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# Evaluation of pH and thermal stability of sorbent based on silica modified with polyaniline using high-resolution continuum source graphite furnace atomic absorption spectrometry and Raman spectroscopy

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ABSTRACT

The stability of stationary phases on temperature and pH is especially important for separation techniques because it extends the possibilities of applications.
In the present paper, the high-resolution continuum source graphite furnace atomic absorption spectrometry HR-CS-GF-AAS and confocal Raman microscopy were successfully used to evaluate stability of silica sorbent modified with polyaniline (Si-PANI) on acidic, neutral and alkaline media and elevated temperature.
The solutions at pH range 1–12 were passed through the SPE cartridges, the eluates were collected and an amount of dissolved silica was analyzed. Furthermore, the quality of polyaniline film and its spatial distribution were verified by confocal Raman microscopy.
The solubility of silica occurred significantly lower for Si-PANI adsorbent comparing to silica and RP-18. Our research shows that covering the particles of silica with polyaniline protects the surface of support material against the drastic pH value. The results obtained by Raman analyses confirm the high stability of polyaniline layer at a temperature range of 30–70 °C and at pH from 1 to 12. The sorbent may be used in separation techniques, e.g. as a stationary phase for liquid chromatography in the wide pH and temperature range.



## 1. Introduction

Polyaniline (PANI) is one of the most interesting conductive polymers (CPs) due to relatively easy preparation and its unique electrical, optical, and chemical properties such as a good conductivity, redox properties [1,2] and high stability against temperature and pH variation [3,4]. Its commercial applications are a subject of interest for many researchers including chemistry, physics, optics, materials and biomedical science [5,6]. Hydrophobicity, π-conjugated structure, polar groups, and ion exchange ability of PANI enabled also its application in separation techniques e.g. in the solid phase extraction (SPE) for isolation of pesticides from aquatic media [7] or fluoroquinolones from honey [8].

Moreover, PANI can be employed to modify the surface of different materials e.g.: glass [9,10], silicon [11,12], polymers [13,14], textile [15,16] and noble metals [17,18]. In our earlier studies, polyaniline was successfully used to cover silica particles to obtain the new stationary phase for ion chromatography [19,20] or SPE [21,22].

The stability of sorbents is a key factor for separation techniques [23–25]. The complexity of analytical problems and diverse matrix of analyzed samples require various conditions of separation process, e.g. elevated temperature or the use of solutions in a wide pH range. Silica and silica based sorbents are the most popular due to good separation properties and high mechanic resistance. However, the main disadvantage of silica is low stability toward an extreme pH value because the Si – O – Si bond hydrolyzes at pH > 8 especially at elevated temperatures (>40 °C) and becomes less stable at acidic pH [23]. There are numerous literature data about modification of silica surface by chemical-bonding or its immobilization to improve its stability [24,25]. Polyaniline has high resistance on drastic temperature and pH values [3,4,12]; thus, the covering of silica particles with PANI may protect its surface and extend the application of silica sorbent.

Usually, the stability of sorbents is investigated by monitoring of changes in chromatographic parameters, e.g.: theoretical plate number, retention factor and peak asymmetry, during the use of eluents with a drastic pH value and/or high temperature [25]. There are also few publications on stability investigation based on determination of dissolved silica in elutes with the use of the silicomolybdate complex colorimetric technique [20,25]. However, AAS is much more sensitive, accurate and

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**Table 1**
Temperature program for GF-AAS analysis of Si.

| Step | Stage | Temperature (°C) | Ramp (°C/s) | Hold (s) | Time (s) |
|---|---|---|---|---|---|
| 1 | Drying | 80 | 6 | 20 | 28.3 |
| 2 | Drying | 90 | 3 | 20 | 23.3 |
| 3 | Drying | 110 | 5 | 10 | 14.0 |
| 4 | Pyrolysis | 350 | 50 | 20 | 24.8 |
| 5 | Pyrolysis | 1200 | 300 | 10 | 12.8 |
| 6 | Gas adaption | 1200 | 0 | 5 | 5.0 |
| 7 | Atomization | 2400 | 1500 | 3 | 3.8 |
| 8 | Clean | 2500 | 500 | 4 | 4.2 |

especially recommended for trace analysis [26,27]. In our research, high-resolution continuum source graphite furnace atomic absorption spectrometry (GF-AAS) was employed for the first time to estimate the degradation of sorbents.

The aim of our work was the evaluation of thermal and pH stability of new stationary phase obtained by deposition of polyaniline film on silica (Si-PANI).

Moreover, the morphology of sorbent with the use of a confocal Raman microscope, the changes of polyaniline chemical form and its spatial distribution within particles of silica under different pH and temperature conditions were verified by Raman analysis.

## 2. Material and methods

### 2.1. Reagents

Aniline (for analysis EMSURE), ammonium peroxydisulphate (extra pure), ammonia solution 25% (suprapur), sodium hydroxide (Titrisol) and certified atomic absorption standard stock solution of Si (1000 mg $L^{-1}$) were purchased from Merck (Darmstadt, Germany). Matrix modifier containing 2 g $L^{-1}$ $Pb(NO_3)_2$ and 10 g $L^{-1}$ $Mg(NO_3)_2$ were from CPAchem (Stara Zagora, Bulgaria). Buffer solutions (pH 1–10) were supplied from POCH (Gliwice, Poland). Water was deionized and purified by ULTRAPURE Milipore Direct-Q® 3UV-R (Merck). The resistivity of water was 18 MΩ cm. High purity argon (99.99% purity) for AAS was from Air Products (Warsaw Poland). Silica gel Lichrospher 60 Si and Lichrospher 60 RP-18 (Merck) were used for investigation.

### 2.2. Preparation of SPE columns

The Si-PANI adsorbent was prepared by in situ polymerization of aniline directly on silica particles at a temperature of 0–2 °C. The ammonium peroxydisulphate was used for oxidation of aniline. The procedure of synthesis and purification was described in detail in our previous publication [19].

200 mg of the Si-PANI, silica and octadecyl silica (RP-18) sorbent was packed into a 3-mL polypropylene column, and the material was retained by two polyethylene frits.

### 2.3. The pH stability experiment

The solutions at pH range from 1 to 12 were passed through the Si-PANI, RP 18 and silica cartridges. The eluates (volume of portion 50 ml) were collected and analyzed by graphite furnace atomic absorption spectrometry method (GF-AAS). The investigated sorbents were washed several times with water, removed from propylene columns and dried in order to verify the degradation thereof by confocal microscope and Raman analysis.

### 2.4. The thermal stability experiments

0.5 g portion of Si-PANI was dispersed in water and heated at 20, 30, 40, 50, 60, and 70 °C temperature under reflux for 60 min. The adsorbent was observed through a microscope and the quality of polyaniline film was investigated through Raman analysis.

### 2.5. Atomic absorption spectrometry (AAS) procedure

The eluates were quantitatively transferred to plastic tubes. Si contents were determined with the use of high-resolution continuum source graphite furnace atomic absorption spectrometer HR-CS-GF-AAS (ContrAA 700, Analytik Jena AG, Germany). A xenon short-arc lamp working in an optimized Hot-Spot-Mode and a CCD array detector (185–900 nm; resolution of 2 pm/pixel) with high quantum efficiency and increased UV-sensitivity were employed. The injection volume was 20 μL. Working standard solutions for the calibration curve, at a concentration range from 0 to 1000 μg $L^{-1}$ were freshly prepared each day by diluting of stock solution (1000 mg $L^{-1}$). The absorbance signal for Si was recorded at 251.6110, 250.6897, 252.8508 and 221.6669 nm wavelengths. The relative sensitivity (%) was 100, 37, 33 and 29, respectively. The best sensitivity of measurements was obtained at $\lambda = 251.6110$ nm, thus this wavelength was used for the quantification. The temperature program applied for Si determination is given in Table 1. The method was validated on the basis of certified atomic absorption standard stock solution of Si.

### 2.6. Raman analysis

The Raman analyses were performed 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. On the basis of literature data, it was expected that with this excitation line the Raman spectra of PANI would be resonance-enhanced [28]. Filters of 780 nm and 400 lines/mm grating

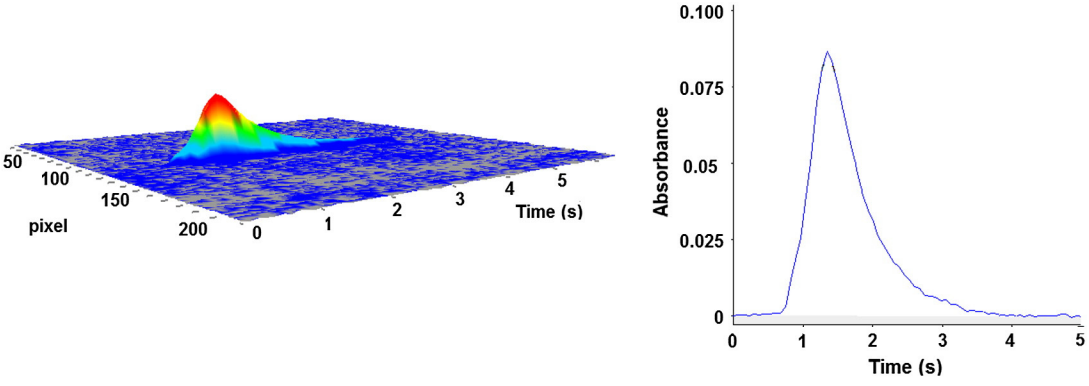


**Fig. 1.** The absorbance profile of silicon.