Rev Anal Chem 30 (2011): 171–175 © 2011 by Walter de Gruyter • Berlin • Boston. DOI 10.1515/REVAC.2011.103

Solid-phase spectrophotometry use for the determination of trace amounts of Rh(III)

Lavinia Tofan*

Department of Environmental Engineering and
Management, Faculty of Chemical Engineering,
"Gh. Asachi" Technical University of Iasi, 71 D.
Mangeron Street, 700050 Iasi, Romania,
e-mail: lavinia_tofan@yahoo.com

*Corresponding author

Abstract

A simple and sensitive solid-phase spectrophotometric method was developed for the determination of rhodium(III) trace amounts. The proposed procedure is based on the reaction product of disodium-1-nitroso-2-hydroxynaphthalene-3,6-disulfonate(Nitroso R salt) previously loaded on Dowex 1×1 anion exchanger. To find the best analytical conditions for the determination, the experimental variables (wavelength, pH, amount of resin, sample solution volume) were optimized. Under the selected conditions, rhodium(III) can be accurately determined in the range of 0.5–2 μg/ml with an RSD of 1.18% and a degree of sensitivity, expressed by the molar absorptivity, of 3.0356×10^4 l/mol cm. The results obtained on synthetic solutions clearly indicate the feasibility of the proposed method for real sample analysis.

Keywords: determination; Nitroso R salt; rhodium; solid-phase spectrophotometry.

Introduction

Rhodium, known for its stability in corrosive environments, physical beauty and unique physical and chemical properties, is a valuable and rare metal of special importance for many industrial processes and products (Bosch Ojeda and Sanchez Rojas 2006). Currently, approximately 73% of the world production of rhodium is consumed in the production of autocatalysts, leading to its emission into the environment; here, it can be deposited along roadways, on vegetable and soil surfaces adjacent to roadways and in the streams, rivers and waterways either directly or as a run-off and can possibly enter the food chain (Ravindra et al. 2001). Rhodium and its complex salts, such as Rh(III) chlorides have been reported as a potential health risk to humans, causing asthma, allergy, rhinoconjunctivitis and other serious health problems (Rauch and Morrison 2008).

The heterogeneous composition of environmental samples and the low concentration level of rhodium make its determination really difficult. Among the analytical techniques currently used for rhodium determination, the spectrophotometric methods have a wide applicability (Bosch Ojeda and Sanchez Rojas 2005). In general, a separation and/or preconcentration step is necessary prior to rhodium determination by spectrophotometry. In this context, a significant improvement might be represented by the use of solid-phase spectrophotometry (SPS).

Applied since 1976, SPS involves techniques in which the spectrophotometric reagent is used simultaneously for preconcentration and determination of the analyte (Yoshimura et al. 1976). SPS combines the preconcentration of the species of interest on a solid substrate with subsequent measurement of the absorbance in solid phase (Brykina et al. 1995, Yadollah and Atefeh 2002, Liu et al. 2004, Pascual-Reguera et al. 2004). The preconcentration step consists either of the sorption of analyte with reagents immobilized on the surface of a solid support or of the sorption of the analyte-reagent complex obtained in solution phase on the solid surface. The right selection of the solid supports taking into account the chemical properties of the analyte or its derivative and the optical properties of the whole is the key factor in SPS methods. The solid phases used in SPS are mostly organic solid particles of diverse granulometry and composition, especially adsorbents or ion exchangers. Among the first, silica gel or modified silica (i.e., C-18 silica gel) and polydextran gels (Sephadex) and as exchangers, cationic or anionic exchangers coming from styrene or polydextran type are very useful (Valencia and Captai-Vallvey 1999). The problem of high background in the absorbance measurements directly on the colored solid phase beads (usually packed in a cuvette of 1-mm thick layer) can be eliminated by using a reference solid phase prepared under the same conditions but without sample component and by measuring at two wavelengths, one characteristic of the sample species and the other in the range where only solid phase causes attenuation of light.

Owing to the preconcentration effect and the selectivity of sorption on the ion exchanger, SPS provides increased sensitivity and selectivity than the solution methods and has been successfully applied to the determination of a wide variety of inorganic or organic species in real samples (Amin 2003, 2009, Bilba et al. 2004, Pellerano et al. 2007, Saputro et al. 2009, Koga et al. 2010, Richter et al. 2011).

This paper presents a procedure for the determination of trace amounts of Rh(III) from aqueous samples by SPS. The developed procedure is based on the reaction product of Rh(III) with 1-nitroso-2-hydroxynaphtalene-3,6-disulfonate (Nitroso R salt) previously immobilized on Dowex 1×1 anion exchanger.

Experimental

Chemicals and instruments

Stock solution of 1000 mg/l was prepared by dissolution of analytical grade reagent $RhCl_3$ in 0.1 M HCl solution. Working solutions of Rh(III) were prepared by the appropriate dilutions of the stock solutions at 50 ml volume.

To study the effect of medium pH on the sorption process, solutions of HCl, CH_3COOH and CH_3COONa have been used and then measured with a pH meter (Radiometer pH M64).

Dowex 1×1 (50–100 mesh) anion exchange resin (Suchuchardt, Germany) in chloride form was used as solid support without any preliminary treatment. The beads were spherical, colorless and optically transparent in the visible region of the spectrum.

A 5×10^{-3} mol/l aqueous solution of Nitroso R salt (disodium-1-nitroso-2-hidroxynaphthalene-3,6-disulfonate; NRS) was freshly prepared.

For absorbance measurements, a VSU-2P spectrophotometer (Carl Zeiss, Jena, Germany) was used.

Analytical procedure

To a 50-ml sample solution containing Rh(III) (up to 100 µg) of pH value adjusted as required 0.06 g of Dowex 1×1 (50–100 mesh) beads were added previously loaded with NRS (20 µmol NRS/g dry resin). The mixture was moderately heated for 30 min and then cooled at room temperature while stirring (1 h).

The colored resin beads were collected by filtration and packed into a glass cell of 1-mm thickness together with a small portion of filtrate using a pipette. The light absorption of the red colored beads was measured against a 1-mm cell packed with the exchanger loaded with NRS and equilibrated with water. The apparent values of absorbance were measured at 500 nm (the absorption maximum of the colored species) and 750 nm (the background absorbance). Thus, the errors due to the variation of filling of the resin beads into cells (the change in path length or scattering) are eliminated. The net absorbance A_{RC} of the complex species sorbed on the resin phase was calculated using Yoshimura's equation (Yoshimura and Waki 1985): $A_{RC}=\Delta A-\Delta A^*$, where $\Delta A=A_{500}-A_{750}$ (for the sample) and $\Delta A^*=A_{500}-A_{750}$ (for the blank).

Results and discussion

NRS forms colored complexes with many platinum group metal ions (Table 1) which can be used in their spectrophotometric determination. It was found that the analytical performances of this method were significantly improved if the palladium(II) ion has been determined by an SPS procedure, based on the retention of analyte from aqueous solutions on a solid phase previously loaded with Nitroso R salt (Bilba et al. 2004).

Strongly basic anion exchangers (Dowex 1×1, Amberlite IRA-402, Amberlite IRA-958) exhibit high affinities for sulfonated NRS. In NRS form they behave like chelating resins and were successfully applied for the preconcentration and separation of trace metal ions, including palladium ions (Moldovan et al. 1998, Wawrzkievicz and Hubicki 2009). The loading of Dowex 1×1 anion exchanger under study with NRS from neutral solutions was explained by an anion exchanger mechanism and polymer matrix of the ion exchanger – condensed rings of the organic reagent interactions (Bilba et al. 1998). It was found that the ion exchange resin modified with organic reagent is characterized by chemical stability in strongly acidic, neutral and weakly alkaline solutions and good thermal stability at 60°C.

To establish the optimum conditions for the application of the proposed method, the influence of the solution pH, resin amount and sample solution volume on the development of Rh(III)-Nitroso R complex color in the resin phase was studied.

Absorption spectra

The Dowex 1×1 beads loaded with NRS have a yellow color with an absorption maximum at 400 nm (Bilba et al. 2004). Their reaction with Rh(III) resulted in a complex of red color, the color being stable at least 48 h. This complex formed in the solid phase exhibits an absorption maximum at λ=500 nm. The electronic spectra of the reagent and its complex with Rh(III) in the solid phase are shown in Figure 1. It can be seen from Figure 1 that the spectra have a shape similar to that of corresponding aqueous solution spectra at the same pH, the slight displacement of absorption bands being explained by the molecule deformation in the resin phase (a bathochromic shift from the solution to the solution phase).

Effect of the solution pH

The influence of the solution pH on the color development of Rh(III)-Nitroso R complex in aqueous solution and resin

Table 1 Characterization of some platinum metal ions – NRS complexes in aqueous solutions.

Platinum metal ion	pH	λ_{max} (nm)	Molar absorptivity (l/mol cm)	Metal to ligand ratio	Stability constant (β)
Pd(II)	1	510	9.55×10^3	1Pd:2NRS	6.994×10^9
Rh(III)	4.8	485	6.482×10^3	1Rh:3NRS	5.5313×10^{12}
Os(VIII)	0	550	3.645×10^3		
	4.8	510	1.695×10^3	1Os:4NRS	1.5203×10^{15}
		620	1.458×10^3		

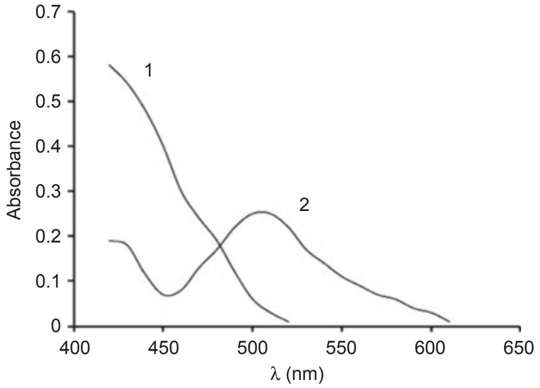

Figure 1 Absorption spectra in Dowex 1×1 resin phase: (1)-Nitroso R salt, 20 μmol/g resin; (2)-Rh(III)-NRS complex, 2.25 μmol/g of resin.

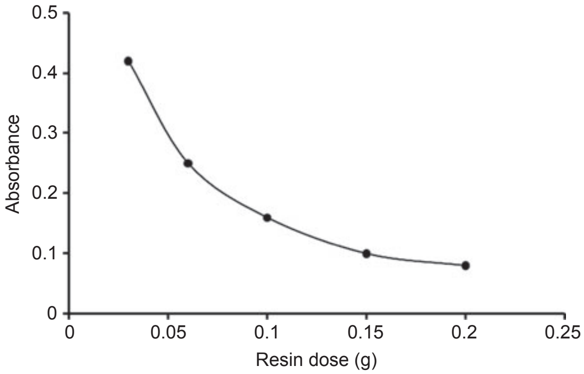

Figure 3 Color development vs. the NRS-Dowex 1×1 resin amount: 1 mg/l Rh^{3+}, pH=4.8.

phase is very similar (Figure 2). Below pH 2, the extent of the reaction is negligible. Over pH 2, the signal increased until a maximum was reached in the range pH 4.5–5. Over this pH value, the signal decreases considerably. This trend is in good agreement with literature data reporting spectrophotometric determination of rhodium with Nitroso R salt (Rollins and Oldham 1971). The optimum pH value for the method was selected as 4.8, also considering that the swelling of the resin is strongly pH dependent.

Effect of resin amount

The effect of the Dowex 1×1 amount on the development of the complex color is depicted in Figure 3. It is obvious from Figure 3 that the absorbance decreases with increasing the amounts of the resin beads impregnated with NRS. From an experimental point of view, the minimum amount of dry resin required to obtain sufficiently high absorbances values is 50 mg.

Effect of sample solution volume

One of the most important advantages of SPS is its inherent capability of preconcentration by increasing the volume of the liquid sample taken for analysis. This effect was studied by measuring the absorbance of the resin (0.06 g portion), which was previously equilibrated with different volumes of solutions (pH=4.8) containing the same concentration of the Rh(III). It was found that the sensitivity of the method can be increased, by decreasing the ratios of solution volume/resin amount.

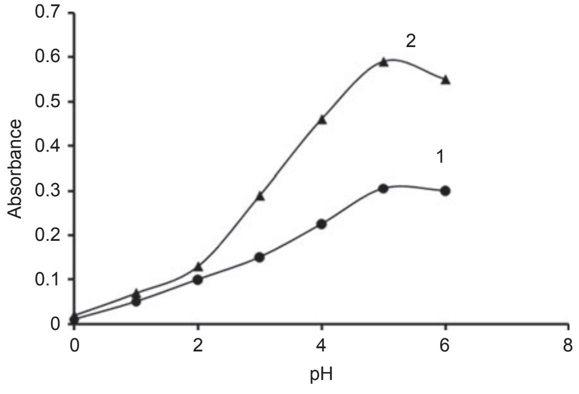

Figure 2 Color development of the Rh(III)-NRS complex in solution (1) and resin phase (2) as function of pH.

Analytical performances of the proposed method

Under the optimum conditions selected, the calibration curve is linear in the concentration range of 0.5–2 μg/ml, for the system with 50 ml of sample volume (pH=4.8) and 60 mg of Dowex impregnated with NRS (20 μmol/g resin). The analytical parameters are recorded in Table 2.

The reproducibility of the determinations was established using eight parallel samples [v=50 ml, C=80 μg/l Rh(III)].

Comparison with conventional spectrophotometric methods

To emphasize the specific features of the proposed method, its performances are compared in Table 3 with that of other spectrophotometric procedures for rhodium determination.

It is obvious from Table 3 that owing to the preconcentration effect, the sensitivity of the SPS method under study, expressed as molar absorptivity, is approximately 4–12 times higher than that of other spectrophotometric methods for Rh(III) determination. This method is simple, reproducible and accurate and can be an inexpensive tool for trace analysis.

Table 2 Analytical parameters.

Parameters	Value
Linear dynamic range (μg/ml)	0.5–2
Correlation coefficient (R^2)	0.9991
RSD (%)	1.18
Detection limit, k=3 (μg/l)	3.842
Molar absorptivity (l/mol cm)	3.0356×10^4

Table 3 Comparison of analytical performance of some spectrophotometric methods for Rh(III) determination.

Reagent (conditions)	Sensitivity ε (l/mol cm)	Analytical range (µg/ml)	Remarks	References
Allthion(8-alkylthioquinoline) (aqueous solution)	7×10^3	0.08–1	λ=400 nm in H_2SO_4	Bosch Ojeda and Sanchez Rojas 2005
Butaperazine dimaleinate (aqueous solution)	2.44×10^3	0.2–28	An orange red 1:1 complex is formed at room temperature in sodium acetate-HCl buffer solution containing Cu(II) sulfate and ascorbic acid	Keshavan and Nagaraja 1984
Tin(II) chloride	4.2×10^3		The other platinum metals interfere in the determination	Marczenko and Balcerzak 2000
5-Sulfoallthion(allyl ester of 5-sulfo-8-mercaptoquinoline) (aqueous solution)	7.4×10^3	0.04–0.8	λ=430 nm; in HNO_3 the method was applied for Rh(III) determination form Pt-base alloys	Bosch Ojeda and Sanchez Rojas 2005
Nitroso R salt (SPS)	3.0356×10^4	0.5–2	pH=4.8; heated for 30 min and then cooled at room temperature	This study

Application of the proposed method

The proposed method was applied to the determination of 80 µg/l Rh(III) in synthetic samples containing different amounts of other platinum group metals. The obtained results are shown in Table 4.

As can be seen from Table 4, the proposed SPS procedure has potential to be used in analysis of Rh(III) from a variety of samples containing other platinum metals over a wide range of concentrations.

Conclusions

To improve the analytical performances of Rh(III) determination by the spectrophotometric method based on Nitroso R salt, the SPS procedure was studied.

- The proposed method is based on the retention of Rh(III) from aqueous solutions of pH 4.8 on the anion exchanger Dowex 1×1 previously loaded with Nitroso R salt (20 µmol/g resin).
- The determinations have been carried out by measuring the absorbance of the red complex formed in the solid phase at λ=500 nm (1 mm glass cell).
- Rh(III) could be determined in the concentration range of 0.5–2 µg/ml with an RSD of 1.18% and a degree of sensitivity, expressed by the molar absorptivity, of 3.0356×10^4 l/mol cm.
- The procedure was successfully applied for the determination of Rh(III) from a variety of samples containing other platinum metals over a wide range of concentrations.

Table 4 Determination of 80 µg/l Rh(III) in synthetic samples.

Sample	Found[a]$\pm S_{n-1}$ (µg/l)	Relative error (%)	Recovery (%)
A	78±2	2.5	97.5
B	81±1.5	1.25	101.25
C	77±2.8	3.75	96.25

[a] n=3; sample A: Pd(II), 500 µg/l; sample B: Os(VIII), 500 µg/l; sample C: Pt(IV), 500 µg/l.

References

Amin, A. S. Solid-phase spectrophotometric determination of trace amounts of vanadium using 2,3-dichloro-6(3-carboxy-2-hydroxynaphthylazo) quinoxaline. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2003**, *59*, 1025–1033.

Amin, A. S. Utilization of solid phase spectrophotometry for the determination of trace amounts of copper using 5-(2-benzothiazolylazo)-8-hydroxiquinoline. *Chem. Pap.* **2009**, *63*, 625–634.

Bilba, D.; Bejan, D.; Tofan, L. Chelating sorbents in inorganic chemical analysis. *Croat. Chem. Acta* **1998**, *71*, 155–178.

Bilba, D.; Paduraru, C.; Tofan, L. Determination of trace amounts of palladium(II) by solid-phase spectrophotometry. *Microchim. Acta* **2004**, *144*, 97–101.

Bosch Ojeda, C.; Sanchez Rojas, F. Determination of rhodium: since the original until today: spectrophotometric methods. *Talanta* **2005**, *67*, 1–19.

Bosch Ojeda, C.; Sanchez Rojas, F. Determination of rhodium: since the original until today: atomic absorption spectrometry. *Talanta* **2006**, *68*, 1407–1420.

Brykina, G. D.; Marchenko, D. Y.; Shapigun, O. A. Solid-phase spectrophotometry. *J. Anal. Chem.* **1995**, *77*, 79–84.

Keshavan, B.; Nagaraja, P. Spectrophotometric determination of rhodium with butaperazine dimaleinate. *Analyst* **1984**, *109*, 835–837.

Koga, M.; Matsuoka, S.; Yoshimura, K. Improved solid-phase spectrometry for the microdetermination of total and dissolved phosphate. *Anal. Sci.* **2010**, *26*, 963–968.

Liu, Y.; Chang, X.; Wang, S.; Guo, Y.; Meng, S. Solid-phase spectrophotometric determination of nickel in water and vegetables samples at sub-µg/L level with o-carboxylphenyldiaminoazobenzene loaded XAD-4. *Talanta* **2004**, *64*, 160–166.

Marczenko, Z.; Balcerzak, M. Separation, Preconcentration and Spectrophotometry in Inorganic Analysis. Elsevier: Netherlands, 2000.

Moldovan, Z.; Vladescu, L.; Neagu, E. Retention of nitroso-R salt on anionic resins: application to the preconcentration and separation of metal ions. *Rev. Roum. Chim.* **1998**, *43*, 193–196.

Pascual-Reguera, P.; Parras, G. P.; Diaz, A. M. Solid-phase UV spectrophotometric method for determination of ciprofloxacin. *Microchem. J.* **2004**, *77*, 79–84.

Pellerano, R. G.; Romero, C. H.; Acevedo, H. A.; Vasquez, F. A.; Marchevsky, E. Determination of lead in water of Parana river by solid-phase spectrophotometry. *Chem. Anal. (Warsaw)* **2007**, *52*, 501–508.

Rauch, S.; Morrison, G. M. Environmental relevance of the platinum group elements. *Elements* **2008**, *4*, 259–263.

Ravindra, K.; Bencs, L.; Van Grieten, R. Platinum group elements in the environment and their health risk. *Sci. Total Environ.* **2001**, *318*, 1–43.

Richter, P.; Canas, A.; Munoz, C.; Leiva, C.; Ahumada, I. Rotating disk sorbent extraction for pre-concentration of chromogenic organic compounds and direct determination by solid phase spectrophotometry. *Anal. Chim. Acta* **2011**, *695*, 73–76.

Rollins, O. W.; Oldham, M. M. Spectrophotometric determination of rhodium with Nitroso R. Formula for the Rh(III)–Nitroso R complex. *Anal. Chem.* **1971**, *43*, 146–148.

Saputro, S.; Yoshimura, K.; Matsuoka, S.; Takehara, K. N. Improved solid-phase spectrometry for the microdetermination of chromium in natural waters. *Anal. Sci.* **2009**, *25*, 1445–1450.

Valencia, M. C.; Captai-Vallvey, A. N. Speciation of selenium (IV) in natural waters by solid-phase spectrophotometry. *Talanta* **1999**, *49*, 915–921.

Wawrzkievicz, M.; Hubicki, Z. Application of nitroso-R salt in modification of strongly basic anion exchangers Amberlite IRA-402 and Amberlite IRA-958. *Desalination* **2009**, *249*, 1228–1232.

Yadollah, Y.; Atefeh, T. Sensing of iron ions by solid phase spectrophotometry. *Iran. J. Chem. Chem. Eng.* **2002**, *21*, 91–96.

Yoshimura, K.; Waki, H. Ion-exchanger phase absorptiometry for trace analysis. *Talanta* **1985**, *32*, 345–352.

Yoshimura, K.; Waki, H.; Ohashi, S. Ion exchanger colorimetry. I. Micro determination of chromium, iron, copper and cobalt in water. *Talanta* **1976**, *23*, 449–454.