Talanta 83 (2010) 596–604

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Assessment of ion imprinted polymers based on Pd(II) chelate complexes for preconcentration and FAAS determination of palladium

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ARTICLE INFO

Article history:
Received 26 May 2010
Received in revised form
28 September 2010
Accepted 2 October 2010
Available online 2 November 2010

Keywords:
Pd separation/preconcentration
Ion imprinted polymer
Solid phase extraction
Flame atomic absorption spectrometry

ABSTRACT

New ion-imprinted polymeric (IIP) materials were synthesized by copolymerization of 4-vinylpyridine (VP) and styrene as functional monomers and divinylbenzene as a cross-linking agent with chelating complexes of Pd(II) in the presence of 2,2-azobisisobutyronitrile as an initiator. The complexes of Pd(II) with ammonium pyrrolidinedithiocarbamate (APDC), N,N′-diethylthiourea (DET), and dimethylglyoxime (DMG) were used for this purpose. Chloroform, ethanol, and cyclohexanol were applied as porogens. The ion-imprinted polymers were tested in a flow mode as sorbents for solid-phase extraction of palladium from aqueous solutions. The conditions of Pd(II) separation on all polymers were optimized. The efficiencies of retention of Pd on different polymers in the presence of high excess of interfering ions were compared. The effect of the used porogen on the analytical performance of the prepared polymers was also investigated. The calculated sorbent capacities for Pd(II) were in the range from 9.25 mg g^{-1} to 13.3 mg g^{-1}. The sorbent with Pd(II) imprinted as Pd–DMG–VP complex in chloroform was used for preconcentration of trace amounts of Pd. The detection limit for 100 mL of the sample was 5 μg L^{-1} using flame atomic absorption spectrometry (FAAS). The developed method was applied for the determination of Pd in water samples.

1. Introduction

Palladium is a metal of economic importance due to its extensive use in metallurgy, in various chemical syntheses, the production of dental and medicinal devices and in jewellery. Due to electrical conductivity and durability Pd is also widely used in electronics applications, for the production of multi-layer ceramic (chip) capacitors, in conductive tracks in hybrid integrated circuits and for plating connectors and lead frames. One of the most important applications of Pd is the production of catalytic converters for car engines [1,2].

The separation and recovery of Pd ions from base metal ions as well as the development of selective and accurate methods for determination of precious metals in waste and different environmental compartments are emergent research area. Solid phase extraction (SPE) has been demonstrated as a very effective and versatile tool for the separation and preconcentration of Pd [3–5]. The most commonly used packing materials for this goal are ion-exchange polymeric resins based on polystyrene, polystyrene-divinylbenzene or cellulose and silica gels functionalized or coated with different chelating groups (containing, e.g. N, S atoms) [6–11]. Non-polar sorbents based on hydrophobic polymeric phase or activated carbon are capable of extracting low polarity Pd complexes from aqueous solutions through reverse phase sorption. For instance, Pd complexed with bis(carboxymethyl)dithiocarbamic acid was preconcentrated on Amberlite XAD-4. The time between 60 and 120 min was necessary for the completion of the chelation reaction [12]. Pd was also enriched in the form of complexes with ammonium pyrrolidinedithiocarbamate (APDC) [13], N,N′-diethylthiourea (DET) [14], dimethylglyoxime (DMG) [15] on fullerene C_{60} and PTFE (the surface of a knotted reactor).

Recently, the polymers with imprinted ions of metals, called ion-imprinted polymers (IIP), have been applied for the selective separation of metal ions from interfering matrix [16,17]. The synthesized polymers contain the imprinting sites of a shape and functionality complementary to the template molecules [18,19]. There are several strategies of the preparation of IIP. One of them is a preparation of binary complex of ion of metal with ligand having vinyl groups, isolation of the complex and then polymerization with matrix-forming monomers. This strategy was applied for the synthesis of a polymer with imprinted ions of copper (in the form of Cu(II)-n-methacrylamidohistidine complex) [20] or uranium (in the form of UO_2^{2+}-5,7-dichloroquinoline-8-ol-4-vinyl pyridine) [21]. The other strategy is based on the preparation of a mixed complex of metal ion with the compounds containing non-vinylated chelating ligands and vinyl ligands. The polymers with Pd(II) imprinted in a form of ternary complexes with DMG and 4-vinylpyridine (4-VP) [22] or different derivatives of quinoline (8-

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doi:10.1016/j.talanta.2010.10.005

aminoquinoline, 8-hydroxyquinoline, 8-mercaptoquinoline) and 4-VP ligands [23] are the examples of this scheme. All polymers, tested in model solutions, showed higher selectivity towards Pd over the other transition metal ions. The complexes of $[PdI_4]^{2-}$ and $[Pd(SCN)_4]^{2-}$ with vinyl pyridinium ion $(VP^+)_2$ were imprinted into a polymeric network using 2-hydroxyethyl methacrylate (HEMA) as a functional monomer, ethylene glycol dimethacrylate (EGDMA) as a cross-linking monomer and methanol or dimethyl sulfoxide (DMSO) as a porogen. The authors, having found the thiocyanate system to be superior to the iodide system with regards to the extraction efficiency and capacity, have used these polymers for the separation of Pd from environmental samples [24]. More examples of using the solid sorbents for the separation of Pd are listed in Table 1.

In this work the new ion imprinted polymers intended for preconcentration of palladium by solid-phase extraction technique were designed and studied. The polymers with imprinted Pd(II) ions were prepared on the basis of their ternary complexes with chelating reagents (DMG, APDC, DET) and 4-VP using styrene as a functional monomer, divinylbenzene (DVB) as a cross-linking monomer and 2,2-azobisisobutyronitrile (AIBN) as an initiator. Since the polarity and hydrogen bonding strength of the solvent will affect some interactions, the effect of different porogens (ethanol, chloroform and cyclohexanol) on analytical properties of the tested polymers was also studied. The experimental parameters that affect the extraction efficiency of Pd(II) ions from aqueous samples were evaluated and optimized. The ability of polymers to separate and preconcentrate of Pd(II) from water samples before its flame atomic absorption spectrometric determination was also tested.

2. Experimental

2.1. Instrumentation and measurements conditions

A Solaar M6 (Thermo Electron Corporation, UK) atomic absorption spectrometer with a deuterium background correction system was used for Pd determination. The measurements were done in air-acetylene flame with commercially available burner (50 mm) located at the height 13.4 mm at acetylene and air flow rates 0.9 L $\min^{-1}$ and 8.0 L $\min^{-1}$, respectively. The absorbance of samples was measured at wavelength 247.6 nm with spectral bandpass 0.2 nm. The Pd hollow cathode lamp (CPI International, USA) was operated at 8 mA.

The FT-IR absorption spectra (in KBr) were recorded in the range between 500 and 4000 cm^{-1} with Nicolet Magna IR 550 Series II (Nicolet, Japan). A scanning electron microscope (SEM), Tesla BS-301 (Tesla, Czech Republic) equipped with a digital unit of image detection satellite, was used to take photographs of the prepared polymers. An inoLab pH Level 1 (WTW, Germany) pH meter equipped with an electrode SenTix 21 (WTW, Germany) was used for pH measurements.

A flow system used for Pd separation consisted of a peristaltic pump Minipuls 3 (Gilson, France), PTFE tubing of i.d. 0.8 mm and laboratory made glassy adsorption columns of i.d. 5 mm. The two ends of the columns were blocked with PTFE membranes.

2.2. Reagents and materials

A stock solution (1 mg mL^{-1}) of Pd(II) was prepared by dissolving 0.833 g of $PdCl_2$ (Merck, Germany) in 3 mL of aqua regia and dilution to 50 mL with Milli-Q water. Standard solutions were prepared from the stock solution daily. Hydrochloric acid (35–38% analytical grade, POCh, Poland) and sodium hydroxide (analytical grade, Standard, Poland) were used to adjust pH of the sample solutions. Nitric acid(V) (65%, Trace Select, Fluka), hydrochloric acid (37% fuming, Trace Select, Fluka) and thiourea (puris p.a., Fluka) were used as desorption agents. Ammonium pyrrolidinedithiocarbamate (APDC), dimethylglyoxime (DMG) and N,N′-diethylthiourea (DET) supplied by Fluka were used for the preparation of Pd(II) complexes. Divinylbenzene (DVB, 80%, mixture of isomers, Aldrich), 4-vinylpyridine (4-VP, 95%, Aldrich), styrene (S, 99%, Fluka), and 2,2′-azobisisobutyronitrile (AIBN, Fluka) were used for the synthesis of polymers. Ethanol, chloroform and cyclohexanol (POCh, Poland) were dried and distilled before use. High-purity argon gas was used to de-aerate the solutions. For interference studies the solutions of nickel(II), copper(II), zinc(II), cadmium(II), magnesium(II) and sodium(I) nitrates(V) and platinum as hexachloroplatinic(IV) acid (30%) (POCh, Poland) were used. All solutions were prepared in de-ionized water obtained from Milli-Q water purification system (Millipore, USA).

2.3. Preparation of Pd(II) complexes

For the preparation of Pd(II)–PDC complex 1 mL of Pd(II) solution (1 mg mL^{-1}, 9.4 μmol) and 4 mg of APDC (24.3 μmol) diluted in 3 mL of nitric acid (0.01 mol L^{-1}) were mixed. The final concentration of APDC in the solution was 0.1%. The solution was stirred for 2 h at room temperature to form a complex and the solvent was azeotropically evaporated with toluene. In this way a yellow solid was obtained.

For the preparation of Pd(II)–DET complex 1 mL of Pd(II) solution (1 mg mL^{-1}, 9.4 μmol) was mixed with 3.1 mg of DET (23.5 μmol) diluted in 2 mL of nitric acid (0.3 mol L^{-1}) (the final concentration of DET in the solution was 0.1%) and stirred for 2 h at 60 °C in an oil bath. The solvent was azeotropically evaporated with toluene. An orange solid was obtained.

For the preparation of Pd(II)–DMG complex 19 mL of Pd(II) solution (1 mg mL^{-1}, 178 μmol) and 10 mL of 1% DMG (689 μmol) in ethanol and hydrochloric acid (0.001 mol L^{-1}) were stirred for 10 min. The formed complex was extracted into a chloroform phase, and the solvent was evaporated. A yellow solid was obtained.

2.4. Preparation of Pd(II)-imprinted polymers

The Pd(II) imprinted polymers were prepared by bulk polymerisation technique according to scheme shown for preparation of Pd–DMG–VP polymer in Fig. 1. To the formed complexes of Pd(II) with APDC, DET and DMG (amount containing 100 μg of Pd(II)) a solution of 4-VP (2.1 μmol) prepared in a given porogen (ethanol, chloroform or cyclohexanol) was added. The resulting solutions were stirred for 2 h at room temperature (when ethanol and chloroform were used as the solvents) or at 30 °C (cyclohexanol as the solvent). In this way ternary complexes of Pd(II)–ligand–VP were prepared. Then, a styrene (20 mmol) as a functional monomer, DVB (15 mmol) as a cross-linking monomer, and AIBN (50 mg) as a chemical initiator were added and the obtained solutions were transferred into glassy polymerisation ampoules. The ampoules were purged with argon for 10 min and sealed. The reaction temperature was kept constant at 60 °C for 2 h and 80 °C for 24 h. The resulting solid polymers were crushed, washed with dichloromethane and ethyl acetate in order to remove the excess of reagents, dried and ground. The prepared polymers had the same colour as the Pd(II) complexes: light yellow for Pd–PDC–VP and Pd–DMG–VP and light orange for Pd–DET–VP. The imprinted Pd(II) ions were leached from the obtained polymers by stirring for 6 h with four portions of HCl (1:1, 20 mL), next the polymers were rinsed with diluted HCl, dried at room temperature and sieved. The concentration of Pd(II) in the leaching solution was determined by FAAS.

The control polymers (CP) were synthesized in a similar way, but in the absence of Pd(II) ions. The control polymers had white colour.

Table 1

Comparison of solid sorbent extraction methods for Pd determination.

Type of sorbent	Retention conditions: sorbent mass/sample pH/contact time or flow rate	Desorption/elution conditions: volume and concentration of eluent/contact time or flow rate	Sorbent capacity, mg g^{-1}	Detection technique/detection limit	Analysed sample	Ref.
Poly(NHMMA-ATU) hydrogel	Batch: 0.05 g/pH 0.5/48 h	2 mL of 0.8 mol L^{-1} TU + 3 mol L^{-1} HCl/48 h	407	GFAAS	Anode slime, photographic developer	8
Melamine-formaldehyde-thiourea resin	Batch: 2 g/pH 4/20 min Column: 5 cm^3/pH 4/0.1 mL min^{-1}	10 mL of 0.5 mol L^{-1} TU + 0.5 mol L^{-1} HCl/0.1 mL min^{-1}	15.3 1.6	FAAS	Model solutions	9
BrPMAAm/AMPS/DVB chelating resin	Column: 0.7 g/pH 9 (buffer NH_3aq/NH_4Cl)/5 mL min^{-1}	10 mL of 1 mol L^{-1} HCl		FAAS 1.1 μg L^{-1}	Spiked tap water, catalytic converters	10
Cellex-T (triethylcellulose)	Column: 0.01 g/pH 4/3 mL min^{-1}	3 mL of 4 mol L^{-1} KSCN (pH 1)/0.3 mL min^{-1}	7.5	FAAS	Spiked tap water, car catalyst	7
		0.3 mL of 1.2 mol L^{-1} TU in HCl (pH 0.5)/0.3 mL min^{-1}		GFAAS 0.2 μg L^{-1}		
Pd(II)-APS functionalized silica gel (surface imprinting)	Batch: 0.05 g/pH 5/30 min	2 mL of 3% TU + 3 mol L^{-1} HCl/1 mL min^{-1}	26.7	ICP-OES	Water (GBW 07293)	11
	Column: 0.05 g/pH 5/1 mL min^{-1}		10.1[a]	0.4 μg L^{-1}	Cooper sediment	
Pd–DMG imprinted polymer	Batch: 0.5 g/pH 0.4-0.7/20 min	2 × 10 mL (1:1) HCl/30 min	21.5 20.0[a]	UV–vis 2.5 μg L^{-1}	Model solutions	22
Pd-AQ imprinted polymer	Batch: 0.05 g/pH 0.3/30 min	2 × 10 mL (1:1) HCl/60 min	28.8 26.1[a]	UV–vis	Model solutions	23
$[PdI_4]^{2-}$ $(VP^+)^2$ imprinted polymer	Batch: 0.1 g/pH 4/30 min	2 × 5 mL acidified methanol in 0.1 mol L^{-1} HCl/60 min	32.4 18.5[a]	FI-FAAS 10.0 μg L^{-1}	Model solutions	24
$[Pd(SCN)_4]^{2-}$ (VP^+) imprinted polymer	Batch: 0.02 g/pH 4/30 min	2 × 5 mL acidified methanol in 0.1 mol L^{-1} HCl/60 min	41.6	FI-FAAS	Road dust	24
	Column: 0.015 g/pH 4/11 mL min^{-1}	1.3 mL of acidified methanol in 0.1 mol L^{-1} HCl/4 mL min^{-1}	29.0[a]	10.0 μg L^{-1} 1.5 μg L^{-1}		
Imprinted polymers	Column	3 mL/0.5 mL min^{-1}	1.3[a]	FAAS	Spiked tap water	This work
Pd-PDC	0.5 g/pH 5/2 mL min^{-1}	0.15 mol L^{-1} TU + 0.8 mol L^{-1} HCl	13.3	5.0 μg L^{-1}		
Pd-DET	0.5 g/pH 5/2 mL min^{-1}	0.15 mol L^{-1} TU + 0.2 mol L^{-1} HCl	12.2			
Pd-DGM	0.5 g/pH 6/2 mL min^{-1}	0.30 mol L^{-1} TU + 1.0 mol L^{-1} HCl	9.3			

NHMMA-ATU—N-(hydroxymethyl)methacrylamide 1-allyl-2-thiourea; BrPMAAm/AMPS/DVB—[N-(4-bromophenyl)-2-methacrylamide-co-2-acrylamido-2-methyl-1-propanesulfonic acid-co-divinylbenzene; APS—3-aminopropyltrimethoxysilane; DMG—dimethylglyoxime; AQ—8-aminoquinoline; VP—4-vinylpyridine; PDC—pyrrolidinedithiocarbamate; DET—N,N′-diethylthiourea.

[a] Adsorption capacity for non-imprinted polymer.

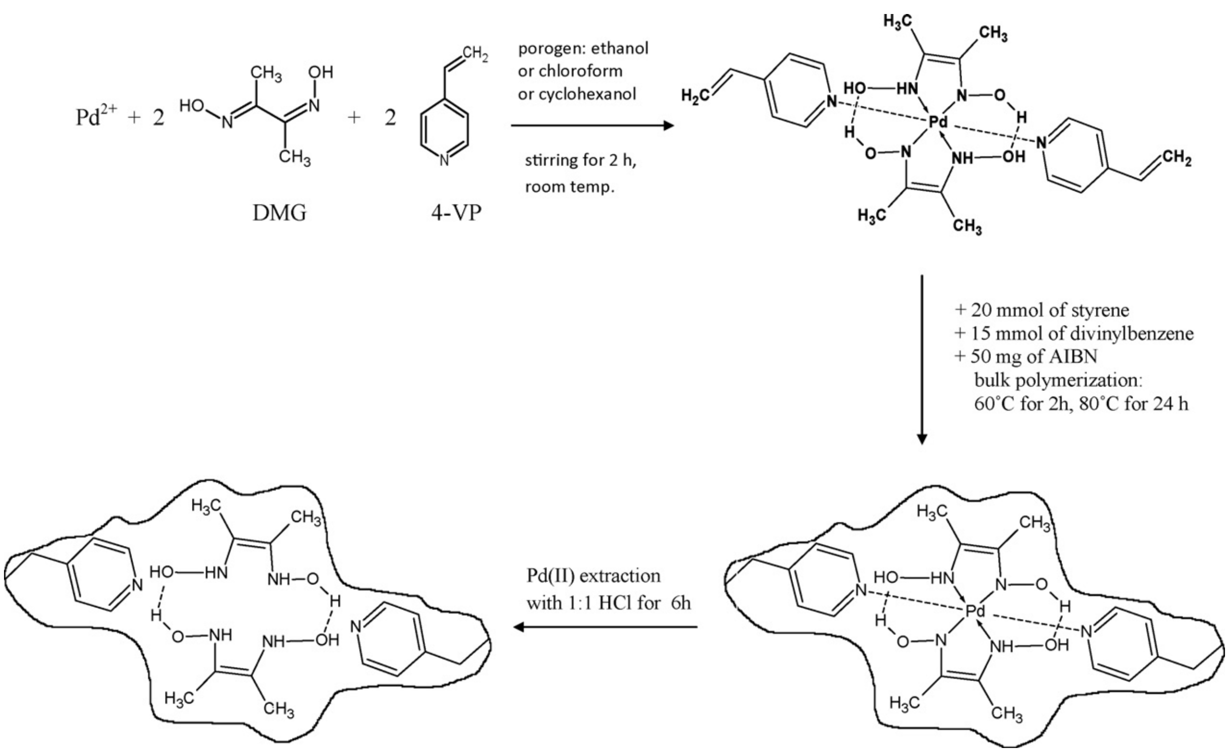

Fig. 1. Schematic illustration of imprinting process for the preparation of ion imprinted polymer Pd–DMG–VP by bulk polymerization technique.

As a result of the procedure described above, 9 polymers with imprinted complexes of Pd(II) with different ligands: APDC, DET, DMG in various porogens: ethanol, chloroform, cyclohexanol were prepared. The fraction of diameter range <50 μm was used as a column filling.

2.5. Separation procedure

The adsorption of Pd(II) from the aqueous solutions was studied in a flow mode. Glassy columns with i.d. 5 mm were packed with 0.5 g of dry ion imprinted polymers. The sorbents were conditioned by passing 3 mL of 0.5 mol L^{-1} HCl and 4 mL of Milli-Q water at the flow rate of 1 mL min^{-1}. For the retention of the analyte 5 mL of Pd(II) solution (0.5–25 mg L^{-1}) adjusted with diluted NaOH to pH 6.0 ± 0.5 were passed through the column at the flow rate of 2 mL min^{-1}. Pd(II) was eluted from the column with 3 mL of the solution of 0.15–0.3 mol L^{-1} thiourea in 0.2–1.0 mol L^{-1} HCl at the flow rate of 0.5 mL min^{-1}.

All the reported retention/elution efficiencies were calculated as a ratio of the mass of Pd retained/eluted on/from the column to the initial mass of Pd in the solution loaded on the column. The Pd concentration in all solutions was determined from the adequate calibration graphs obtained by the FAAS method.

3. Results and discussion

The new sorbents prepared via the imprinting of ion-associated complexes: Pd–PDC–VP, Pd–DET–VP and Pd–DMG–VP in the presence of various porogens: ethanol, chloroform and cyclohexanol in polymeric network were used for the selective separation of Pd(II) from the aqueous solutions. The chelating complexes of Pd(II) with APDC and DMG, non-specific group reagents, and with DET, selective reagent for platinum group metals, were used as template molecules. The studies were performed under dynamic conditions. Numerous parameters like the effect of pH and the flow rate of the sample solution, the type and concentration of the stripping agent, the volume and the flow rate of the eluent were optimized in order to obtain the highest retention and recovery of Pd(II) from the polymers.

3.1. Characteristic of the polymers

FT-IR spectra were registered for all prepared polymers. The characteristic bonds of the polymeric matrix (VP-styrene-DVB) were observed in all materials. The bands observed at 3082, 3050 and 3024 cm^{-1} correspond to the C–H stretching vibrations of the aromatic system. The symmetrical and asymmetrical stretching vibrations due to the presence of methyl and methylene groups were observed at 2980 and 2920 cm^{-1}. The ring bending vibrations of the aromatic ring were observed at 1600, 1508, 1450 cm^{-1}. The bands at 750 and 700 cm^{-1} correspond to C_{Ar}–H out of the plane vibration from the aromatic ring. For the Pd–PDC–VP polymers the absorption at 1336 cm^{-1} can be attributed to the stretching vibration of C–N from the imprinted ligand, while the band at 1164 cm^{-1} corresponds to the stretching vibration of C=S from N–C(=S) of the imprinted ligand. For the Pd–DET–VP polymers the absorption at 3220 cm^{-1} could be assigned to the stretching vibration of the associated –NH group of the imprinted ligand. The bands at 1340 and 1164 cm^{-1} can be assigned to the stretching vibrations of C–N and S=C–N of the imprinted Pd–DET complex. For Pd–DMG–VP polymers the presence of the O–H stretching vibration at 3500–3300 cm^{-1} corresponds to the –OH groups indicating that DMG ligands occur in the polymeric structure.

The size and shape of Pd(II)-imprinted polymer particles measured by SEM are shown in Fig. 2a and b. It was observed that the size of particles of Pd–PDC–VP and Pd–DET–VP polymers was in the range 50–200 μm, while after removing of Pd(II) the size of particles of polymers decreased to 10–20 μm. The particles had an irregular shape and a rough surface (the upper left side of photographs). For comparison the surface of non-imprinted DET–VP polymer (control polymer) is shown in Fig. 2c.

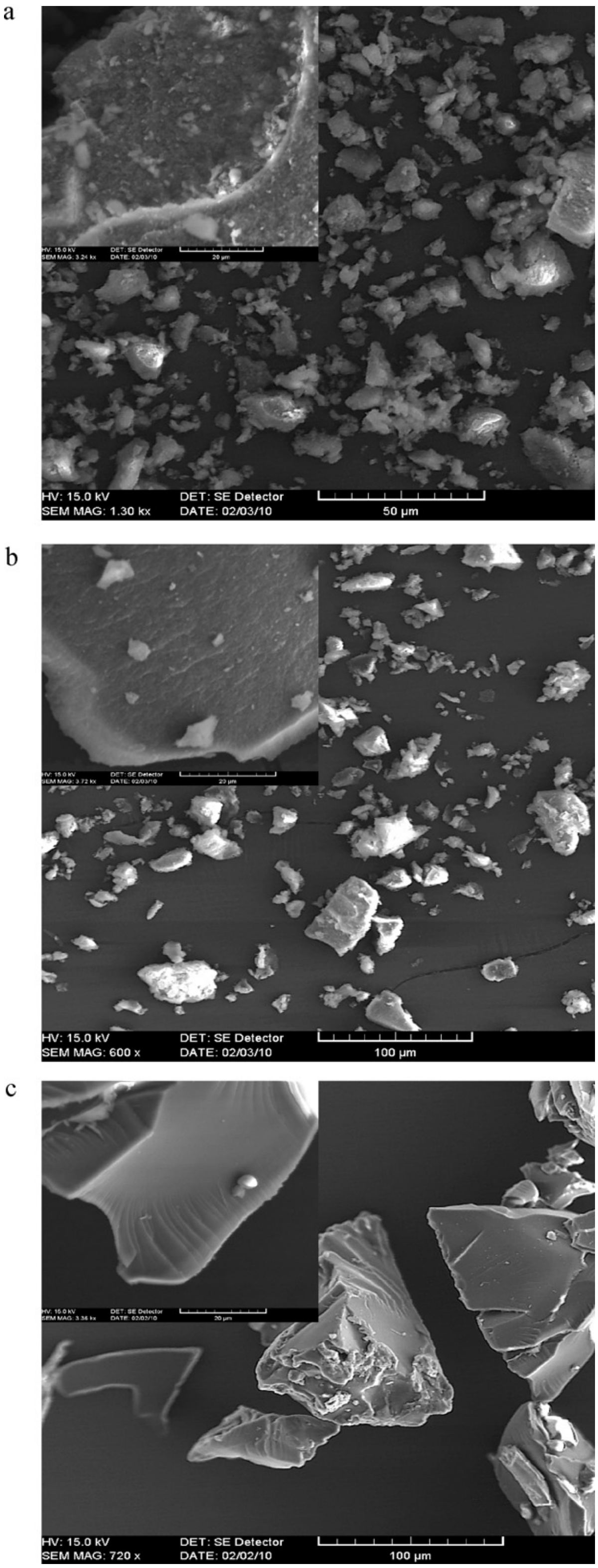

Fig. 2. SEM photographs of particles of polymers: (a) Pd–PDC–VP (after leaching of Pd(II)), (b) Pd–DET–VP (after leaching of Pd(II)), (c) control polymer. Surface morphology and bulk structure (upper left side).

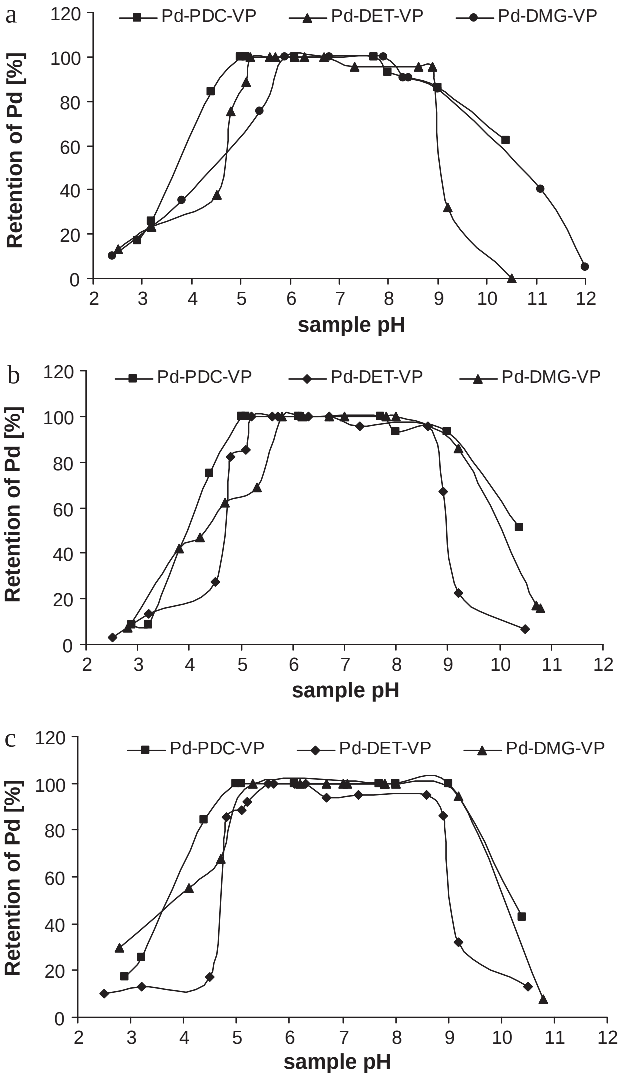

Fig. 3. Effect of sample pH on the retention of Pd(II) ions on the Pd–PDC–VP, Pd–DET–VP, Pd–DMG–VP polymers prepared in various porogens: (a) chloroform, (b) cyclohexanol, (c) ethanol (sample: 125 µg of Pd(II), flow rate: 2 mL min^{-1}).

3.2. Optimization of the retention conditions

The effect of a sample pH on the retention of 125 µg of Pd(II) from the aqueous solutions on all tested polymers was thoroughly investigated at pH range from 2 to 12. The sample pH was adjusted with the diluted solutions of HCl or NaOH. The quantitative retention of Pd(II) ions on the Pd–PDC–VP polymers prepared in chloroform and cyclohexanol occurred at pH range 5.0–7.7, while on the polymer prepared in ethanol was observed at pH range 5.0–9.0. The total uptake of Pd(II) ions on the Pd–DMG–VP polymers prepared in chloroform and cyclohexanol was at pH from 5.8 to 8.0, while for the one prepared in ethanol it was at pH from 5.3 to 8.0. The retention of Pd(II) ions on the Pd–DET–VP polymers was quantitative at a slightly narrow pH range, namely at pH: 5.2–6.7, 5.2–6.3 and 5.6–6.3, when chloroform, cyclohexanol and ethanol were used as the porogens, respectively. The low efficiency of the Pd(II) sorption on all polymers was observed below pH 4. As can be seen in Fig. 3 the retention of the analyte on the polymers prepared in different porogens was influenced by the sample pH in a similar way. The efficiency of the retention of Pd(II) on CP polymers in the studied pH range was 10–20% lower than on the imprinted sorbents, indicating the occurrence of non-specific interactions between the analyte and the polymers (results not shown). The similar difference between retention of analyte on imprinted and non-imprinted polymers was observed on sorbents with imprinted Pd [23,24], Cu [25] and Cr ions [26].

It is well known that Pd forms many different species in aqueous solutions [27]. In acidic solutions containing chloride ions Pd(II) occurs in anionic form (mainly as $PdCl_4^{2-}$ and $PdCl_3(H_2O)^-$) and cannot interact with the active sites of the polymers while in more neutral solutions the hydrolyzed Pd(II) ions can bind to negatively charged functional groups. Additionally, at acidic media the donating sulfur (APDC, DET) or nitrogen (DMG) atoms of ligands can be protonated, hence, the negligible amounts of Pd(II) ions are adsorbed on the polymers. In a highly alkaline pH (above 8) the precipitation of $Pd(OH)_2$ occurs [28], which reduces the amount of Pd(II) ions able to interact with the sorbent. In order to avoid the precipitation of metal hydroxides originating from the potential matrices the sample pH was kept as low as possible for further studies.

The effect of the sample flow rate on the retention of Pd(II) on the polymers was studied in the range 1–7 mL min^{-1} at pH 5.0 for the Pd–PDC–VP polymers, at pH 5.6 for the Pd–DET–VP polymers and at pH 6.0 for the Pd–DMG–VP polymers. The retention of Pd(II) was quantitative up to the flow rate of 6 mL min^{-1} on the Pd–PDC–VP polymers prepared in chloroform and ethanol, but only up to 2 mL min^{-1} on the sorbent prepared in cyclohexanol. At higher flow rates the efficiency of Pd(II) retention dropped to 60%. The retention of Pd(II) on the Pd–DET–VP polymers prepared in chloroform and cyclohexanol was complete and independent of the sample flow rate in the range from 1 to 6 mL min^{-1}. A slightly worse efficiency of Pd(II) uptake (90%) at the flow rate higher than 3 mL min^{-1} was observed on the Pd–DET–VP polymer prepared in ethanol. The retention of Pd(II) on all Pd–DMG–VP polymers was quantitative up to the flow rate of 3 mL min^{-1}, but on the sorbent prepared in cyclohexanol with the higher flow rates it decreased very fast to 60%. Longer contact time was necessary for the efficient binding of the analyte to the polymers based on Pd–DMG–VP complex. As the illustration of the experiment, the results obtained for the polymers prepared in chloroform are shown in Fig. 4a. From these results it is evident that the sorption of the analyte on all polymers is fast. In order to provide the total retention of Pd(II) on all polymers further studies were performed at the sample flow rate of 2 mL min^{-1}.

3.3. *Effect of the interfering ions*

Different metal ions often present in environmental and industrial samples were examined for their effect on the retention of Pd(II) on the polymers. The selection of the interferents was also based on their affinity for the imprinted ligands, the size of metal covalent radius and the effect on the analytical signal of Pd measured by FAAS. In the presence of the excess of Cu(II), Zn(II), Ni(II), Ca(II), Co(II) ions the relative absorbance of Pd is in the range of 90–92% compared to the Pd standard [7]. The interfering ions (listed in Table 2) were added individually in the concentration range of 1–500 mg L^{-1} to the Pd(II) solution (20 mg L^{-1}), and the separation procedure was applied. The tolerable amount of each foreign ion was taken as the largest concentration, yielding an error below 10% in the sorption efficiency of the analyte. As can be seen in Table 2 the effect of the interfering ions on the retention of Pd on polymers more significantly depends on the imprinted ligand than the used porogen. The retention of the analyte on Pd–DMG–VP was practically not affected by the added ions in the entire studied range of the concentrations. The most considerable effect was caused by the Pt(IV) ions. At the platinum concentrations above 1 mg L^{-1} the retention of Pd(II) decreased to 20–50% on the Pd–PDC–VP, 78–85% on the Pd–DET–VP and 87% on the Pd–DMG–VP polymers, probably due to Pt(IV) chemical similarity to Pd(II) and competitive binding to the imprinted ligands. Considering the effect of porogen, the effect of the presence of the interfering ions on the Pd(II) retention is negligible on the polymers prepared in chloroform, which can be attributed to the lower polarity of this solvent.

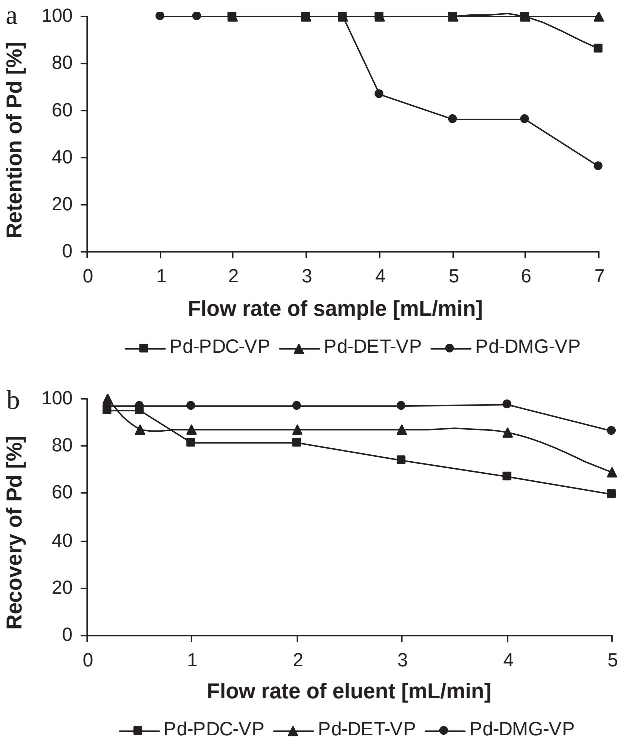

Fig. 4. Effect of (a) sample flow rate on the retention of Pd(II) on the Pd–PDC–VP, Pd–DET–VP, Pd–DMG–VP polymers, (b) eluent flow rate on the recovery of Pd(II) from polymers (porogen: chloroform, sample: 125 μg of Pd(II), pH 5–6, eluent: as in Table 3, volume 3 mL).

3.4. *Optimization of the elution conditions*

The repeated use of sorbent materials is very important from the economical point of view. The elution of the metal ions retained on ion-imprinted polymers can be performed using mineral acids or agents forming stable complexes [18,22]. Initially, EDTA, hydrochloric and nitric acids of different concentrations were tested for their ability to remove Pd from sorbents. The flow rate of the eluent was 0.5 mL min^{-1}. It was found that the efficiency of Pd(II) elution with nitric acid at the concentrations of 1–4 mol L^{-1} was almost independent of the reagent concentration, but was affected by the type of ligand imprinted in the polymeric network (Fig. 5). The efficiency of Pd(II) elution from the Pd–PDC–VP polymer with 3 mL of hydrochloric acid solutions (in the concentration range of 1–5 mol L^{-1}) was only 40%, while from the Pd–DET–VP and the Pd–DMG–VP polymers it was 65% and 74%, respectively. The recovery of Pd from all polymers was almost independent of the porogen used in the synthesis process. The recovery of Pd with EDTA of the concentrations in the range of 0.05–0.1 mol L^{-1} in all cases did not exceed 20%. Since thiourea (TU) forms stable cationic complexes with Pd in acidic medium, the solutions containing different concentrations of TU (from 0.15 to 1.0 mol L^{-1}) and HCl (from 0.2 to 1 mol L^{-1}) were examined for metal recovery. It was found that more than 85% of Pd was eluted with such solutions from the polymers. The optimal concentrations of TU and HCl solutions used for the elution of the analyte from the polymers prepared in chloroform and the results of the recovery are given in Table 3. It is worth mentioning that the differences in Pd recovery on the polymers

Table 2
Influence of interfering metal ions on the retention of Pd(II) ions on studied ion imprinted polymers (sample: 80 μg of Pd, pH 5–6, flow rate 2 mL min^{-1}). Efficiency of the retention of Pd(II) in the presence of given amount of Pt(IV) is shown in brackets.

Type of polymer	Type of porogen	Tested matrix ions	Tolerable concentration of interfering ions, μg mL^{-1}
Pd–PDC–VP	Chloroform	Cu(II), Ni(II), Cd(II), Zn(II)	100
		Pt(II)	1 (41%)
	Cyclohexanol	Cu(II), Ni(II), Cd(II)	100
		Zn(II)	50
		Pt(IV)	1 (21%)
	Ethanol	Cu(II), Ni(II)	100
		Cd(II), Zn(II)	50
		Pt(IV)	1 (52%)
Pd–DET–VP	Chloroform	Ni(II), Zn(II), Mg(II)	400
		Cu(II), Cd(II), Na(I)	100
		Pt(IV)	5 (81%)
	Cyclohexanol	Cd(II), Zn(II), Mg(II)	400
		Na(I)	100
		Ni(II)	20
		Pt(IV)	1 (85%)
	Ethanol	Cd(II), Zn(II), Mg(II)	400
		Ni(II),	100
		Cu(II), Na(I)	40
		Pt(IV)	1 (78%)
Pd–DMG–VP	Chloroform	Cu(II), Ni(II), Cd(II), Zn(II)	500
		Pt(IV)	5 (87%)
	Cyclohexanol	Cu(II), Ni(II), Cd(II)	500
		Zn(II)	50
		Pt(IV)	15 (87%)
	Ethanol	Cu(II), Ni(II), Cd(II), Zn(II)	500
		Pt(IV)	1 (87%)

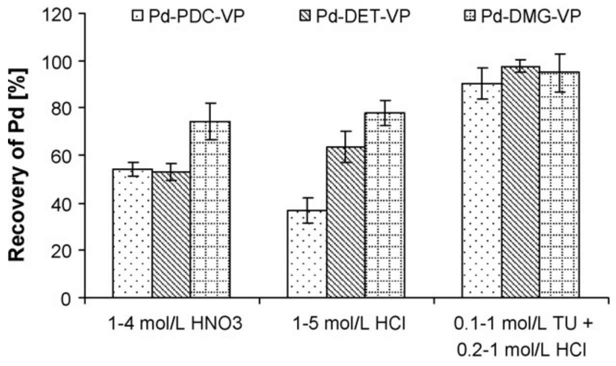

Fig. 5. Efficiency of the elution of Pd(II) with stripping agents from the Pd–PDC–VP, Pd–DET–VP, Pd–DMG–VP polymers (porogen: chloroform, sample: 125 μg of Pd(II), pH 5, flow rate 2 mL min^{-1}, eluent: volume 3 mL, flow rate 0.5 mL min^{-1}).

prepared in different porogens were not statistically significant.

The influence of the eluent volume (from 0.5 to 4 mL) and its flow rate (0.2–5 mL min^{-1}) on metal recovery was also studied. The quantitative elution of the analyte was obtained with 3 mL of stripping agent at 0.5 mL min^{-1} flow rate from Pd–PDC–VP and Pd–DET–VP polymers, while from Pd–DMG–VP polymer the total elution was obtained at flow rate up to 4 mL min^{-1} (Fig. 4b). The small volume of the used eluent is one of the advantages of the evaluated procedure when compared to the literature data [9,10] (Table 1). The high flow rate of eluent (similar to presented in [24]) make possible the application of Pd–DMG–VP polymer as a sorbent in a flow-injection FAAS system.

3.5. *Analytical performance*

The total retention of Pd(II) was obtained on all polymers with repeatability better than 3%. The recovery of Pd was in the range 92–100% with the repeatability of the elution process below 8% (Table 3). The good reproducibility of the results, obtained even after one hundred preconcentration cycles, testifies the good stability of the sorbents.

The breakthrough volume of the polymers prepared in chloroform was determined by passing the solution of Pd (25 mg L^{-1}) through the column filled with 0.2 g of the appropriate polymer and measuring of the absorbance of Pd in the effluent. The experiment was completed when the efficiency of the Pd retention decreased to 80% [29]. On this basis the sorbent capacity for Pd(II) was calculated as 13.3 mg g^{-1} for the Pd–PDC–VP, 12.2 mg g^{-1} for the Pd–DET–VP, 9.3 mg g^{-1} for the Pd–DMG–VP polymers. The capacity of non-imprinted polymers for Pd(II) was only 1.3 mg g^{-1} what indicates the advantage of using ion-imprinted polymers in separation step.

Table 3
Repeatability of the retention process and the recovery of Pd(II) on different polymers (porogen: chloroform, sample: 80 μg of Pd(II), flow rate 2 mL min^{-1}, eluent: volume 3 mL, flow rate 0.5 mL min^{-1}), $n = 6$.

Polymer	Retention of Pd(II)		Elution of Pd(II)	
	Sample pH	Efficiency of retention, %	Eluent	Recovery of Pd (II), %
Pd–PDC–VP	5.0	100 ± 1	0.15 mol L^{-1} TU in 0.8 mol L^{-1} HCl	92 ± 5
Pd–DET–VP	5.0	99 ± 3	0.15 mol L^{-1} TU in 0.2 mol L^{-1} HCl	95 ± 6
Pd–DMG–VP	6.0	100 ± 1	0.30 mol L^{-1} TU in 1.0 mol L^{-1} HCl	96 ± 9

Table 4
Recovery of Pd(II) from various samples after its separation on Pd-DMG-VP polymer (porogen: chloroform; sample: pH 6, flow rate 2 mL min^{-1}; eluent: 0.3 mol L^{-1} TU in 1.0 mol L^{-1} HCl, volume 3 mL, flow rate 0.5 mL min^{-1}).

Sample matrix	V, mL	C_{Pd}, mg L^{-1}	Pd mass added, µg	Pd mass determined, µg	Recovery, %
MQ water	2	10.0	20.0	19.3	97
	4	5.0	20.0	18.1	91
	10	5.0	50.0	47.4	95
	20	2.0	40.0	39.1	98
	50	0.8	40.0	36.5	91
	100	0.4	40.0	36.5	91
Pd(II) + 5 mg L^{-1} Fe(III)	10	5.0	50.0	46.6	93
Pd(II) + 5 mg L^{-1} Cu(II)	10	5.0	50.0	49.4	99
Pd(II) + 5 mg L^{-1} Cd(II)	10	5.0	50.0	45.0	90
Pd(II) + 5 mg L^{-1} Ni(II), Cu(II), Cd(II), Zn(II), Mg(II)[a]	10	5.0	50.0	52.4	105
Pd(II) + 10 mg L^{-1} Ni(II), Cu(II), Cd(II), Zn(II), Mg(II)[b]	10	5.0	50.0	32.1	64
Tap water (n = 6)[c]	15	0.5	7.5	6.87 ± 0.37	91.6 ± 4.4
	10	5.0	50.0	47.7 ± 2.0	95.5 ± 4.1

[a] Total amount of matrix ions > 250 µg.
[b] Total amount of matrix ions > 500 µg.
[c] Mean of the results of determination at 95% confidence interval.

The obtained values are close to the results reported in the literature for other ion-imprinted materials (Table 1).

On the basis of the studies performed on the effect of interfering ions (Table 2) the Pd–DMG–VP polymer prepared in chloroform was chosen for the analysis of the real samples. The ability of this polymer to preconcentrate the trace amounts of Pd(II) was tested in the following experiment. The different volumes (2–100 mL) of the solution of Pd(II) containing 20–50 µg of Pd(II) were passed through the column in optimized conditions, then the analyte was eluted with 0.3 mol L^{-1} TU in 1 mol L^{-1} HCl solution. The calibration graph of Pd(II) prepared in this solution was linear in the range 1–80 mg L^{-1}. The recovery of Pd (Table 4) calculated from the calibration graph demonstrates that the procedure may be applied to the separation of low amounts of Pd(II) from large sample volumes. The preconcentration factor obtained for 100 mL of the sample was 33.3. The limit of the detection of Pd by FAAS was 0.18 mg L^{-1}, while the limit of the quantification was 0.59 mg L^{-1}. After the preconcentration step these values decreased to 5 µg L^{-1} and 18 µg L^{-1}, respectively. From these results it is apparent that the application of the proposed procedure allows the preconcentration and determination of trace level of Pd by FAAS technique.

The proposed method was applied for the determination of Pd in spiked tap water samples. The tap water was spiked with 0.5 mg L^{-1} and 5 mg L^{-1} of Pd(II) and equilibrated for 2 h. In order to destroy the organic matrix 2 mL of 30% H_2O_2 was added to the sample and was irradiated under a UV lamp (180 W) for 3 h. The recovery of the analyte (92–96%) (Table 4) demonstrates the suitability of this sorbent for the selective extraction and determination of Pd(II) in water samples.

4. Conclusions

The new sorbents based on non-covalently imprinted Pd(II) complexes with PDC, DMG, DET ligands and 4-VP within polymeric network were designed and tested as SPE materials for the selective separation/preconcentration of Pd(II) ions in a flow mode before its FAAS determination. Polymerization is considered the initial step of a successful selectivity. Hence, in order to obtain the material characterized by good analytical properties various chelating ligands were used for formation of Pd complexes as template molecules, as well as various solvents (chloroform, cyclohexanol, ethanol) were tested as porogens in polymerization process. It was observed that the type of used porogen does not significantly influence the analytical properties of sorbent. However the application of polar porogen in synthesis step can be advised in case the polymer is planned to be used for separation of analyte from aqueous samples. It was also found that the retention of Pd on the polymers in the presence of interfering ions is more significantly dependent on the imprinted ligand than the used porogen. The using of DVB as a cross-linker avoided problems with template leaching during analytical cycles. The applied synthesis procedure allows to prepared polymers with good mechanical stability, what was proved by a year using without losing sorption capacity even in harsh media such as concentrated acids.

Among all tested polymers that synthesized with the Pd–DMG–VP complex in chloroform had the best analytical performance, as good efficiency of extraction, reproducibility of separation process, selectivity, and stability. Its application resulted in decreasing of the limit of detection of Pd by FAAS technique to 5 µg L^{-1} (for 100 mL of sample) and achieving 33-fold enrichment factor of analyte. The optimized separation conditions of Pd on prepared polymers indicate the possibility of using such polymers in a flow-injection FAAS procedure. Such on-line coupling of separation column with FAAS detection requires using of high flow rates of the eluent solution, what was presented in [24]. In such procedure the flow rates of sample and eluent as high as 4 mL min^{-1} could be used providing quantitative retention and extraction of analyte from Pd–DMG–VP sorbent and as well as efficient introduction of sample to the flame of AAS detector.

Summarizing, with a proper choice of the ligand complexing of analyte and synthesis process, ion imprinted polymers could satisfactorily replace other solid phase materials due to their advantages as simplicity in their preparation, low cost, flexibility in manufacturing, mechanical and chemical stability, kinetically faster interactions and rebinding mechanism, reusability, high retention capacity, and simplicity in automation of extraction process.

Acknowledgment

The authors kindly acknowledge the financial support from the Polish Ministry of Science and Higher Education (project N N 204 246 135).

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