanol had higher elution strength in comparison to methanol; 3 mL of this solution proved sufficient for elution of about 98% of bonded oleanolic acid (Fig. 4).

3.3.4. Recovery experiments

The optimized SPE conditions were used for recovery experiments at two different levels. The cartridges were conditioned with water, and then 1 mL of methanol/water 80:20 (v/v) solutions of triterpenic acids was applied. 3 mL of the washing solution was passed through the adsorbent, and next the investigated compounds were eluted as follows: 3 mL of 2.5% ammonia in methanol was used for elution from Si-PANI; and 3 mL and 7 mL of methanol from RP-18 and aminopropyl silica, respectively. The results obtained were satisfactory, as the percentage of recovery was higher than 92% for all the tested cartridges (Table 3).

3.4. Application of the SPE procedure using Si-PANI cartridges for plant extract analyses

The samples of the extract before and after SPE purification (*) were analyzed in triplicate and the amounts of triterpenic acids were calculated from the calibration plot. The data were analyzed by the least-square linear regression model. The detection (LOD) and quantification (LOQ) limits were evaluated on the basis of a signal-to-noise ratio of 3:1 and 10:1, respectively. The validation parameters such as the correlation coefficient, linear regression equation, precision (RSD values), LOD, and LOQ are summarized in Table 4. The obtained chromatograms are presented in Fig. 5.

The results of quantification of oleanolic, ursolic and betulinic acid in the extract samples before and after SPE procedures are given in Table 5.

3.5. The efficiency of SPE purification

As can be seen in Fig. 5, the investigated extracts possess a large matrix of other compounds, which are eluted at 2–4 min. The gradient elution was used in order to verify the efficiency of SPE clean-up. The extracts were chromatographed with a mobile phase with constantly decreasing amounts of water in acetonitrile from 90% to 0% during 60 min and monitored in the region between 190 nm and 400 nm. The results obtained are presented on 3D chromatograms (Fig. 6).

The fewest components or their lowest concentrations were observed on chromatograms of all the investigated samples after the SPE procedures, compared to extracts without purification. The purification was the most effective for *S. officinalis* and *O. vulgare* extracts.

4. Conclusion

In this work, the application of a new sorbent Si-PANI for the solid phase extraction technique was described. The adsorbent proposed can be easily obtained in a process of *in situ* polymerization of aniline directly on silica particles. It is relatively inexpensive and could be an alternative for commercially available cartridges for SPE. The investigated triterpenes were bonded more strongly on aminopropyl silica than on silica covered with polyaniline; on the other hand, an important advantage of the proposed sorbent was the lower amount of the solvent required for elution.

The advantage of Si-PANI is its high chemical resistance to drastic inorganic and organic reagents and possibility of working in a wide pH range [27,35], which makes Si-PANI cartridges reusable. On the basis of Raman analysis, no significant changes of polyaniline film quality were observed after the series of SPE experiments.

The Si-PANI sorbent was successfully used for purification of plant extracts to determine triterpenic acids.

Table 5
The content of triterpenic acids in plant material before and after SPE procedures ($n=3$).

Plant	Oleanolic acid				Ursolic acid				Betulinic acid			
	Before SPE		After SPE		Before SPE		After SPE		Before SPE		After SPE	
	Content (mg/g)	RSD (%)	Content (mg/g)	RSD (%)	Content (mg/g)	RSD (%)	Content (mg/g)	RSD (%)	Content (mg/g)	RSD (%)	Content (mg/g)	RSD (%)
Salvia officinalis L.	5.13	1.59	4.84	1.61	7.81	1.66	7.36	1.71	–	–	–	–
Syzygium aromaticum (L.)	11.5	1.51	10.96	1.50	0.58	2.41	0.55	2.45	0.092	2.61	0.088	2.73
Origanum vulgare L.	6.73	1.71	6.33	1.62	1.23	2.01	1.16	2.02	0.099	2.65	0.093	2.81

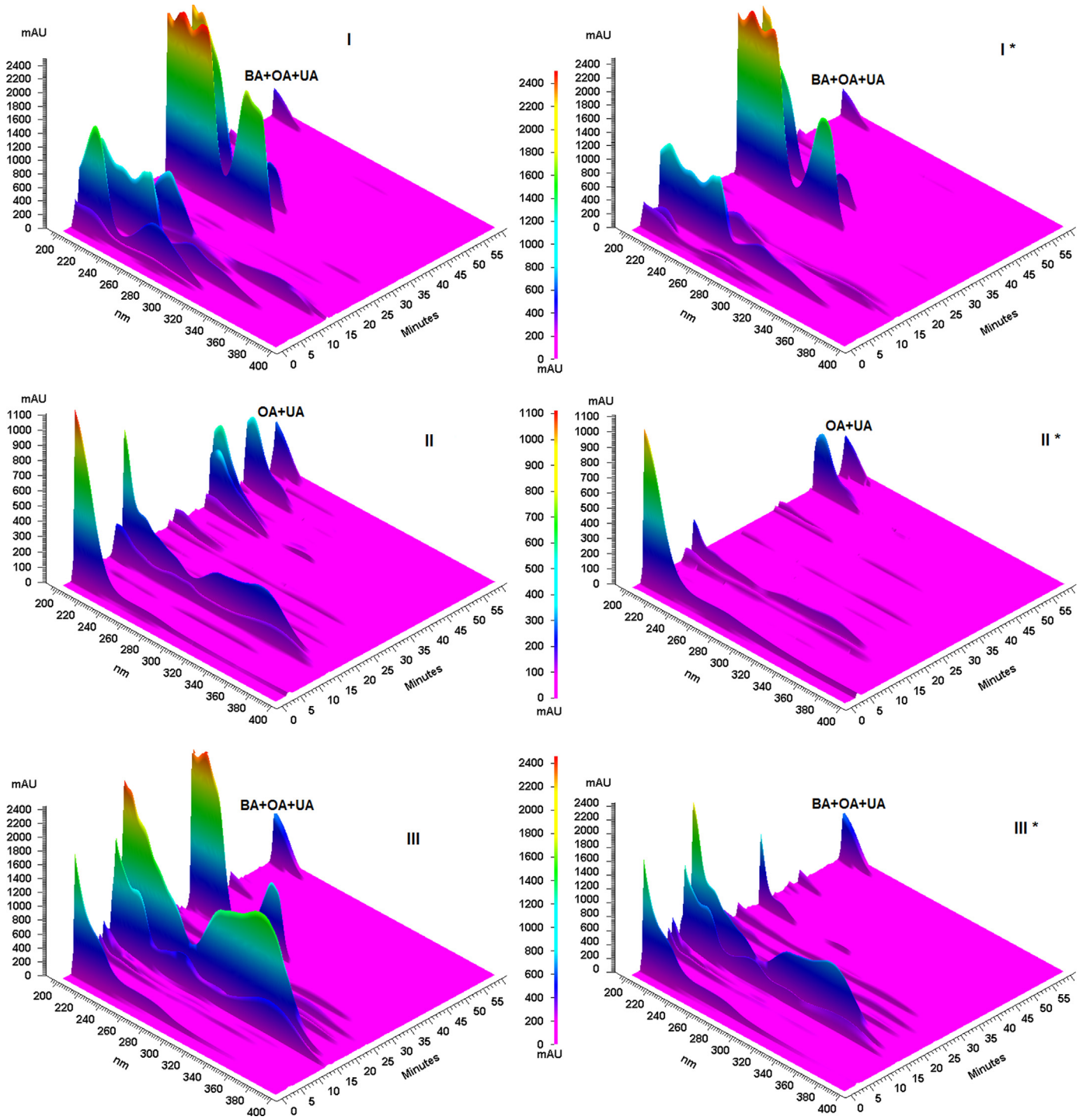

Fig. 6. 3D chromatograms of extracts before and after SPE purification* obtained by gradient elution ($\lambda=190$–400 nm). Samples: (I) *Syzygium aromaticum*, (II) *Salvia officinalis*; and (III) *Origanum vulgare*.

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