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Tracking changes in rhodium nanoparticles in the environment, including their mobility and bioavailability in soil



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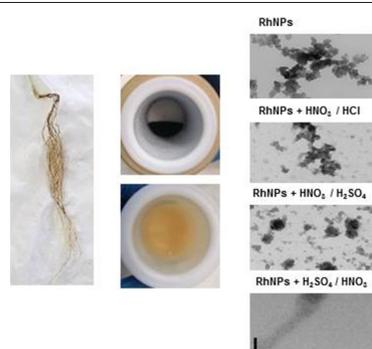
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HIGHLIGHTS

- Combination of AdSV and ICP-MS allows to distinguish ionic and metallic Rh forms.
- Two-step procedure with H₂SO₄ and HNO₃ is recommended for digestion of Rh NPs.
- Rh from the environment can be accumulated by plants.
- Rh interaction with soil increases its biogeochemical inertness.

GRAPHICAL ABSTRACT



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ABSTRACT

The goals of the undertaken studies included assessment of the mobility of Rh nanoparticles (Rh NPs) and ionic forms (Rh(III)) in soil, optimization of the digestion procedure of environmental samples containing Rh NPs, and comparison of Rh NPs and Rh(III) uptake and bioaccumulation by hydroponically cultivated plants. Mass spectrometry with inductively coupled plasma (ICP MS) was used to determine the total content of Rh in solutions obtained after the processes of digestion and extraction. Transmission Electron Microscopy (TEM) supported the investigation of Rh NPs decomposition and proved the presence of uptaken nano forms in plant tissues. Adsorptive stripping voltammetry (AdSV) allowed to distinguish ionic and metallic forms of Rh, based on the fact that Rh NPs are electrochemically inactive. A two-step digestion procedure with H₂SO₄ and HNO₃ was proposed for efficient decomposition of Rh NPs. Based on single extractions with selected extractants, it was found that independently of its chemical form Rh is substantially immobilized in soil. The mobility of Rh(III) and Rh NPs was below 38% and 0.02%, and the accumulation factor in leaves equaled 0.2 and 4.4, respectively.

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1. Introduction

Rhodium together with platinum and palladium belongs to the platinum group elements (PGEs). Its content in the earth's crust is estimated at about 0.1 ng g⁻¹ (Fortin et al., 2011; Greenwood and Earnshaw, 1989). It is one of the few elements that has only one stable isotope -

¹⁰³Rh (Czerczak et al., 2012). Rhodium accompanies nickel and cobalt deposits. It can also appear as an admixture of platinum ore - sperrylite (PtAs₂), sulphide ore of ruthenium (RuS₂) and a natural alloy of osmium and iridium - osmiiride, which accompanies native platinum. It can also contribute to gold deposits. The most abundant sources of rhodium are nickel - copper sulphide ores located in Sudbury, Ontario, Canada, and in South Africa. Local deposits contain up to 0.1% of rhodium (Greenwood and Earnshaw, 1989). Being exceptionally inactive, and at the same time very rare in the earth's crust, rhodium is an extremely valuable and

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expensive raw material of high economic importance. Therefore rhodium is recognized as one of the technology critical elements (TCEs) (European COST Action TD1407: Network on Technology Critical Elements) (Cobelo-García et al., 2015).

Due to its unique chemical and physical properties, rhodium is applied in many industries, including automotive, jewelry, medicine and electronics. Car catalysts are the main source of this element's emission to the atmosphere. PGEs have been the primary catalysts used in the automobile industry since the mid - 1970s in USA, Canada and Japan, since the mid - 1980s in Europe, Australia and parts of Asia, since the 1990s in Mexico, Brazil and India (Fortin et al., 2011), and since 1997 in Poland (Leśniewska et al., 2004). As a result of abrasion of the catalyst's surface, more and more platinum group elements are released to the atmosphere and deposited in soils, especially in the vicinity of highways. It was noted in a number of scientific works dealing with the distribution and behavior of rhodium in roadside soils (Leśniewska et al., 2004), road dust (Leśniewska et al., 2004) and plants (Huszał et al., 2005; Leśniewska et al., 2004). Despite its negligible chemical activity, rhodium can be transformed from the insoluble metallic form into some soluble ones. The environmental factors influencing this process are soil pH and redox potential, pH of water, salinity and the presence of inorganic (mainly chlorides) and organic ligands (humic acids). Rh(III) forms complexes with soft ligands such as chlorides, sulfides, polysulfides, cyanides, and natural organic acids (Dahlheimer et al., 2007; Mulholland and Turner, 2011). Part of Rh naturally migrating in the environment becomes bioavailable, and therefore it can be assimilated by organisms and accumulated in their tissues (Colombo et al., 2008). The content of rhodium was examined in various samples collected in areas with high traffic density. Its content found in airborne particles was 4.6 ng g^{-1} (Gómez et al., 2002), tunnel dust 24.0 ng g^{-1} (Helmers and Mergel, 1998), road dust 101.8 ng g^{-1} (Gómez et al., 2002), surface soil 18 ng g^{-1} (Zereini et al., 1997), grass 0.65 ng g^{-1} (Helmers and Mergel, 1998), and sediments core $0.06\text{--}0.46 \text{ ng g}^{-1}$ (Almécija et al., 2016).

Rhodium in the environment still remains at a very low level, so analytical techniques applied for its determination must be characterized by very low detection limits. One of appropriate techniques is adsorptive stripping voltammetry (AdSV). This method is based on formation of surface-active metal complexes and their interfacial accumulation on a hanging mercury drop electrode (HMDE). Improvement in the sensitivity of the measurements is obtained by coupling of the adsorption and catalytic hydrogen evolution in strongly acidic medium (Helmers and Mergel, 1998; Huszał et al., 2005; Kowalska et al., 2004; León et al., 1997; Tae-Kee et al., 1994). The obtained detection limit for rhodium equals 0.2 ng L^{-1} (Huszał et al., 2005). Moreover, second derivative transformation can be used to obtain further significant decrease in the detection limit, which allows to detect 200 fmol L^{-1} Rh in the voltammetric cell (Almécija et al., 2016).

More often than AdSV, inductively coupled plasma mass spectrometry (ICP MS) is applied for Rh determination (Liu et al., 2018; Rinkovec, 2019; Suoranta et al., 2016). The only stable isotope of rhodium is ^{103}Rh . Determination of Rh in the ng L^{-1} range is impaired by spectral interferences originating from $^{63}\text{Cu}^{40}\text{Ar}^+$; $^{86}\text{Sr}^{17}\text{O}^+$; $^{86}\text{Sr}^{16}\text{O}^{1}\text{H}^+$; $^{87}\text{Sr}^{16}\text{O}^+$; $^{87}\text{Rb}^{16}\text{O}^+$; $^{66}\text{Zn}^{37}\text{Cl}^+$; $^{68}\text{Zn}^{35}\text{Cl}^+$; $^{206}\text{Pb}^{2+}$ (Abdulbur-Alfakhoury and Leermakers, 2021; Savignan et al., 2021). The problem of spectral interferences can be dealt with in two ways, either by the removal of interfering ions or by correction of the measured signal. Theoretical and instrumental approaches can be applied: mathematical corrections, application of a nebulizer with cryogenic desolvation, matrix separation of interfering species using offline/online chromatographic systems, cold plasma conditions, collision/reaction cell technologies (Meeravali and Jiang, 2008; Savignan et al., 2021), and high resolution mass spectrometers (Bencs et al., 2003; Gomez et al., 2000; Suoranta et al., 2016).

Application of both techniques (AdSV and ICP MS) requires liquid samples, so digestion process must be performed before Rh determination. In case of PGEs following reagents are proposed for sample

digestion: *aqua regia* with an addition of HF (Gomez et al., 2000), *aqua regia* with additional heating with HCl (Higney et al., 2002) and a mixture of conc. HNO_3 and conc. HCl in ratio 3:4 (Kowalska et al., 2014) or 5:2 (Mittra et al., 2021). To assess the real risk related to environmental contamination with PGEs, and their mobility and bioavailability, fractionation studies should be done. Mobility of the elements in soil is evaluated based on single extraction with acetic acid (Lilleengen and Wibetoe, 2002; Pelfrène et al., 2020). Hydroxylamine hydrochloride is used to define the reducible fraction (Anawar et al., 2008; Krasnodębska-Ostęga et al., 2001; Palumbo-Roe et al., 2015), and hydrogen peroxide to define the organic fraction (Arunachalam et al., 1996; Couturas et al., 2000). Recommended procedure lasts 16 h (Krasnodębska-Ostęga et al., 2006; Leśniewska et al., 2017; Miličević et al., 2017; Wali et al., 2014), so application of ultrasounds was suggested to shorten the extraction time (Arain et al., 2008; Canepari et al., 2005; García-Casillas et al., 2014; Krasnodębska-Ostęga et al., 2006; Leśniewska et al., 2016; Rusnák et al., 2010; Sihlahla et al., 2020). Rhodium speciation was also studied in freshwater samples. Although hydroxylated rhodium complexes dominate in the water environment, it was indicated that organic matter can effectively bind rhodium, nevertheless with very slow reaction kinetics (Cobelo-García, 2013).

The aims of the presented research were: to optimize the digestion procedure of samples containing Rh NPs, to assess the uptake of Rh NPs and Rh salt by *Sinapis alba* and to compare the translocation and accumulation factors obtained for both Rh forms, to track the presence of Rh NPs in plant tissues by TEM, to estimate the mobility of both Rh forms in soil (fractionation study), to differentiate ionic and metallic forms of Rh by applying selective decomposition coupled with voltammetric detection.

2. Materials and methods

2.1. Instrumentation

The following instruments were used: ETHOS 1600 microwave digestion system with Teflon bombs (Milestone, USA); $\mu\text{AUTOLAB TYPE II}$ (ECO-CHEMIE, BV, Netherlands) comprising a hanging mercury drop electrode (HMDE) as a working electrode, a saturated Ag/AgCl reference electrode, and a glassy carbon auxiliary electrode; Transsonic T-570 ultrasonic water bath 160 W, 35 kHz (Elma, Poland); KBCG-100/250 electric dryer (Promed, Poland); Ceran 500 hotplate (Robax, Germany); ball mill (FRITSCH, Germany); Nexion 300D spectrometer equipped with a Meinhard type nebulizer and a cyclone fog chamber (Perkin Elmer, USA); EF-TEM Libra 120 transmission electron microscope (Zeiss, Germany).

2.2. Reagents

The following acids were used: HNO_3 ($d = 1.40 \text{ g mL}^{-1}$), HCl ($d = 1.15 \text{ g mL}^{-1}$), H_2SO_4 ($d = 1.84 \text{ g mL}^{-1}$), and CH_3COOH ($d = 1.06 \text{ g mL}^{-1}$) (Suprapur, Merck, Denmark); formaldehyde 36% (C.P. POCh Gliwice, Poland); deionized water (Sartorius arium mini); rhodium nanoparticles (average particle size 20–30 nm, spherical morphology, purity 99.95%, density 12.41 g cm^{-3}) (Nanostructured and Amorphous Materials Inc., USA); hydrogen peroxide 30% (C.P. Cheman, Poland); hydroxylamine hydrochloride (C.P. POCh Gliwice, Poland).

2.3. Plant sample preparation

Sinapis alba L. was cultivated in a nutrient solution containing 500 mg L^{-1} $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 150 mg L^{-1} KNO_3 , 150 mg L^{-1} MgSO_4 , 150 mg L^{-1} KH_2PO_4 , 0.482 mg L^{-1} $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$, 0.0185 mg L^{-1} $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, 8.0 mg L^{-1} EDTAFeNa, 1.25 mg L^{-1} $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 0.575 mg L^{-1} $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, and 1 mmol L^{-1} Tris (hydroxymethyl) aminomethane (all reagents were of analytical

grade). The containers with plants (9 seedlings per a 4 L container) were placed in a growth chamber at 22 °C/20 °C (16 h day/8 h night) and continuously aerated. After one week, nutrient solutions were supplemented with 0.5 mg L⁻¹ Rh(III) chloride, 1.0 mg L⁻¹ Rh(III) chloride or 5.0 mg L⁻¹ Rh NPs, introduced as a 1 g L⁻¹ stock solution, and the plants were exposed to the presence of the xenobiotic for 2 weeks. Then, they were harvested and split into leaves, stems, and roots. In the case of plants grown in the presence of rhodium nanoparticles, the roots were divided into two parts: “bright” and “dark”. Oven-dried plant material (60 °C) was pulverized in an agate ball mill (Kinska and Kowalska, 2019), transferred to polyethylene containers and stored until mineralization.

2.4. Soil samples spiked with Rh

Into each of two polyethylene containers 20 g of dry soil (pH (H₂O) = 5.5–6.5) were weighed. To one of them 200 µL of 1.000 mg mL⁻¹ of rhodium(III) standard was added (to obtain the final content of 10 µg g⁻¹ Rh), to the second one 400 µL of 5.1 mg mL⁻¹ of rhodium(0) nanoparticles (Rh NPs) suspension was added (to obtain 102 µg g⁻¹ Rh). The samples were then regularly wetted with deionized water, shaken and stirred for 30 days. According to the literature data, the samples should be allowed to equilibrate after spiking for more than 15 days to let rhodium reach equilibrium with the inorganic and organic ligands present in the matrix (Cobelo-García, 2013). After that time, the bulk samples were left to air-dry. Dried material was ground in a mortar and then sieved through a 1 mm sieve. The fraction above 1 mm was re-grounded. Both parts of the bulk sample were combined. The pH(H₂O) of soil was controlled before and after spiking with the ionic form of Rh. Only for one of three sub-samples a negligible pH decrease (about 0.05) was observed.

2.5. Digestion procedures

2.5.1. Closed system - microwave heating

50–100 mg of plant samples from the control cultivation was weighed to high-pressure Teflon vessels and Rh (III) salt or Rh NPs were added. 50–100 mg of previously dried soil samples containing Rh (III) salt or Rh NPs were weighed to high-pressure Teflon vessels. 2 mL *aqua regia*, 2 mL conc. HNO₃ or 2 mL conc. H₂SO₄ were added to each vessel and closed tightly. The HPR rotor with vessels was placed on a turntable of the microwave oven. A three-stage program with a maximum temperature of 200 °C and a maximum microwave power of 1000 W was applied (5 min: 20–90 °C; 10 min: 90–170 °C; 50 min: 170–200 °C). In the case of mineralization with H₂SO₄ this was the first step of the procedure, after which the vessels were cooled down, opened, and 1 mL of conc. HNO₃ was added to each vessel. Then, the mineralization program was repeated (second step). After the mineralization the content of each vessel was transferred to a 25.00 mL volumetric flask, and filled to the mark with deionized water. Obtained solutions were stored in PE vessels at the temperature of 4 °C till analysis. The scheme of digestion is visualized on Fig. 1.

2.5.2. Open system – conventional heating

50–100 mg of plant samples from the control cultivation were weighed to quartz crucibles and 0.1 mg Rh NPs were added. Then, 2 mL conc. H₂SO₄ was added to each crucible. The samples were evaporated nearly to dryness (for 5 h). After cooling, 1 mL conc. HNO₃ was added and the process was repeated. Next, 500 µL conc. HNO₃ was added and again evaporated nearly to dryness. After the process was completed, DI water was added to each crucible (up to 10.0 g). The solution was transfer to PP tube and centrifuged. An aliquot of the samples was piped and diluted before analysis.

The digestion was also carried out with 2 mL of conc. HNO₃ and 1 mL of conc. H₂SO₄ in sequence; according to the same scheme. The

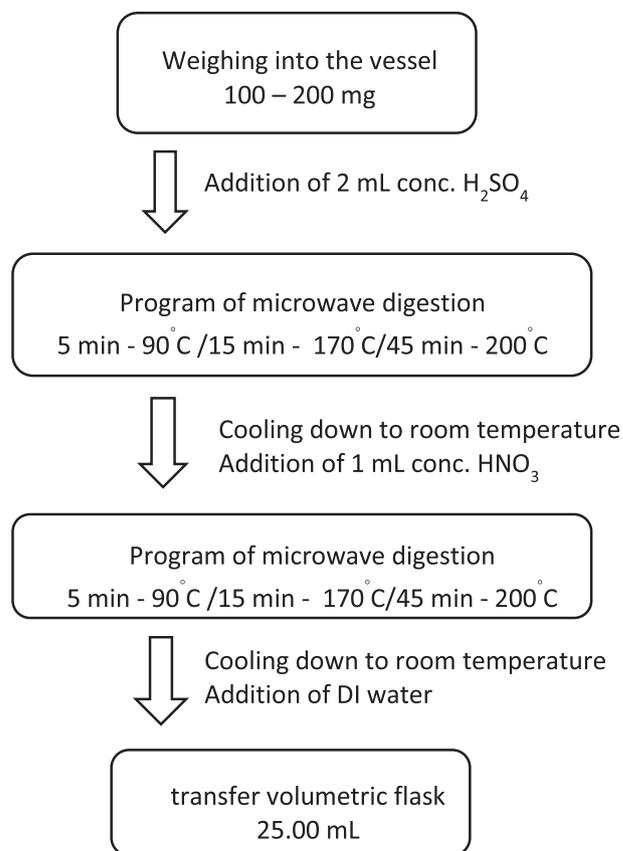


Fig. 1. Scheme of sample pretreatment using closed microwave system before Rh determination.

decomposition of NPs was also carried out without the presence of plant matrix.

2.6. Fractionation study

Mobile fraction of Rh was extracted using acetic acid (Krasnodebska-Ostrega et al., 2006): 1 g of soil was transferred to an Erlenmeyer flask and 50.00 mL of 0.43 mol L⁻¹ CH₃COOH was added. The mixture was placed in the ultrasonic water bath for 45 min. Reducible and mobile fraction was defined by utilizing a single extraction with hydroxylamine hydrochloride in acetic acid (Krasnodebska-Ostrega et al., 2001): 1 g of soil was transferred to an Erlenmeyer flask and crystals of NH₂OH·HCl were added to obtain the concentration of 5 mmol L⁻¹ in 50.00 mL of 0.43 mol L⁻¹ CH₃COOH. The mixture was placed in the ultrasonic water bath for 45 min. Organic and mobile fraction was defined using a single extraction with hydrogen peroxide and acetic acid used in sequence (Arunachalam et al., 1996): 0.2 g of soil was transferred to a quartz crucible, 3.0 mL of 30% H₂O₂ was added and the sample was heated at 90 °C to dryness. The procedure was repeated twice. Then, 3 mL of 0.43 mol L⁻¹ acetic acid was added to the residue. The mixture was placed in the ultrasonic water bath for 45 min. All extracts were immediately filtered through a filtering paper. The solutions were collected in PE bottles. The extracts were stored at 4 °C till analysis. Blank extractions were carried out for each set of analysis using the same reagents as above.

2.7. Instrumental analysis

Rh(III) was determined by AdSV in a supporting electrolyte containing 0.240 mol L⁻¹ sulfuric(VI) acid and 0.020 mol L⁻¹ formaldehyde

(Huszał et al., 2005). The solutions were purged with argon for 10 min. Preconcentration was carried out in a stirred solution at a potential of -0.7 V (E_d) for 60 s (t_d). After a resting time of 5 s, voltammetric curves were recorded in the potential range from -0.65 V to -1.25 V using differential pulse technique with a scan rate of 20 mV s $^{-1}$, modulation time of 0.05 s and amplitude of 50 mV. Double standard addition method with background subtraction was applied for quantitative determination.

ICP MS was used for determination of total content of rhodium. Analysis was performed under the following conditions: atomizing gas flow 0.85 – 1.0 L min $^{-1}$, plasma gas flow 15 – 18 L min $^{-1}$, auxiliary gas flow 1.20 – 1.40 L min $^{-1}$, generator power 1100 – 1600 W, monitored isotope ^{103}Rh . For quantitative determination calibration curve was applied.

TEM images were taken at EHT 120 kV and high vacuum. Copper grids (mesh 300) covered with a carbon layer were used for samples imaging.

3. Results and discussion

3.1. Selective distinction of rhodium chemical forms in environmental samples

One of the tasks of the undertaken studies was to propose procedures giving the possibility of selective leaching of ionic and metallic forms of rhodium from plant and soil samples. Additionally, application of two analytical techniques (AdSV and ICP MS) for rhodium determination in solutions obtained after extraction/digestion of environmental samples made it possible to distinguish between labile and non-labile Rh forms.

In the studied samples, rhodium was present in two chemical forms: as Rh(III) salt or Rh NPs. During the sample preparation process the ionic forms only need to be dissolved/leached from soil or plant matrix. As it was already mentioned, for that purpose *aqua regia* alone or with addition of hydrofluoric, hydrochloric or nitric acid can be applied (Gómez et al., 2001; Gomez et al., 2002; Higney et al., 2002). In turn, Rh NPs can be leached from the sample matrix in an unchanged metallic form or can be transformed into ionic ones. It should be noted that the properties of rhodium indicate that this metal is especially resistant to concentrated acids, with the exception of hot sulfuric acid.

Preliminary experiments started with Rh NPs standard in a form of suspension. Known amounts of Rh NPs were placed in quartz crucibles and heated in the presence of *aqua regia*, or in sequence with conc. HNO_3 and then conc. H_2SO_4 or conc. H_2SO_4 and then conc. HNO_3 . The dissolving potential of proposed acid mixtures was assessed on the basis of the images of the residues, obtained by transmission electron microscopy after evaporation of the reagents. The obtained images are presented in Fig. 2. It can be noticed that Rh NPs in the suspension form aggregates. Nanoparticles aggregate also after their dissolution in

aqua regia, and in conc. HNO_3 and conc. H_2SO_4 in sequence. There are visible changes in their diameters and morphology, size distribution significantly increases, single nano-objects occur. Only application of conc. H_2SO_4 and conc. HNO_3 in sequence ensured effective dissolution of metallic Rh, therefore the studies of environmental samples were continued taking into account the differences in the efficiency of NPs dissolution under various conditions.

In the presence of plant matrix, the efficiency of dissolution of Rh NPs with a mixture of HNO_3 and H_2SO_4 was compared for open and closed digestion systems. Leaves of *Sinapis alba* from the control cultivation (without addition of any pollutants) spiked with a known amount of Rh NPs were digested in two ways: 1) with conc. HNO_3 and conc. H_2SO_4 in sequence, 2) with conc. H_2SO_4 and conc. HNO_3 in sequence. For Rh determination, beside ICP MS, adsorptive stripping voltammetry was applied to determine the amount of ionic form of Rh in the obtained solutions.

Both used analytical techniques offer sufficiently low limits of detection of Rh but only AdSV is able to separately detect the ionic form in the presence of the metallic one. It is because Rh NPs are not electrochemically active. The voltammograms recorded for the solutions containing only Rh(III), and Rh(III) with Rh NPs are presented in Fig. 3. It can be noticed that the signal recorded for the ionic form of Rh does not increase after the addition of Rh NPs. Moreover, the addition of Rh NPs to the supporting electrolyte does not disturb the signal of Rh(III) and it does not change the linearity of the signals detected during quantitative analysis using a double standard addition method (R^2 was in the range 99.86–99.98%). The results of Rh determination in the solution obtained after digestion with $\text{HNO}_3/\text{H}_2\text{SO}_4$ in sequence are presented in Table 1. The highest Rh recovery was obtained when NPs were decomposed in a closed system with microwave heating in the presence of H_2SO_4 and HNO_3 in sequence, and Rh was determined by ICP MS. It should be emphasized that the results obtained by AdSV for the same solutions were much lower. It indicates that not all nanoparticles were transformed into ionic forms, and they are not active during voltammetric determination. However, their dimensions were sufficiently reduced to be successfully determined by ICP MS. During further studies digestion in a closed system (with various acids) was performed to differentiate between two forms of Rh present in plant and soil samples.

Leaves of *Sinapis alba* from the control cultivation (without addition of any pollutants) spiked with a known amount of Rh NPs or a known amount of Rh(III) were placed in Teflon vessels and different acids were added: 1) conc. HNO_3 , 2) *aqua regia*, 3) conc. H_2SO_4 and conc. HNO_3 in sequence. In the third case the temperature program of microwave heating was repeated twice (according to the conditions described in the experimental section). In the case of soil samples enriched with Rh(III) salt or Rh NPs decompositions were done with conc. HNO_3 only, as well as conc. H_2SO_4 and conc. HNO_3 in sequence. Digestion efficiencies were calculated based on the results obtained by ICP MS measurements (Table 2).

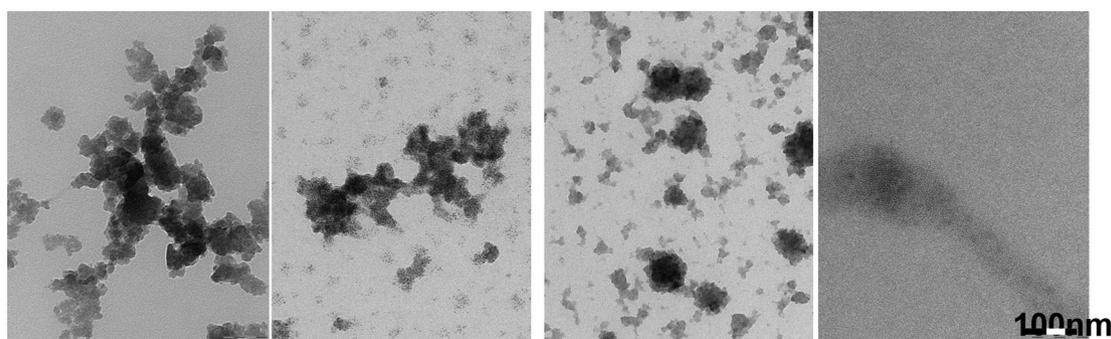


Fig. 2. Comparison of dissolution efficiency of Rh NPs after different variants of digestion. Variants visualized using TEM images of RhNPs before (a) and after microwave assisted decomposition by *aqua regia* (b), $\text{HNO}_3/\text{H}_2\text{SO}_4$ in sequence (c), $\text{H}_2\text{SO}_4/\text{HNO}_3$ in sequence (d).

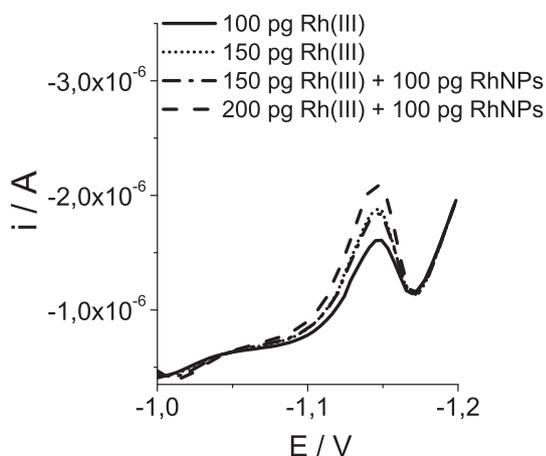


Fig. 3. The recorded voltammogram using AdSV mode at HMDE in supporting electrolyte containing $0.240 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ and 0.020 mol L^{-1} formaldehyde ($E_d = -0.70 \text{ V}$; $t_d = 60\text{s}$) with addition of 100 pg of ionic rhodium(III), 150 pg of ionic rhodium (III), 150 pg of ionic rhodium (III) and 100 pg of RhNPs, 200 pg of ionic Rh(III) and 100 pg of RhNPs.

Regardless of digestion conditions in the case of plant samples spiked with Rh(III) the recovery of Rh was above 90%, while in the case of soils enriched with Rh(III) the results were much lower. It can be a consequence of inhomogeneity of the soil samples or immobilization of Rh(III) ions by the soil components.

When plant and soil samples containing Rh NPs were digested, sufficiently high Rh recoveries were obtained only when conc. H_2SO_4 and conc. HNO_3 acids were applied in sequence. It proves that this procedure is adequate for preparation of samples containing metallic forms of Rh before determination of the total content of this element, while sample digestion with HNO_3 or *aqua regia* gives the possibility to differentiate between two forms of this element – ionic and metallic.

3.2. Bioavailability of rhodium

During the bioavailability study the total content of Rh was examined in various plant organs to assess Rh accumulation and translocation. *Sinapis alba* plants were cultivated in the presence of solution containing Rh ions or Rh nanoparticles. Leaves, stems and roots were analyzed separately. Additionally, the roots were divided into two sets, “bright” and “dark” (with visible absorption of nanoparticles). The total contents of Rh determined by ICP MS are summed up in Table 3. Simultaneous analysis of control plants, cultivated without Rh addition, showed Rh concentrations not exceeding $0.1 \mu\text{g g}^{-1}$.

The obtained data was also used to calculate the bioaccumulation (AF) and translocation (TF) factors. The first parameter is the ratio of the metal's content in the plant to its concentration in the medium, and TF is the ratio of the metal's content accumulated in upper organs to its content in the roots. It can be noted that rhodium is taken up from the nutrient solution and transported to plant organs independently on its form, with the highest amount found in roots. Sorption of

Table 1

Comparison of Rh NPs digestion efficiency under different conditions. Data are presented as a range of rhodium recovery [%] obtained by AdSV and ICP MS.

Digestion variant	Rh recovery [%]							
	Open system				Closed system			
	ICP MS		AdSV		ICP MS		AdSV	
	NPs	Plant + NPs	NPs	Plant + NPs	NPs	Plant + NPs	NPs	Plant + NPs
3) $\text{HNO}_3/\text{H}_2\text{SO}_4$	–	36 ÷ 68	–	12 ÷ 21	–	1.0 ÷ 1.3	–	–
4) $\text{H}_2\text{SO}_4/\text{HNO}_3$	71 ÷ 75	62 ÷ 81	14 ÷ 17	37 ÷ 47	87 ÷ 95	86 ÷ 90	23 ÷ 30	14 ÷ 21

“–” Not studied.

Table 2

Comparison of digestion efficiency obtained under different conditions. Data are presented as a range or as a mean value \pm sample standard deviation of the results of ICP MS measurements and expressed in %.

Digestion variant	Rh recovery [%]	
Plant	With Rh NPs	With RhCl_3
1) HNO_3	2–7	91 \pm 4
2) HNO_3/HCl (<i>aqua regia</i>)	5–17	90 \pm 5
4) $\text{H}_2\text{SO}_4/\text{HNO}_3$	93 \pm 3	93 \pm 3
Soil	With Rh NPs	With RhCl_3
1) HNO_3	1.7 \pm 0.2	63 \pm 4
4) $\text{H}_2\text{SO}_4/\text{HNO}_3$	83 \pm 4	81 \pm 2

NPs on the surface of the roots is also very important. The content of rhodium in the “dark” parts of the roots was significantly higher. Translocation factors are rather low: 0.01–0.02 (in the case of NPs the “bright” parts of root were taken into consideration). Their values in the case of NPs and Rh salt were equal, while the concentration of Rh NPs in the nutrient solution was 5 times higher than the concentration of Rh salt. The values of accumulation factors are much higher. In the case of plants cultivated with Rh salt the AF equals 650–1300, 7 and 4 for roots, stems and leaves respectively. In the case of plants cultivated with Rh NPs the AF values are 400 for roots, 0.2 for stems and 0.2 for leaves.

The presence of NPs in plant tissues was confirmed based on TEM imaging (Fig. 4). Analysis of the images indicates that leaves and roots of white mustard grown in the presence of rhodium nanoparticles contain Rh NPs, which diameters are in the range of 2–3 nm. Considering the morphology of applied nanoparticles added to the nutrient solution during plant cultivation, a significant reduction of their diameters can be noticed. In the case of root tissues, small NPs probably accumulate mainly in the cell membranes of the organelles.

3.3. Potential transformations of rhodium in the soil environment

Fractionation study using solid-liquid extraction (SLE) was performed in order to determine the influence of the soil environment e.g. on the mobility of nano- and ionic forms of Rh. Four protocols for single SLE extractions with carefully selected extractants were applied. To define: the mobile fraction a solution of $0.43 \text{ mol L}^{-1} \text{ CH}_3\text{COOH}$ (1E) was used, the reducible and mobile fraction – $5 \text{ mmol L}^{-1} \text{ NH}_2\text{OH}/\text{HCl}$ in $0.43 \text{ mol L}^{-1} \text{ CH}_3\text{COOH}$ (2E), the organic or organic and mobile fraction – hot leaching with 30% H_2O_2 followed by extraction with $0.43 \text{ mol L}^{-1} \text{ CH}_3\text{COOH}$ (4E) or with DI water (3E). The results of the fractionation study are shown in Table 4. Soil used for this experiment contained $10 \mu\text{g}$ of ionic form of Rh and $100 \mu\text{g}$ of Rh NPs in 1 g of d.m.

Combination of the obtained data and some indirect evidence (Arunachalam et al., 1996) leads to conclusions about transformations of ionic and metallic forms of Rh in soil environment. Leachable fraction of Rh under proposed extraction conditions does not exceed 40% of the amount of Rh(III) added to the soil, which means that the soil immobilized the ionic forms of Rh. Obtained results suggest that

Table 3

Total content of Rh in plants' organs. Data are presented as a mean \pm sample standard deviation obtained by ICP MS.

Rh content in the medium [mg L ⁻¹]	Plant organ	Rh [$\mu\text{g g}^{-1}$ of d.m.]	AF	TF
0.50 Rh(III)	Leaves	2.2 \pm 0.1	4.4	0.003
	Stems	3.9 \pm 0.1	7.8	0.006
	Roots	647 \pm 10	1294	–
1.0 Rh(III)	Leaves	3.5 \pm 0.1	3.5	0.006
	Stems	7.0 \pm 0.2	7.0	0.01
	Roots	647 \pm 25	647	–
5.0 NPs	Leaves	1.0 \pm 0.4	0.2	0.01
	Stems	1.0 \pm 0.1	0.2	0.01
	"Bright" roots	113 \pm 16	22.6	–
	"Dark" roots	1820 \pm 20	364	–

oxidizing conditions decrease the retention ability of soil for that element, as the extraction efficiency using the 4E scheme of extraction is about 10% higher than the efficiency for the 3E scheme. Particularly noteworthy are the results obtained for nano-forms of rhodium. The mobile fraction of Rh in soil enriched with Rh NPs does not exceed 0.1%, while after oxidation the mobility noticeably increases. The amount of Rh leached using the 4E scheme of extraction was nearly two times higher than the efficiency of the extraction done according to the 3E scheme.

4. Conclusion

The proposed two-step digestion procedure (conc. H₂SO₄ and conc. HNO₃ in sequence) ensures efficient Rh NPs dissolution and allows to determine the total content of Rh (both ionic and metallic forms) in environmental samples by ICP MS. Application of different methods of sample pretreatment gives the possibility of selective leaching of ionic and metallic forms of rhodium from plant tissues and soil matrix. Voltammetry can be successfully applied for speciation study of Rh, as it differentiates between labile (ionic) and non-labile (NPs) forms of Rh. The bioavailability studies proved that Rh is uptaken by plants independently on its form, although with different efficiency, and that it is accumulated mainly in roots. Bioaccumulation and translocation factors indicate that the transport of this element to the above-ground parts

Table 4

Extraction efficiency of Rh from soil. Data are presented as a mean \pm sample standard deviation obtained by ICP MS, expressed in %.

Soil spiked with	Leaching of added Rh [%]			
	Mobile (1E)	Mobile + reducible (2E)	Organic (3E)	Mobile + organic (4E)
RhCl ₃	2.5 \pm 0.4	2.0 \pm 0.5	20 \pm 4	38 \pm 6
Rh NPs	0.1	0.1	0.1	0.17

is negligible. Soil components strongly immobilize nano- as well as ionic forms of rhodium. To sum up, the proposed procedures can be used to track changes that Rh nanoparticles undergo in the environment.

Application of single particle ICP MS and hyphenated technic HPLC ESI MS in further studies gives possibility to get more detailed information about rhodium speciation in environmental matrixes.

CRedit authorship contribution statement

J. Kowalska: Conceptualization, Formal analysis, Investigation, Methodology, Project administration, Visualization, Writing – original draft. **E. Biaduń:** Conceptualization, Formal analysis, Funding acquisition, Investigation, Methodology, Visualization, Writing – original draft. **K. Kińska:** Conceptualization, Investigation, Methodology, Validation, Formal analysis. **M. Gniadek:** Investigation, Methodology, Visualization. **B. Krasnodębska-Ostrega:** Conceptualization, Formal analysis, Methodology, Project administration, Supervision, Visualization, Writing – original draft.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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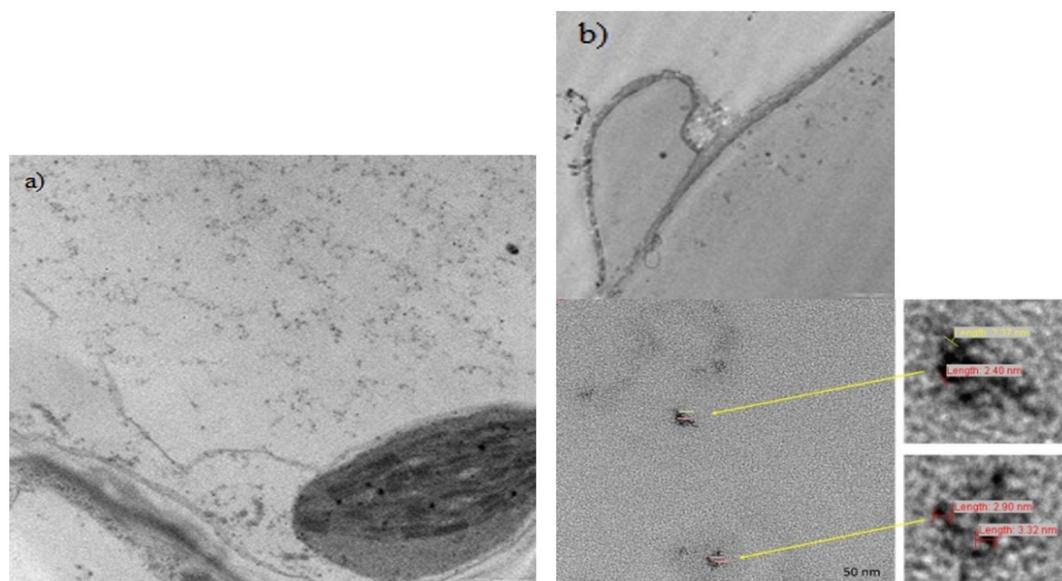


Fig. 4. TEM images of *Sinapis alba* tissues (a) leaf (b) root grown in the presence of rhodium nanoparticles.

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