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Separation of ruthenium from environmental samples on polymeric sorbent based on imprinted Ru(III)-allyl acetoacetate complex

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ABSTRACT

A new ion imprinted polymer (IIP) for ruthenium recognition/pre-concentration was prepared via bulk polymerization using methacrylic acid as the functional monomer and ethylene glycol dimethacrylate as the cross-linking agent in the presence of Ru(III)–allyl acetoacetate complex as a template. The synthesized IIP was used as a new support for solid phase extraction (SPE) of ruthenium from environmental samples before electrothermal atomic absorption spectrometric determination. Variables affecting the SPE process, such as pH, load and elution flow rates, as well as concentration and volume of the eluting solution, were evaluated. The optimized procedure consists of a sample loading (sample pH of 6.5 ± 0.5) through IIP-SPE columns containing 200 mg of the synthesized IIP at a flow rate of $1.0\,\mathrm{mL\,min^{-1}}$. Elution was performed by passing $0.3\,\mathrm{mol\,L^{-1}}$ thiourea in $0.1\,\mathrm{mol\,L^{-1}}$ HCl at a flow rate of $1.0\,\mathrm{mL\,min^{-1}}$. For 10 mL of sample pre-concentration factor of 20 was achieved. The limit of detection of the method was $0.32\,\mathrm{ng\,mL^{-1}}$, while the relative standard deviation for six replicated separation processes was 2.5%. Good selectivity of the synthesized material for Ru(III) ions against other transition metal ions assures efficient removal of matrix of analyzed samples (tap and river water, municipal and road sewages, and grass) by the proposed IIP-SPE procedure.

1. Introduction

Ruthenium, which belongs to platinum group metals, is typically present in common terrestrial rocks at $\mathrm{ng\,g^{-1}}$ level. Due to its unique physical and chemical properties, such as high melting temperature, inertness towards many chemical reagents, hardness, good conductivity, and versatile catalytic effect, growing use of ruthenium in different fields has been observed. The total ruthenium demand in 2006 year reached 52 tons, and was higher that demand for rhodium and iridium [1]. However, the demand fell by 40% from 2006 to 2010 due to the global economic crisis which also affected the prices of all noble metals. The metal was mainly used in the electronic (73%), electrochemical (13%) and chemical industries (10%), with smaller amounts being used in other applications. The chemical industry consumes significant volumes of ruthenium in process catalysts used for the production of acetic acid from methanol, ammonia from natural gas, and special chemicals [1,2]. In electronics, ruthenium is largely used for manufacture of electrical contacts and chip resistors [3]. Recently, ruthenium together with platinum have been applied as effective catalysts in fuel cells and dye-sensitized solar cells [4–6]. Potential anticancer properties of ruthenium complexes have been also extensively studied. As a result of the numerous research activities, two ruthenium compounds, i.e. NAMI A and KP1019, have already entered clinical trials, while a few others, in particular the ruthenium arenes, are currently undergoing advanced preclinical testing [7–9].

Extensive use of ruthenium based catalysts in industrial processes and more common generation of e-wastes as well as its use in medicine result in raising of ruthenium content in the environment. The content of ruthenium in aquatic system, sewage sludge, road dust, and soil has been found in the range 0.1–13 $\mathrm{ng\,g^{-1}}$ [10,11] while in raw incinerator ash has exceeded 100 $\mathrm{ng\,g^{-1}}$ [11]. A survey of literature indicates that few methods for the determination of ruthenium at trace level have been applied [12–28]. Generally, the sensitivity and selectivity of spectrophotometric methods, even based on catalytic effect of ruthenium on redox reactions, are not sufficient [12–15]. In order to enhance method's selectivity, the application of derivative spectrophotometric determination has been proposed [16,17]. Many interference of matrix origin influence the accuracy of determination of ruthenium by atomic absorption spectrometry [18–24], spectrofluorimetry [25,26], and inductively coupled plasma mass spectrometry (ICP MS) [9,10,27]. Therefore, different separation procedures, such as volatilization [28], co-precipitation [29], solvent extraction [30], and solid phase extraction (SPE) [22,31–36], have been used to isolate and pre-concentrate ruthenium from samples containing noble and base

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Table 1
The survey of methods applied for the determination of ruthenium by spectrometric techniques.

Preconcentration/separation procedure	Detection technique	Limit of detection	Analyzed sample	Ref
–	FAAS	$0.515\,\mathrm{mg\,mL^{-1}}$ $1.17\,\mathrm{mg\,mL^{-1}}$	Powder catalysts Pt:Ru 1:1 Pt:Ru 1:3	[18]
–	ETAAS	$0.065\,\mathrm{ng\,mL^{-1}}$	Chemicals: $Ru(bpy)_3Cl_2{\cdot}6H_2O$, dendrimers	[20]
–	ETAAS	$1.52\,\mathrm{ng\,mL^{-1}}$	Pharmaceutical compounds	[23]
–	ID ICP MS	$0.014\,\mathrm{ng\,g^{-1}}$	Roadside soil, certified reference materials: BCR-723, WGB-1, TDB-1	[10]
–	ETV ICP MS	$1\,\mathrm{pg\,g^{-1}}$	Photographic emulsions and films	[27]
Electrochemical preconcentration – electrodeposition on graphite tube	ETAAS	$0.236\,\mathrm{ng\,mL^{-1}}$ $59.0\,\mathrm{ng\,g^{-1}}$	Road tunnel dust CW7, vehicle exhaust particulates: CRM NIES 8 (0.1 g)	[24]
Co-precipitation with chitosan	ETAAS	$0.6\,\mathrm{ng\,mL^{-1}}$	Spring and river water, sewage	[29]
Activated carbon TPTZ-AC	ETAAS	$0.8\,\mathrm{ng\,mL^{-1}}$	River, sea and waste water	[31]
Cation exchange resin Amberlite CG-120	ICP MS	$< 4\,\mathrm{ng\,g^{-1}}$	Copper–nickel sulphide ore (0.02 g)	[32]
TEVA (Aliquat 336 on Amberchrom CG-71)	ICP MS	$5\,\mathrm{pg\,g^{-1}}$	Peridotite powder, certified reference material: PML P-2 (0.2 g)	[34]
Anion-exchanger Dowex 1-X8	ICP MS ICP OES	$0.22\,\mathrm{ng\,mL^{-1}}$ $14\,\mathrm{ng\,mL^{-1}}$	Geological certified reference materials: PTM-1, PTC-1, SARM 7 (1 g)	[33]
Anion-exchanger Dowex 1-X8	ID ICP QMS	$0.015\,\mathrm{ng\,g^{-1}}$	Road dust, soil (0.2 g)	[35]
Anion-exchanger AG 1-X8	ID ICP MS	$0.2–0.5\,\mathrm{ng\,g^{-1}}$	Certified reference materials: WPR-1, WMS-1 Meteorite sample (Orgueil) (0.6–1.5 g)	[36]
Ion imprinted polymers Ru–TSd Ion imprinted polymers Ru–AcTSn	ETAAS	$0.16\,\mathrm{ng\,mL^{-1}}$ $0.25\,\mathrm{ng\,mL^{-1}}$	Tap and river water, municipal sewage, grass, hair	[22]
Ion imprinted polymer Ru–AAA	ETAAS	$0.32\,\mathrm{ng\,mL^{-1}}$	Tap and river water, municipal and road sewage, grass	This paper

FAAS: flame atomic absorption spectrometry; ETAAS: electrothermal atomic absorption spectrometry; ICP MS: inductively coupled plasma mass spectrometry; ICP OES: inductively coupled plasma optical emission spectrometry; ID: isotope dilution; ETV: electrothermal vaporization; TEVA: (for tetravalent actinide) resin; TPTZ-AC: 2,4,6-tri-2-pyridyl-1,3,5-triazine activated carbon; TSd: thiosemicarbazide; AcTSn: acetaldehyde thiosemicarbazone; AAA: allyl acetoacetate.

metals. A brief summary of the literature published on this topic is presented in Table 1. Generally, atomic absorption spectrometry with electrothermal atomization (ETAAS) due to its wide availability, versatility and low costs of analysis was mostly used for determination of ruthenium.

The field of separation is continuing to expand, driven by the promise of increased market opportunities in the water purification and waste material treatment. Ion imprinted polymers (IIP) are novel sorbent materials widely applied in SPE procedures for separation and preconcentration of metal ions [37,38] and organic molecules [39,40]. The synthesis of such sorbents is made by assembly of monomers around a template molecule (usually a complex of metal ion with the organic ligand) and a subsequent polymerization using a cross-linker. Low-molecular weight compounds containing functional groups that can engage in hydrogen bonding or acid–base reactions with the monomer are useful as templates. The formation of complexes of monomers with analyte (template) may be based on covalent or non-covalent bonds. Non-covalent imprinting protocol, thanks to its versatility, is the most widely used. Type and amount of cross-linker has profound influence on selectivity and binding capacity of IIP. It also controls the morphology of the polymeric matrix and its mechanical stability. After polymerization, template molecules are removed by extensive washing steps to disrupt the interactions between the template and the monomers. Prepared polymers contain imprinting sites of a complementary shape and functionality to the template molecules [41–44].

Presently, materials with imprinted ruthenium ions have found application as catalysts in organic synthesis [2,45]. The single study on application of polymers with imprinted ruthenium ions for analytical purposes was carried out by our research group [22]. The analytical properties of sorbents, prepared by imprinting of complexes of Ru(III) with thiosemicarbazide (Ru–TSd) and acetaldehyde thiosemicarbazone (Ru–AcTSn) into polymeric network, were studied. Methacrylic acid (MAA) was used as a functional monomer, due to its unique characteristics, being capable to act as a hydrogen-bond donor and acceptor, and showing good suitability for ionic interactions. Ethylene glycol dimethacrylate (EGDMA) was used as cross-linking agent. The polymers were prepared using free radical addition polymerization by bulk method. The comparison of both polymers demonstrated better suitability of Ru–TSd polymer for SPE extraction and determination of ruthenium in environmental samples by ETAAS. However, in order to remove the excess of matrix ions retained on the polymer simultaneously with the analyte, the washing step was introduced into the procedure.

In this work the IIP were prepared using a complex of Ru(III) with allylacetoacetate (Ru–AAA) as a template molecule. Allylacetoacetate is a very interesting organic compound that acts as bidentate ligand in complexes with many transition metal ions [46,47]. The protocol of polymerization was similar as in the previous work (MAA as functional monomer, EGDMA as cross-linker, radical bulk polymerization) [22], but different template molecule and molar ratio of functional monomer to cross-linker were used. The optimization of separation conditions of ruthenium from aqueous solutions was performed in a flow mode. The effectiveness of prepared sorbent was tested for separation and determination of ruthenium by ETAAS in environmental samples (river water, municipal and road sewage, and grass).

2. Experimental

2.1. Instrumentation

A Solar M6 (Thermo Electron Corporation, UK) atomic absorption spectrometer, equipped with an electrothermal atomizer and a Zeeman background correction system, was used for the determination of ruthenium. The ruthenium hollow cathode lamp (Thermo SCIENTIFIC, USA) was operated at 10 mA current. The integrated absorbance signal of ruthenium was measured at 349.9 nm with a spectral bandpass 0.2 nm, using pyrolytically coated graphite tubes. The following optimized furnace heating program was used for the ruthenium determination: drying at 110 °C for 30 s, ashing at 1600 °C for 20 s, and atomization at 2650 °C for 3 s.

The FT-IR absorption spectra were recorded in the range between 500 and 4000 cm^{-1} with a Nicolet Magna IR 550 Series II (Nicolet, Japan). The Surface Area and Porosity Analyser Gemini VII 2390 (Micrometrics, USA) was used for the determination of surface area by BET method. Scanning electron microscope Hitachi S 3000 N (Hitachi, Japan), equipped with X-ray microanalyzer QUEST, was applied to take images of the surface of the prepared polymers. An inoLab pH Level 1 (WTW, Germany) pH meter, equipped with an electrode SenTix 21 (WTW, Germany), was used for the pH measurements.

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

The digestion of samples was performed in a microwave system ETHOS PLUS (Milestone, Italy).

2.2. Reagents and materials

A ruthenium atomic spectroscopy standard solution in HCl (1 g L^{-1}, Fluka, Switzerland) was used. Hydrochloric acid (37%, fuming, POCh, Poland) and sodium hydroxide (pure, POCh, Poland) were used to adjust the pH of samples and standards. Hydrochloric acid (37% fuming, Trace Select, Fluka,) and thiourea (puris p.a., Fluka, China) were used as a desorption agents.

Ruthenium(III) chloride hydrate (purum, 41% Ru, Fluka, UK) and allyl acetoacetate (AAA purum ≥98.5%, Sigma Aldrich, USA) were used for the preparation of Ru(III) complexes. Ethylene glycol dimethacrylate (EGDMA) (98%, Sigma Aldrich, USA), methacrylic acid (MAA) (99%, Sigma Aldrich, USA), and 2,2′-azobisisobutyronitrile (AIBN) (Fluka, France) were applied for the synthesis of polymers. Dichloromethane (POCh, Poland) and ethyl acetate (POCh, Poland) were used to remove an excess of reagents after the synthesis process. Methanol (99.8%, POCh, Poland) was dried and distilled before use. High-purity argon gas (99.999%) was used to de-aerate the solutions.

Solutions of palladium(II), rhodium(III) iron(III) chlorides, cobalt(II), nickel(II), aluminum(III) nitrates and platinum as hexachloroplatinic(IV) acid (30%) (POCh, Poland) were used to study the matrix interference. All solutions were prepared in de-ionized water obtained from a Milli-Q water purification system (Millipore, USA).

2.3. Preparation of Ru(III)-imprinted polymer

The complex of Ru(III)–allyl acetoacetate (Ru–AAA) was prepared according to the following procedure: 26 mg (0.099 mmol) of hydrated crystal ruthenium(III) chloride and 99 μL (0.720 mmol) of allyl acetoacetate (AAA) were dissolved in 0.4 mL of methanol and stirred for 15 min. In this way the dark green solid of Ru–AAA complex was obtained. FT-IR (KBr pellet), cm^{-1}: ν(OH) 3448s; ν(C—H) 2922 m; ν(C═O) 1618 vs; δ(CH═CH) 1560s; ν(C—O) 1254s, 1161 m.

The formed complex of Ru–AAA (0.038 mmol) was dissolved in methanol and mixed with MAA (17.7 mmol), as a functional monomer, and EGDMA (52.5 mmol), as a cross-linking monomer. Next the AIBN (150 mg), as chemical initiator, was added and the solution was stirred and transferred into glassy polymerization ampoules. The ampoules were purged with argon for 10 min and sealed. The reaction temperature was kept constant at 55 °C for 24 h. The resultant solid polymer was crushed and washed with dichloromethane and ethyl acetate in order to remove the excess of the reagents. Then, the polymer was dried, ground and sieved. The fraction of diameter range <150 μm was used as a column filling. FT-IR (KBr pellet), cm^{-1}: ν(OH) ~ 3500; ν(C—H) 2981–2853 m; ν(C═O) 1727vs; ν(C—O) 1178 m.

The imprinted Ru(III) ions were leached from individuals portions of the polymer (0.2 g) by passing 40 mL solution of 0.3 mol L^{-1} thiourea in 0.5 mol L^{-1} HCl. The concentration of ruthenium in leaching solution was measured by ETAAS. The scheme of the preparation of the Ru(III)-AAA-MAA polymer is shown in Fig. 1.

The control polymer (CP) was synthesized in a similar way, but in the absence of Ru(III) ions. The CP polymer has a similar IR spectrum as the ion imprinted polymer indicating the similarity in the backbone structure. Differences have been observed in the fingerprint region.

2.4. BET surface area

Nitrogen sorption analysis was carried out on approximately 0.65 g portions of polymers. The samples were degassed for 16 h at 80 °C. The surface area of the imprinted polymers was derived from the adsorption isotherms using a BET (Brunauer, Emmett and Teller) method.

2.5. Separation procedure

Glassy column with an i.d. of 5 mm was packed with 0.2 g of dry ion imprinted polymer. The sorbent was conditioned by passing 3 mL of 0.05 mol L^{-1} NaOH and next 3 mL of 0.1 mol L^{-1} HCl at a flow rate of 1 mL min^{-1}. For the retention of the analyte, the Ru(III) standards (50 ng mL^{-1}) and the samples were adjusted with diluted NaOH to pH 6.5 ± 0.5 and passed through the column at a flow rate of 1 mL min^{-1}. Then, Ru(III) was eluted from the column with 2 mL of solution of 0.3 mol L^{-1} thiourea in 0.1 mol L^{-1} HCl at a flow rate of 1 mL min^{-1}.

All reported retention efficiencies were calculated as the ratio of the mass of ruthenium retained on the column to the initial mass of ruthenium loaded onto the column. The mass of the analyte retained on the column was derived from the difference in analyte concentration in the solution before and after loading on the column. The efficiency of elution was calculated as the ratio of the mass of ruthenium eluted from the column by a stripping agent to the mass of ruthenium retained on the column. The metal concentration in the solutions was determined by ETAAS.

2.6. Preparation of samples

Tap water and river water taken from the Biała river (Białystok, Poland) were spiked with 1 ng mL^{-1}; 50 ng mL^{-1} of ruthenium. Sample of sewage was obtained from the sewage treatment plant in Białystok. The sewage was spiked with 50 ng mL^{-1} of ruthenium. After 2 h equilibration, samples were filtered through PVDF filters (Whatman, 0.45 μm) and adjusted to the required pH with diluted NaOH. Grass was collected in suburban area (Białystok, Poland) and prepared for analysis according to the procedure described in [48]. Each grass sample (500 mg) was mineralized in a closed microwave system with 6 mL HNO_3 and 1 mL H_2O_2. The residue was evaporated near to dryness with 2 mL HCl on a hot place and next diluted with Milli-Q water to 20 mL. The samples of grass were spiked with 50 ng mL^{-1} of ruthenium.

3. Results and discussion

The new material prepared by imprinting of complexes of Ru(III) with allylacetoacetate and methacrylic acid into polymeric network was examined for solid phase extraction of ruthenium. The surface morphology of the CP and Ru–AAA–MAA polymers is shown in Fig. 2. It can be seen that the CP polymer has a smooth surface. The particles of ion imprinted polymer are smaller (50–150 μm in diameter) and rougher than the particles of the control polymer. This roughness of the surface of imprinted polymer after removing

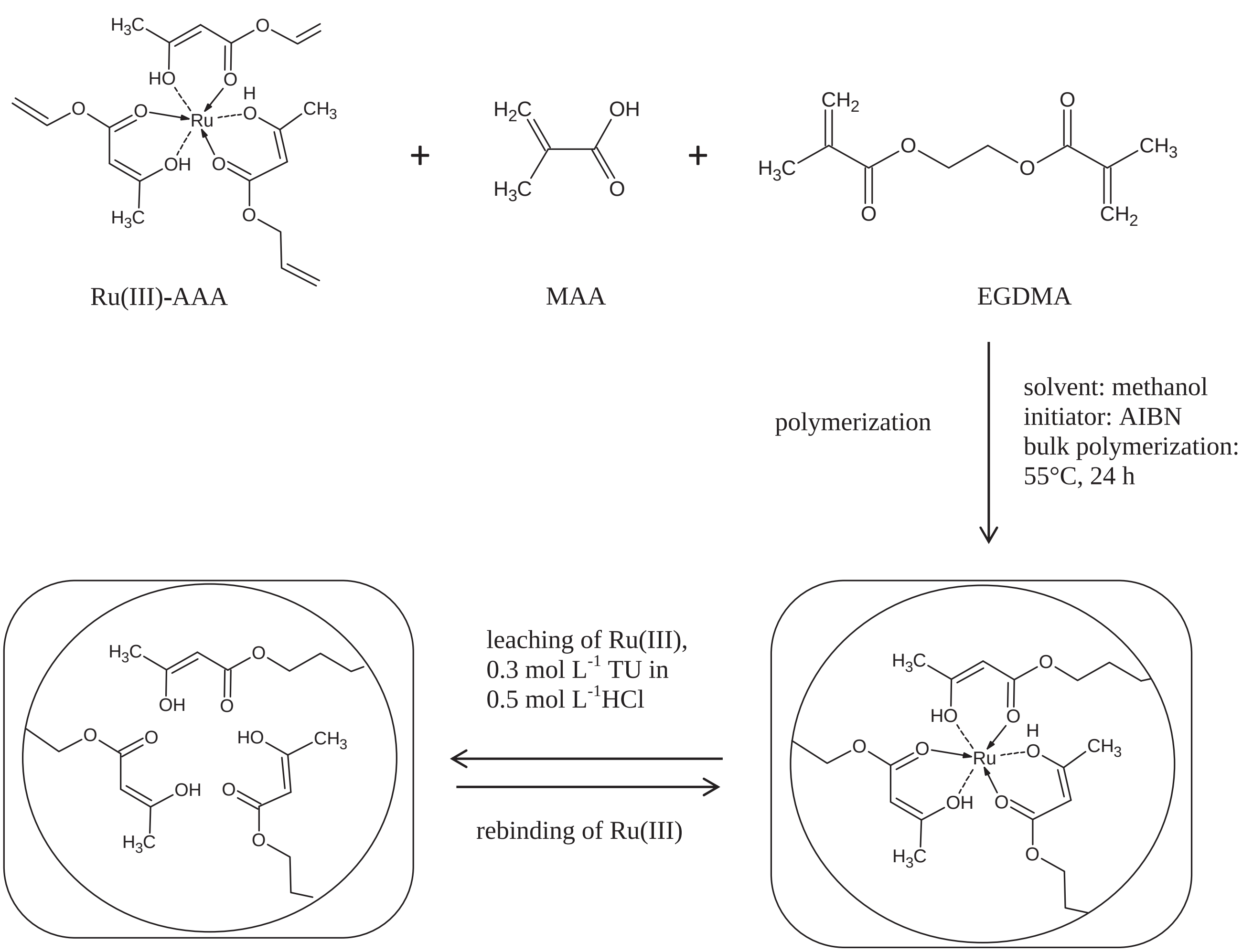

Fig. 1. Scheme of the preparation of Ru(III)–AAA–MAA imprinted polymer.

of Ru(III) ions should be considered as a factor providing an increase in the surface area. The BET surface area and average pore diameter for unleached and leached particles of imprinted polymers were 1.03 and 2.39 $m^2\,g^{-1}$ and 10.53 and 11.18 Å, respectively. The surface area of particles of leached IIP is 2.3-fold higher than particles of unleached IIP.

3.1. Optimization of separation conditions

Numerous parameters, like the effect of pH and flow rate of sample, the eluent concentration, volume and its flow rate, were optimized to obtain the maximal extraction of Ru(III) from the solution. Initially, the polymers were conditioned with 0.05 $mol\,L^{-1}$ HCl. The influence of sample pH on the retention of 100 ng of Ru(III) ions on polymers was studied at pH range from 1 to 12. The retention of analyte from acidic and highly basic solutions was low (10–30%), but it increased to 90% from solutions of pH 6.0–9.0 (Fig. 3). The simple hexachlororuthenium complex ($RuCl_6{}^{3-}$) is stable only in strong hydrochloric acid (6 $mol\,L^{-1}$). In solutions of lower acidity ruthenium forms several complexes which contain various amounts of chloride-, hydroxo- and aqua-ligands, such as $[RuCl_5(H_2O)]^{2-}$, $[RuCl_4(H_2O)_2]^{-}$, $[RuCl_3(H_2O)_3]$, $[RuCl_3OH(H_2O)_2]^{-}$, $[RuCl_3(OH)_2(H_2O)]^{2-}$. Ruthenium in neutral solutions forms also complex multinuclear species, such as $[Ru_2OCl_{10}]^{4-}$ or $[Ru_2OCl_8(H_2O)_2]^{2-}$ [49,50]. The aqua and hydroxocomplexes carry either a lower negative charge than the chlorocomplexes or even a slight positive charge, depending on equilibration time and kinetics of the reaction involved. Probably, these forms are retained on the polymer from weakly basic solutions. In order to avoid precipitation of other ions, potentially present in analyzed samples, sample pH was adjusted to 6.5 ± 0.5 with diluted NaOH in further experiments.

The effect of type (methanol, thiourea, HCl), concentration (0.01–0.2 $mL\,L^{-1}$ HCl) and volume (1–4 mL) of conditioning reagent on the efficiency of Ru(III) retention was studied at optimal pH. The highest retention of analyte (93%) was obtained after conditioning of column with 3 mL of 0.1 $mol\,L^{-1}$ HCl. The influence of sample flow rate on the retention of Ru(III) ions was studied in the range 0.2–5 $mL\,min^{-1}$. As the efficiency of retention of Ru(III) was almost constant in the studied range (93–84%), the sample was passed through the column at flow rate of 1.0 $mL\,min^{-1}$ in subsequent experiments.

Initially, the elution of Ru(III) ions retained on ion-imprinted polymers was carried out with solutions of hydrochloric acid. As the efficiency of ruthenium elution with 3 $mol\,L^{-1}$ HCl did not exceed 50%, acidic thiourea solutions were later used. Thiourea forms with Ru(III) ions monothiourea $[RuTU]^{2+}$ and trithiourea $[RuTU_3]$ complexes with a formation constant K_1 equal to 16.3 ± 0.5, and formation constant K_3 equal to 5.3 ± 0.1 [51,52]. It was reported that the formation of complexes of Ru(III) with TU was faster and easier along with the increasing concentration of hydrochloric acid and temperature [53]. For this reason, the efficiency of elution of ruthenium with HCl and TU solutions (0.3 $mol\,L^{-1}$) of different acidity (0.1–3.0 $mol\,L^{-1}$) has been studied. However, as can be seen

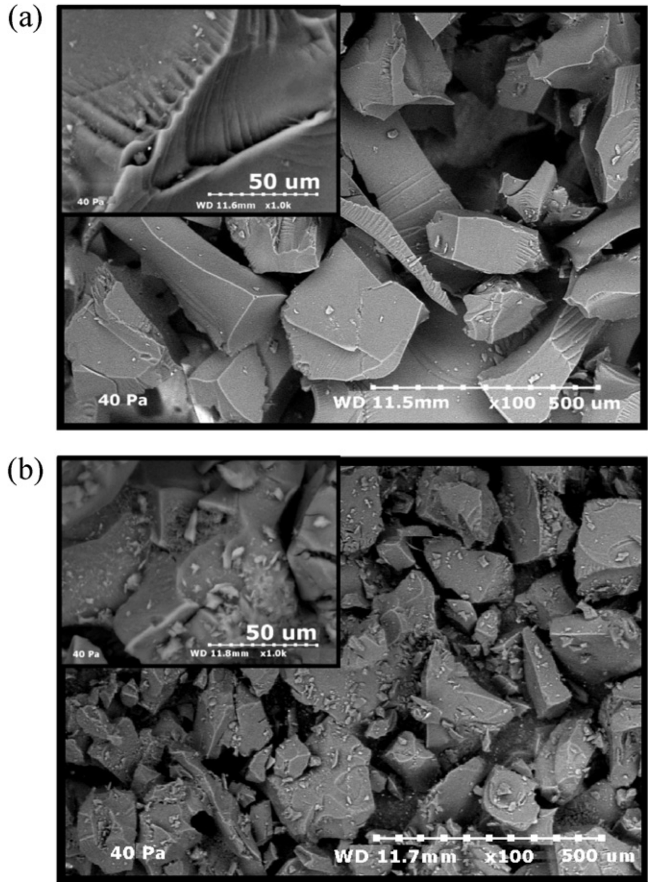

Fig. 2. SEM images of the surface of polymers (100-fold magnification): (a) AAA–MAA control polymer, (b) Ru(III)–AAA–MAA imprinted polymer after leaching of Ru(III) ions. SEM images in upper left side show 1000-fold magnification of the surface of polymers.

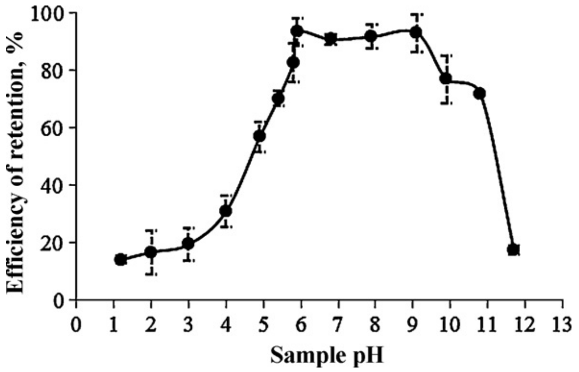

Fig. 3. Effect of sample pH on the retention of Ru(III) ions (200 ng) on the IIP (flow rate 0.5 mL min^{-1}). The error bars represent the standard deviation of results for $n = 3$.

in Fig. 4, the quantity of ruthenium eluted from the column was decreasing with increasing concentration of HCl. The efficiency of ruthenium elution was independent on thiourea concentration in the range 0.3–0.6 mol L^{-1}. The best recovery of analyte from polymer was obtained with solution of 0.3 mol L^{-1} TU in 0.1 mol L^{-1} HCl. That agent was used for examination of the influence of flow rate of eluent on elution of metal. The increase of flow rate from 0.2 to 1.5 mL min^{-1} caused the decrease in the efficiency of analyte elution from 95% to 78%. The flow rate equal to 1.0 mL min^{-1} was used for subsequent experiments. It is worth mentioning, that in order to remove the residue of analyte from the column at the end of desorption cycle the column was washed with 3 mL of 0.05 mol L^{-1} NaOH.

The volume of eluent necessary to remove analyte from the column quantitatively was also studied. The efficiency of elution of ruthenium from the polymer with 2 mL of eluent was 96.9 ± 1.2% ($n = 6$). In order to enhance the preconcentration factor, the volume of stripping agent should be as low as possible. The detailed study of elution profiles (Fig. 5a), using approximately 0.15 mL aliquots of eluent, showed that with 0.55 mL volume of stripping agent the recovery of analyte was 85.6 ± 4.9%, while with 0.95 mL was equal to 95.7 ± 1.2% (Table 3).

For the comparison, a similar experiment was performed on the CP polymer. The cumulative recovery of the analyte with increasing volume of eluent (Fig. 5b) shows that the quantitative elution of analyte from IIP and CP polymers may be achieved with 1.4 mL and 2.5 mL of eluent, respectively. This experiment demonstrates that different interactions are responsible for binding the analyte to ion imprinted and non-imprinted polymers.

3.2. *Competitive adsorption*

Competitive adsorption of Ru(III) and foreign metal ions (listed in Table 2) on the polymer was studied in solutions containing equivalent concentrations of analyte and individually added interferent (50 ng L^{-1}). Distribution ratios (D, mL g^{-1}), selectivity coefficients (α) of Ru(III) with respect to Pd(II), Pt(IV), Rh(III), Co(II), Ni(II), and Fe(III) ions were calculated in a dynamic system from the equations described in [22,54]. The distribution ratio of Ru(III) ions on IIP polymer from single standard solution (50 ng mL^{-1}) was 92.7 mL g^{-1}, while on CP polymer was 71.2 mL g^{-1}. The values calculated for solutions containing two competitive ions are summarized in Table 2. The value of distribution ratio for Ru(III) is a mean of D_{Ru} values obtained for all studied systems containing analyte and competitive ion. A comparison of D values for Ru(III) ions on CP and IIP polymers shows that higher distribution ratio has been achieved on ion imprinted polymer. The selectivity coefficient expresses how the sorbent responds to a particular ion with respect to the imprinted Ru(III) ions. The greater selectivity coefficient indicates greater preference for the imprinted ion. In all examined systems the selectivity coefficients were higher on IIP than on CP polymer. A relative selectivity coefficients (α_{r}), calculated as the ratio of α_{IIP} to α_{CP}, represent the selectivity factor of IIP against CP. The relative selectivity coefficients were the highest for Ru(III)/Co(II) and Ru(III)/Ni(II) systems. Lower values of α_{r}, but always exceeding 1.5, were obtained in the presence of platinum group metals. It is probably a result of great chemical similarity between these elements and small differences in ionic radius of platinum group metals (Ru(III) = 0.68 pm, Pt(IV) = 0.625 pm, Pd(II) = 0.64 pm, Rh(III) = 0.665 pm [55]). The high distribution ratio of Pd(II) on both polymers is probably the effect of faster ligand-exchange process of Pd(II) than Ru(III) ions. Palladium(II) ions exhibit the highest rate of aqua ligand exchange (~10 s^{-1}) among all platinum group elements [56]. Ruthenium and platinum belongs to "slow" metal ions that exchange some of their ligands even within the range of hours.

As can be seen in Fig. 5a, the elution profiles of analyte from the polymer in the presence of interfering ions of matrix origin (tap and river water, and municipal sewage) correspond to equivalent profile obtained for the standard solution. It confirms that ruthenium is more selectively bound to imprinted sites of the polymer than other transition ions. Moreover, selectivity of the Ru–AAA–MAA sorbent is higher than that one of the Ru–TSd polymer, which contains the same functional and cross-linking monomers, but different template [22].

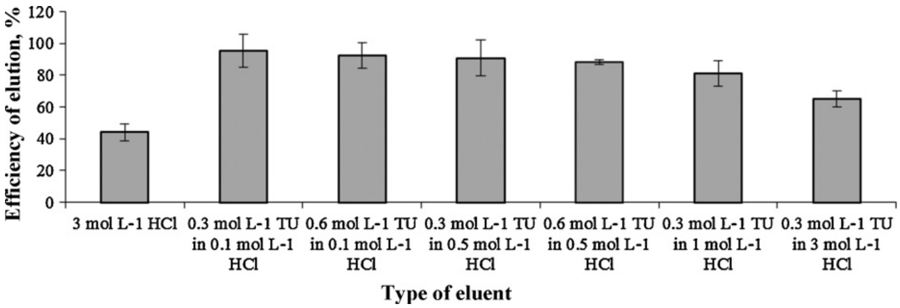

Fig. 4. Efficiency of the elution of Ru(III) from IIP with different stripping agents (eluent volume 3 mL, flow rate 0.5 mL min^{-1}). The error bars represent the standard deviation of results for $n = 3$.

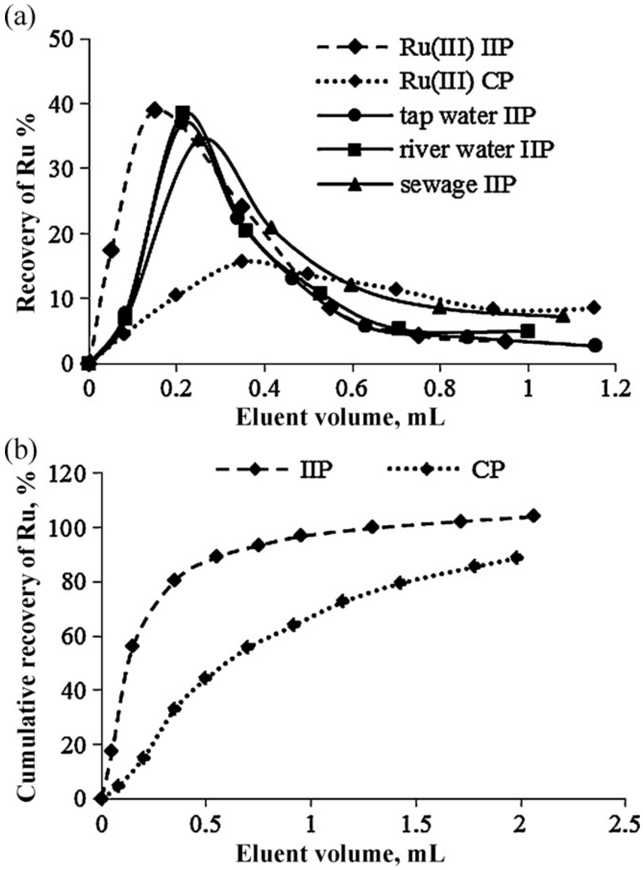

Fig. 5. Recovery of Ru(III) (100 ng) from IIP and CP polymers with 0.3 mol L^{-1} TU in 0.1 mol L^{-1} HCl (flow rate 1.0 mL min^{-1}) recovery of Ru(III) from standard solutions, and spiked tap water, river water and municipal sewage with 0.15 mL aliquots of eluent cumulative recovery of Ru(III) from standard solutions.

3.3. *Analytical characteristic and application*

The analytical performance of the method was evaluated under optimized experimental conditions mentioned above. The reproducibility of the separation procedure was studied in six successive retention and elution cycles. The efficiency of the retention process of Ru (100 ng) on the polymer was 90.0 ± 2.5%, while the elution efficiency was 99.2 ± 2.5%. The precision of the procedure is better that 3%.

Ruthenium standard solutions used for the preparation of calibration graphs were submitted to the evaluated separation procedure. The calibration graphs have been prepared using different volumes of the eluent solution (0.5 mL and 2 mL). The calibration graph was linear up to 25 ng mL^{-1} of ruthenium using 0.5 mL of TU solution. The enhancement factor, defined as the ratio of the slopes of the calibration graphs before and after the preconcentration step, was equal to 5. The limit of detection of ruthenium after preconcentration of 10 mL of sample (LOD = blank + $3\text{SD}_{\text{blank}}$) was 0.32 ng mL^{-1}, while limit of quantification (LOQ = blank + $10\text{SD}_{\text{blank}}$) was 0.52 ng mL^{-1}. These values are 3–6 times lower than those obtained for direct determination of ruthenium in acidic thiourea solution (0.3 mol L^{-1} TU in 0.1 mol L^{-1} HCl) by ETAAS technique (LOD = 1.1 ng mL^{-1}, LOQ = 3.2 ng mL^{-1}). Moreover, they are comparable to the results obtained by ICP MS method after ruthenium separation on ion exchangers Amberlite CG-120 [32], Dowex 1-X8 [33], and AG 1-X8 [35] (Table 1).

The calibration graph prepared using 2 mL of eluent volume was used for analysis of environmental samples. Larger volume of eluent was applied in order to provide the total recovery of ruthenium from the column (Fig. 5). The graph was linear in the concentration range of 5–102 ng mL^{-1} of ruthenium. Limits of detection and quantification of ruthenium obtained from this graph were equal to 1.8 ng mL^{-1} and 4.4 ng mL^{-1}, respectively.

The breakthrough capacity of the polymer was determined by passing the standard solution (50 ng mL^{-1}) through the

Table 2
The effect of imprinting on selectivity. Competitive sorption of ruthenium and other metal ions on the Ru(III)-imprinted and control polymer (sample: 100 ng Ru + 100 ng of other ion, pH 6.5, flow rate: 1.0 mL min^{-1}, $n = 3$).

Metal ion	Distribution ratio (D), mL g^{-1}		Selectivity coefficient ($S_{\text{Ru/Inf}}$)		α_r
	CP	IIP	CP	IIP	
Ru(III)	35.5	50.7	–	–	–
Pt(IV)	23.2	20.2	1.5	2.5	1.7
Pd(II)	124.1	102.5	0.3	0.5	1.7
Rh(III)	2.0	1.1	17.7	46.1	2.6
Fe(III)	4.2	2.1	8.4	24.1	2.9
Co(II)	4.6	0.7	7.7	72.4	9.4
Ni(II)	4.3	0.7	8.2	72.4	8.8

Table 3
Recovery of Ru(III) from various samples after its separation on Ru–AAA–MAA polymer (sample: pH 6.5, flow rate: 1.0 mL min^{-1}; elution: 0.3 mol L^{-1} TU in 0.1 mol L^{-1} HCl, 2 mL, flow rate: 1.0 mL min^{-1}, $n = 3$).

Sample matrix	V, mL	C_{Ru}, ng mL^{-1}	Ru mass added, ng	Recovery of Ru ± RSD%
MQ water	2	50	100	85.6 ± 4.9[a]
	2	50	100	95.7 ± 1.2[b]
	2	50	100	96.9 ± 1.2
	10	1	10	97.5 ± 0.1
	20	1	20	98.7 ± 1.9
Tap water	2	50	100	95.0 ± 3.2
	3	60	180	84.1 ± 1.2
River water	20	1	20	95.0 ± 0.7
	40	1	40	93.5 ± 1.6
	60	1	60	84.9 ± 0.6
	2	50	100	91.8 ± 1.6
Municipal sewage	2	50	100	86.3 ± 3.5
Road sewage	2	50	100	95.1 ± 0.5
Grass	2	50	100	99.6 ± 0.4

[a] Elution with 0.55 mL.
[b] Elution with 0.95 mL.

column filled with 0.2 g of polymer. Fractions of effluent (1 mL) were collected and analyzed for ruthenium content by ETAAS. The experiment (repeated three times) was completed when the efficiency of ruthenium retention decreased to 80%. The sorbent capacity for ruthenium was calculated as 2.25 μg g^{-1} for IIP and 0.60 μg g^{-1} for CP.

The polymer was subjected to several loading and elution operations. The good efficiency of retention and reproducibility of the results was obtained even after 75 sorption–desorption cycles. This experiment testifies the good stability of the sorbent, much better than these obtained for other ion imprinted polymers, e.g. [54,57]. The sorbent in dry state can be stored at room temperature for long period of time.

Considering the molar ratio of functional monomer to cross-linking agent, we confirmed its influence on polymer properties – such as sorption capacity and mechanical stability. Lower molar ratio of monomers used in this work (1:3) as compared to [22] (1:4) resulted in lower sorbent capacity and slightly lower durability of the polymer.

The ability of polymers to preconcentrate Ru(III) ions (1 ng mL^{-1}) from large volumes of river water (10–100 mL) was tested. It was found that the procedure may be applied for the separation of trace amounts of Ru(III) from volumes up to 60 mL (Table 3).

The proposed procedure, based on separation of analyte on studied polymers, was applied for the determination of ruthenium in tap and river water, municipal and road sewage, and grass samples spiked with 20–180 ng of Ru(III). The accuracy of the procedure was checked by analysis of spiked environmental samples, because an environmental reference materials with certified ruthenium content are not presently available. The recovery of analyte from polymer was in the range 86.3–99.6% (Table 3). The reproducibility of the procedure, expressed as RSD, was in the range 0.1–3.5%. This indicates the suitability of this polymer for selective extraction of ruthenium from environmental samples. It is worth mentioning, that washing step between retention and elution of the analyte is omitted in this procedure, what confirms the good selectivity of the prepared polymeric material.

4. Conclusions

It was demonstrated that ion imprinted polymer prepared by imprinting of Ru–AAA complex in polymeric network has the ability to extract ruthenium from aqueous solutions of pH 6.0–9.0, and can be applied to the separation of analyte from environmental samples. The optimization of separation procedure was performed in a flow mode with ETAAS detection. The developed method of determination of Ru is characterized by a low limit of detection (0.32 ng mL^{-1}), good sensitivity and precision (<3.5%). The preconcentration factor obtained for 10 mL of sample was 20, while the enhancement factor was equal to 5. The sensitivity of the procedure is comparable to the results obtained after ruthenium separation on ion exchangers but with ICP MS detection [32,33,35]. The calculated selectivity coefficients clearly shows the positive effect of ion imprinting on the separation process. Selectivity of the developed IIP-SPE procedure ensures effective separation of interfering matrix and accurate determination of ruthenium in complex samples, e.g. municipal and road sewages or grass.

The use of IIP, based on imprinted Ru–AAA complex, has several advantages over the use of the IIP, based on imprinted Ru–TSd complex [22], including higher efficiency of analyte elution and procedure precision and shorter time of analysis. In spite of the lower adsorption capacity of the polymer, the main merit of the procedure is its selectivity, which is a result of the ligand chosen for complexing of the metal ion to form the template of the polymer.

With proper choice of the template and synthesis process, IIP could satisfactory replace other solid phase materials with additional advantages such as stability under high temperature and pressure, ease of production, low cost, mechanical resistance and simplicity of automation.

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