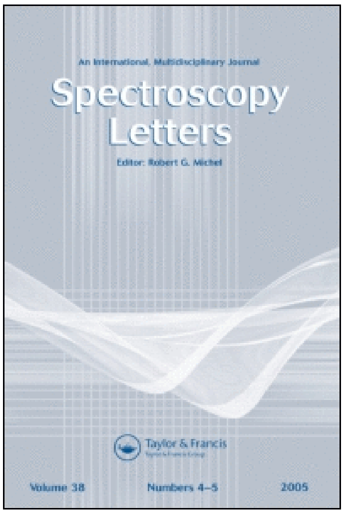

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

DETERMINATION OF Pd(II) AND Rh(III) IN SILICATE ROCKS BY DIRECT AND FIRST-ORDER DERIVATIVE SPECTROPHOTOMETRY

A. Youssef El-Sayed[a]
[a] Department of Chemistry, Al-Azhar University, Assiut, Egypt

To cite this Article El-Sayed, A. Youssef(2002) 'DETERMINATION OF Pd(II) AND Rh(III) IN SILICATE ROCKS BY DIRECT AND FIRST-ORDER DERIVATIVE SPECTROPHOTOMETRY', Spectroscopy Letters, 35: 6, 821 — 834

To link to this Article: DOI: 10.1081/SL-120016283

URL: http://dx.doi.org/10.1081/SL-120016283

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

SPECTROSCOPY LETTERS
Vol. 35, No. 6, pp. 821–834, 2002

DETERMINATION OF Pd(II) AND Rh(III) IN SILICATE ROCKS BY DIRECT AND FIRST-ORDER DERIVATIVE SPECTROPHOTOMETRY

A. Youssef El-Sayed*

Department of Chemistry, Faculty of Science,
Al-Azhar University, Assiut, Egypt

ABSTRACT

The determination of Pd and Rh in silicate rocks by normal and derivative spectrophotometry has been proposed. The reactions of Pd(II) and Rh(III) with 5-(2,4-dihydroxybenzylidene) rhodanine have been studied using zero- and first-derivative spectrophotometry. The 1:3 and 1:4 (metal-reagent) complexes are formed in the pH ranges 10.4–10.8 and 5.0–5.5 – with molar absorptivities of 9.0×10^4 and $7.4 \times 10^4\,\mathrm{L\,mol^{-1}\,cm^{-1}}$, at 558 and 460 nm, respectively. Derivatization of the zero-order spectra leads to an improvement of the sensitivities and selectivities of the methods. The first-derivative procedures permit determining down to 8 and 20 ng $\mathrm{mL^{-1}}$ of Pd and Rh, respectively, with good accuracy and reproducibility. The methods have been applied to

---

*E-mail: abd_el_yousef@hotmail.com

DOI: 10.1081/SL-120016283
0038-7010 (Print); 1532-2289 (Online)

www.dekker.com

determine Pd and Rh in silicate rocks and to the determination of Pd in a Pd-activated charcoal and compared with the neutron activation method with good agreement between the results.

Key Words: Palladium; Rhodium; Rocks; Rhodanine; Derivative spectrophotometry

INTRODUCTION

The development of analytical methods for determination of the noble metals is still growing as a result of importance of their applications, e.g., in catalysis. The need for fast, simple sensitive and selective methods are obvious, especially when routine determinations are required. Many chromogenic reagents have been utilized to the spectrophotometric determination of Pd[1–6] and Rh.[7–12] However, most of them either exhibits low sensitivity,[1,2,7,8] or require a time-consuming extraction step[3,4,9,10] and suffers from a large number of interferences from metal ions that often accompany Pd and Rh.[5,6,11,12]

Interest in the analytical applications of derivative spectrometry has been on the increase for the past few decades, owing to the introduction of commercial spectrometers capable of operating in the derivative mode. Derivative spectrophotometry was of greatly utility in determination of metal ions because of its great sensitivity[13–18] and selectivity[19–21] as well as its relatively low cost.

In the present woke, a good chromogenic reagent, 5-(2,4-dihydroxybenzylidene) rhodanine is easily synthesized and utilized for Pd and Rh determination with simple, safe, rapid and precise procedure. The sensitivity and selectivity of the developed methods have been improved using first-derivative spectrophotometry.

EXPERIMENTAL

Materials and Solutions

All chemicals used were of analytical-reagent grade and doubly-distilled water was used throughout. Stock solutions (1×10^{-2} M) of Pd(II) and Rh(III) are prepared as reported[22] Polyvinylpyrrolidone (PVP) was prepared as 2% (m/v). 5-(2,4-dihydroxybenzylidene) rhodanine. [5-(2,4-dihydroxyphenylmethylene)-2-thioxo-4-oxo-1,3-thioxo-4-oxo-1,3-thiazolidene] was synthesized and a 1×10^{-3} M ethanolic solution is prepared according to El-sayed.[23] Acetate buffer solution of pH 5.2 and borate buffer of pH 10.2 were prepared as reported.[22]

Instrumentation and Procedure

A Perkin–Elmer 3B double-beam UV-visible spectrophotometer, loaded with Pc computer running spectrophotometric software PECSS was used. The computer calculated the derivative according to method, a value of Dlta lambda = 2 found optimal for first-derivative spectra.[24] The pH measurements were made using a Janco electronics LTD digital pH-meter with combined glass calomel electrode.

Determination of Pd(II) Using Zero-Derivative Spectrophotometry

Place an aliquot containing 0.05–1.4 μg mL^{-1} of Pd(II) in a 25-mL standard flask. Add 2.0 mL of the reagent solution. Complete to the volume with borate buffer of pH 10.6. After 10 min, measure the absorbance at 558 nm against a reagent blank.

Determination of Pd(II) Using First-Order Derivative Spectrophotometry

Into a 25-mL calibrated flask, transfer a sample solution containing 0.03–0.5 μg mL^{-1} of Pd(II), 1 mL of DHBR and complete to the mark with buffer of pH 10.6. The first derivative was recorded from 650–450 nm against a reagent blank at a scan speed of 120 nm min^{-1}.

Record the absorption spectrum of the solution against a reagent blank with the following instrumental parameters: wavelength 520–380 nm; slit 1 nm; scan speed 120 nm min^{-1}; wavelength interval, 1 nm. Calculate the first-derivative absorption spectrum of the solution Measure the absolute values of the derivative spectrum from the baseline to a peak at 537 nm.

Determination of Rh(III) Using Zero-Derivative Spectrophotometry

To sample solution containing 0.1–1.4 μg mL^{-1} Rh(III), add 2.0 mL of reagent solution, 2.0 mL of PVP solution, 5.0 mL of acetate buffer solution of pH 5.2 and 10.0 mL of distilled water. Heat the mixture for 20 min on water bath at 85 ± 1°C. Cool the solution rapidly and transfer quantitatively into 25-mL standard flask. Complete to the mark with distilled water. Measure the absorbance at 460 nm against an identically prepared reagent blank.

Determination of Rh(III) Using First-Order Derivative Spectrophotometry

Mix a sample solution containing 0.05–0.15 μg mL^{-1} of Rh(III) with 1 mL of DHBR and the above procedure was followed. Record the absorption spectrum of the solution against a reagent blank under the same instrumental parameters mentioned above. Calculate the first-derivative absorption spectrum of the solution and measure the absolute values of the derivative spectrum from the baseline to a peak at 447 nm.

Determination of Pd and Rh in Silicate Rocks

To Teflon beaker, transfer an accurately weight portion of finely powdered silicate rock (between 2.00 and 3.25 g). Treat the sample with a few drops of water, 20 mL of perchloric acid and 20 mL of concentrated hydrofluoric acid.[25] Evaporate the mixture in a sand-bath to fumes of perchloric acid and allow the residue to cool. Add a new portion of concentrated hydrofluoric acid and again evaporated to dryness. Treat the cooled residue with 20 mL 1.0 M hydrochloric acid. Warm and stir to dissolve the residue then evaporate to ca. 5 mL. Transfer the sample solution into 25-mL volumetric flask and the procedures for determination of Pd and Rh using zero and first-derivative spectrophotometry were followed in the presence of 5 mL of 1 M sodium bromide.

RESULTS AND DISCUSSION

Pd(II) forms a colored complex with the reagent in alkaline medium. The zero-order absorption spectra of reagent and its Pd complex are recorded in Fig. 1, curve 1 and 2, respectively. On the other hand, Rh(III) forms a colloidal complex with the reagent in acidic medium. In an attempt to solubilize or prevent coagulation of this complex, different types of surfactants and protective colloids were utilized.

The surfactants used were sodium dodecyl sulfate and sodium alkylbenzene sulfonate (anionic), polyoxyethylene sorbitan monolaurate,

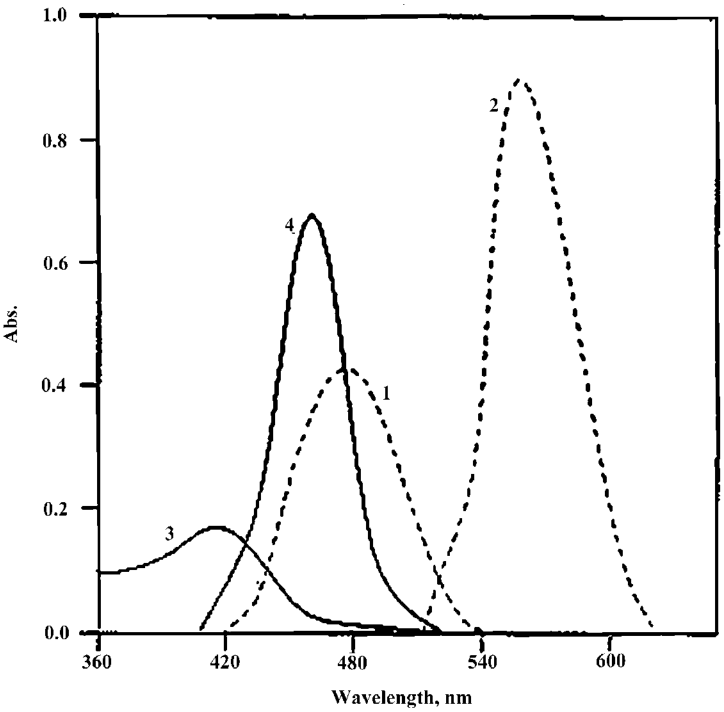

Figure 1. Zero-order absorption spectra of Pd(II)- and Rh(III)-DHBR complexes and their reagent blank. [Pd(II)] = 1.1 μg mL^{-1}, [Rh(III)] = 0.95 μg mL^{-1}, [DHBR] = 8.0×10^{-5} M, 0.016% PVP, 10 mm cell. Curve 1, 1×10^{-5} M DHBR at pH 10.6 vs. buffer; 2, Pd(II)–DHBR complex vs. DHBR at pH 10.6; 3, 1×10^{-5} M DHBR + PVP at pH 5.2 vs. PVP + Buffer; 4, Rh(III)–DHBR-PVP complex vs. DHBR + PVP at pH 5.2.

polyoxyethylene sorbitan monopalmitate, polyoxyethylene sorbitan monostearate, polyoxyethylene sorbitan monooleate and polyoxyethylene-p-tert-octylphenol (non-ionic) and cetyltrimethylammonium bromide, cetylpyridinium bromide, and benzyldimethyl-tetradecylammonium chloride (cationic); whereas gelatin, poly(vinyl alcohol) and polyvinylpyrrolidone protective colloids were also utilized. The study is performed using 8.2×10^{-6} M of rhodium, 8.5×10^{-5} M of reagent and 2×10^{-3} M of reagent and 2×10^{-3} M of surfactant (0.2% protective colloid) at pH 5.2. Anti-coagulation or solubilization of the complex has been achieved by all the studied protective colloids and surfactants. However, maximum absorbance is obtained in the presence of polyvinylpyrrolidone (PVP). The absorption spectra of the reagent and complex, in the presence of PVP, are shown in Fig. 1, curves 3 and 4 respectively.

Optimization of Experimental Conditions

Optimum pH ranges for formation of Pd(II)- and Rh(III) complex is 10.4—10.8 and 5.0—5.5, respectively. Use of borate and acetate buffer in this pH range slightly improved the absorbance of Pd(II) and Rh(III) complexes, respectively. Thus, pH 10.6 and 5.2 is recommended in the procedures for determination of Pd(II) and Rh(III), respectively. A complete color development of Pd(II) and Rh(III) complexes in aqueous and aqueous medium of PVP are obtained in the presence of 5.0×10^{-5}–1.4×10^{-4} and 6.5×10^{-5}–2.0×10^{-4} M of DHBR, respectively. In the recommended procedures, 2.0×10^{-3} M reagent solution are utilized (8×10^{-5} M final concentration). On the other hand, the concentration of ethanol (reagent solvent) has no effect on the color of Pd(II)- and Rh(III)-DHBR complexes. The effect of PVP concentration on the absorbance of Rh(III) complex is studied, maintaining fixed concentration of Rh(III) and reagent at pH 5.2. A PVP concentration $\geq 0.01\%$ prevents coagulation of the colloidal complex.

The rate of color development of Rh(III) complex increased rapidly with temperature up to 85°C. A temperature of 85 ± 1°C is adopted for the standard procedure. The absorbance of the solution increased rapidly during the first several minutes of heating; after 30 min the average change in absorbance is only 0.001 absorbance unit per minute. Good reproducibility is obtained by heating for 30 min. After cooling the complex color is stable for more than 4 h. On the other hand, the absorbance of Pd(II) complex is maximum and constant up to 35°C. At the 25°C, the color is stable for more than 3 h.

Derivative Spectra

A study of the first-, second-, third-, and fourth-derivative spectra of Pd(II) and Rh(III) complexes revealed that the first-derivative spectra gave results of highest sensitivity and lowest detection limits. Higher-order derivatives yield very yet irreproducible signals. On the other hand, the noise level increases proportionality with the derivative order. Derivative spectra are obtained by numerical calculation with the aid of PECSS program. The main instrumental parameter that affect the shape of the derivative spectra are the wavelength scanning speed and the wavelength increment over which the derivative is obtained (Δλ), all of which need to be optimized to give a large peak. A scan speed of 120 nm $\min^{-1}$ is found to be convenient. To obtain a satisfactory signal-to-noise ratio, the derivative spectrum is recorded at different Δλ (1–8). Generally, the noise level deceases with increase in Δλ. An optimum Δλ has been obtained using the auto-option uses a width of $\Delta\lambda = 2$ according to the Savitzky-Golay algorithm.[20] The first derivative values of Pd(II) and Rh(III) complexes are recorded at 537 and 447 nm, respectively.

When the Pd(II) and Rh(III) content of the colored solution is too low to give a measurable absorbance, the first-derivative technique is utilized. The influence of DHBR concentration on the colored solution, having an absorbance value lower than 0.1, is studied. The study revealed that the DHBR, concentration higher than 1 mL of 10^{-3} M are accompanied by a significant increase of the blank intensity, which affected the spectral characteristic of the complex. To avoid any change in the maximum absorption of the Pd(II) and Rh(III) complex due to increasing Pd(III) (or Rh(III)): DHBR concentration ratio, 1 mL of 10^{-3} M DHBR (in the final 25- mL) is utilized for determination of Pd(II) and Rh(III) with first-derivative mode. The first-derivative spectra for different concentrations of Pd(II) and Rh(III) are given in Fig. 2a and 2b, respectively.

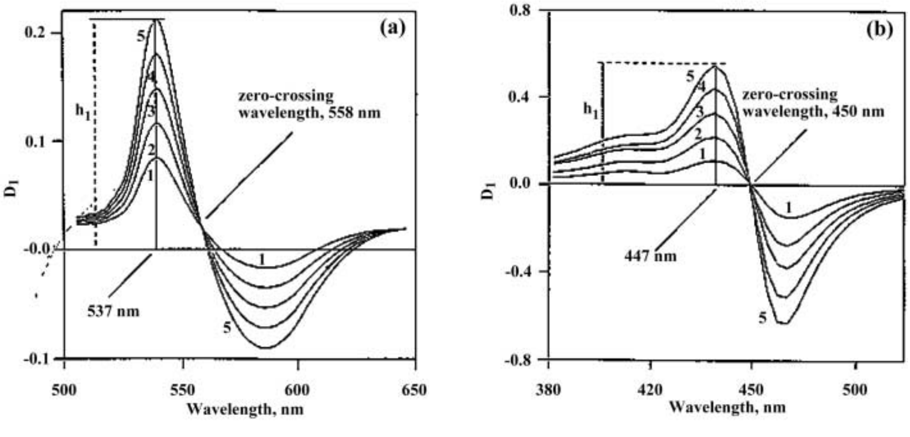

Figure 2. First-derivative spectra of (a) Pd(II)- and (b) Rh(III)-DHBR complexes. [Pd(II)] = 0.045, 0.068, 0.09, 0.11 μg mL^{-1} for curves 1–5, respectively. [Rh(III)] = 0.08, 0.16, 0.24, 0.33 and 0.41 μg mL^{-1} for curves 1–5, respectively. [DHBR] = 4.0×10^{-5} M; 0.016% PVP; scan speed 120 nm $\min^{-1}$; $\Delta\lambda = 2$; 10 mm cell.

Analytical Characteristics of the Methods

The calibration graphs for zero-order determination of Pd(II) and Rh(III) are linear in the ranges 0.06–1.4 and 0.1–1.4 μg mL^{-1}, respectively. The results obtained by measuring the absorbance values (A) of Pd(II) and Rh(III) complexes vs. concentration (C, μg mL^{-1}) fit the regression equations $A = 0.85C \pm 0.019 - 0.008 \pm 0.005$ ($r = 0.9999$) and $A = 0.72 \pm 0.03C + 0.03 \pm 0.018$ ($r = 0.9991$), respectively. The confidence limits[26] calculated for $t = 2.14$ (at $n = 14$ and 95% confidence level). The molar absorptivities, calculated from the slopes of regression equations, limits of detection and the relative standard deviation ($n = 10$) for 0.5 μg mL^{-1} of Pd or Rh are given in Table 1.

The calibration graphs prepared by plotting the First-derivative values (D) measured from the baseline-to-peak vs. Pd(II) or Rh(III) concentration (C, μg mL^{-1}) fit the equations $D = 1.36 \pm 0.05C + 0.0002 \pm 0.0001$ ($r = 0.9995$) and $D = 1.4 \pm 0.03C + 0.012 \pm 0.005$ ($r = 0.9996$), respectively. The *t*-value for $n = 8$, and the 95% confidence level is 2.31. The linear dynamic ranges, the limits of detection and the R.S.D for 40 ng mL^{-1} Pd or Rh (number of replicates; $n = 10$) are also illustrated in Table 1. As can be observed from Table 1, limit of detection for determination of Pd or Rh with derivative procedure is lower than those obtained in zero procedure.

From Table 1, it can be deduced that the proposed method for Pd the determination are more sensitive and simple than spectrophotometric procedure utilizing 5-(p-dimethylaminobenzylidene) rhodanine ($\varepsilon = 4.3 \times 10^4\ L\,mol^{-1}\,cm^{-1}$)[27] and 5-(3,4-methoxybenzylidene)rhodanine ($\varepsilon = 7.5 \times 10^4\ L\,mol^{-1}\,cm^{-1}$ at nm).[22] Also, the suggested procedure for the determination of Rh are more sensitive than the procedures utilizing sulphochloropenolazorhodanine ($\varepsilon = 3.5 \times 10^4\ L\,mol^{-1}\,cm^{-1}$)[28] and 5-(3,4-methoxybenzylidene)rhodanine ($\varepsilon = 5.1 \times 10^4\ L\,mol^{-1}\,cm^{-1}$ at nm).[22]

Effect of Foreign Ions

To test efficiency and selectivity of the proposed analytical procedures to real sample, the effect of foreign ion, in a wide range of concentrations, on the determination of Pd(II) and Rh(III) at 0.4 μg mL^{-1} by zero- and first-derivative mode is studied. The tolerance limits, defined as the concentration (molar in the final solution) causing a deviation of less than ±4% in the analytical response, are depicted in Table 2. As can be seen tolerance limits of noble metals as well as many transition metals obtained first-derivative procedure higher than zero-order procedure. The tolerance level for noble metal ions can be increased by addition of sodium bromide, potassium

Table 1. Analytical Characteristics of the Procedures

	Pd			Rh
Analytical Parameter	Ordinary Spectrophotometric	First Spectrophotometric	Ordinary Spectrophotometric	First Spectrophotometric
Molar absorpitivity	9.0×10^4 L mol^{-1} cm^{-1}	1.45×10^5 L mol^{-1} cm^{-1}	7.4×10^4 L mol^{-1} cm^{-1}	1.4×10^5 L moL^{-1} cm^{-1}
Linear dynamic range	0.08–1.4 μg mL^{-1}	20–400 ng mL^{-1}	0.1–1.4 μg mL^{-1}	30–600 ng mL^{-1}
Limit of detection	0.05 μg mL^{-1}	8 ng mL^{-1}	0.08 μg mL^{-1}	20 ng mL^{-1}
Limit of quantification	0.17 μg mL^{-1}	27 ng mL^{-1}	0.27 μg mL^{-1}	74 ng mL^{-1}
Coefficient of variation (RSD)	0.12%	0.27%	0.78%	0.85%

Table 2. Tolerance Limits for Foreign Ions in the Determination of 0.42 μg ml^{-1} of Pd(II) or Rh(III)

	Tolerance Limit [Ion]/Pd(II)		Tolerance Limit [Ion]/Rh(III)	
Foreign Ion	Zero-Order	First-Order	Zero-Order	First-Order
Na^+, K^+, Cl^-, NH_4^+, NO_3^-, SO_4^{2-}	> 10,000	> 10,000	> 10,000	> 10,000
I^-, Br^-	> 10,000	> 10,000	2500	2500
Ca^{2+}, Mg^{2+}	5000	5000	> 10,000	> 10,000
Ba^{2+}, Citrate, malonate, tartarate	5000	5000	5000	5000
Al^{3+}	5000	5000	2500	2500
Co^{2+}, Cr^{3+}, Gd^{3+}, La^{3+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Pr^{3+}, Th^{4+}, Ti^{4+}, U(VI)	500	600	700	900
Fe^{2+}, Fe^{3+}	200	500	300	700
Cd^{2+}, Pt^{4+}, Rh^{3+}, Ru^{3+}	200	400	300	450
F^-, EDTA, DCTA, V(v)	150	150	300	350
$Ag^{+(a)}$, $Au^{3+(a)}$, $Cu^{2+(b)(d)}$, $Hg^{2+(c)(d)}$, $Ir^{4+(a)}$, $Os(VIII)^{(a)}$	100	200	100	140

[a] 5 mL of 0.1 M sodium bromide.
[b] 5 mL of 0.1 M ammonium citrate.
[c] 5 mL of 0.1 M potassium iodide.
[d] 1 mL of 0.02 M EDTA (in case of Rh procedure).

iodide, ammonium citrate and EDTA. These results show that great tolerance ratios of many ions frequently accompanying Pd and Rh in real samples are well tolerated without any prior separation technique.

Composition and Formation Constant of the Complexes

The composition of Pd(II) and Rh(III) complexes are determined using the molar ration, continuous variation and slope ratio methods. These methods reveal the formation of 1:3 and 1:4 (metal–reagent) complexes, respectively. The corresponding formation constants of the complexes, as determined by Job's continuous variation method,[29] are 4.8×10^9 and 2.3×10^{13}.

Analytical Application

The recommended procedures have been satisfactorily applied to the determination of Pd and Rh in silicate rock obtained from Sebaiya West, Egypt. In order to test the accuracy of this method results are compared with those obtained by neutron activation method by means of t-test at 95% confidence level and respective degrees of freedom. Results presented in Table 3, show that the proposed methods does not differ significantly from the neutron activation analysis. As an additional check of accuracy, recovery experiments are performed by adding a fixed amount of Pd(II) and Rh(III) to the pre-analysed rocks. As can be seen the quantitative recoveries for Pd and Rh ranges between 97%–101% The proposed Pd methods are also applied to the determination of Pd in three standard solid samples palladium-activated charcoal catalyst obtained from S.D. Fine (India). The acid decomposition procedure of Rosales and Ariza[30] for sample preparation was followed. The results as shown in Table 4 are in good agreement with the certified values.

CONCLUSIONS

Although methods such as neutron-activation analysis and inductively plasma optical emission spectrometry have been used for the determination of trace amounts of various noble metals, access to the necessary equipment is not always available. The proposed method is suitable as a rapid alternative method to expedite routine analysis of Pd(II) and Rh(III) using inexpensive apparatus. The short analysis time and low costs are the main

Table 3. Determination of Pd and Rh in Silicate Rocks

				Pd, μg					Rh, μg				
		Added, μg		Zero Method		First Method			Zero Method		First Method		
Sample	Weigh G	Pd	Rh	Found*	Rsd	Found*	Rsd	NAA	Found*	Rsd	Found*	rsd	NAS
Rock-1	1.00	–	–	0.198 ± 0.005	2.1	0.202 ± 0 .004	1.8	0.20	0.375 ± 0.008	1.8	0.38 ± 0.007	1.4	0.38
	1.00	1.0	1.0	1.18 ± 0.02	1.4	1.19 ± 0.01	0.92		1.386 ± 0.01	0.83	1.374 ± 0.01	0.70	
Rock-2	1.00	–	–	0.0488 ± 0.002	2.6	0.0506 ± 0.001	2.3	0.05	0.256 ± 0.006	1.9	0.262 ± 0.005	1.6	0.26
	1.00	1.0	1.0	1.06 ± 0.03	2.1	1.06 ± 0.02	1.5		1.268 ± 0.02	1.03	1.265 ± 0.01	0.82	

*Average of five separate determinations (n = 5);
$t_{\text{theoretical}} = 2.78$ at confidence level = 95%;
NAS, Neutron Activation Analysis.

Table 4. Determination of Pd in Activated Charcoal

	Pd, %					
		Zero-Order		First-Order		
Sample No.	Content	Found*	SD	Found*	SD	F Calc.[a]
1	2	2.02	0.05	1.99	0.03	2.78
2	5	4.97	0.09	5.01	0.07	1.65
3	10	10.13	0.06	10.05	0.05	1.44

*Average of five separate determinations.
[a] F theory = 6.39.

advantages of these procedures for routine analysis. The method is advantage over many of the reported spectrophotometric methods with respect to sensitivity, selectivity and simplicity (Introduction). The method could be easily applied to determine trace amounts of Pd and Rh in material samples.

ACKNOWLEDGMENTS

The author is grateful to Dr. Abdel Wahab, at the Department of Geology, Faculty of Science, Ain Shams University, for providing the sample of silicate rocks, and to Dr. F. Siegel, Professor of Geochemistry, George Town University, Washington, D.C., for conducting the reference analysis of these samples by neutron activation analysis (N. A. C., Toronto, Canada).

REFERENCES

1. Gowda, A.I.; Gowada, H.S.; Gowada, N.M.M. Anal. Chem. **1983**, *55*, 1816.
2. Shetty, A.N.; Gadag, R.V. Bull. Chem. Soc. Jpn. **1993**, *66*, 2536.
3. Rizvi, G.H.; Natarajan P.R. Fresenius J. Anal. Chem. **1990**, *336*, 498.
4. Singh, I.; Kadyan, P.S.; Garg, B.S.; Barua, S. Bull. Chem. Soc. Jpn. **1989**, *62*, 1316.
5. Gregorowicz, G.; Gorka, P.; Kowalski, S.; Cebula, J. Mikrochim. Acta **1983**, *II*, 181.
6. Marczenko, Z.; Kus, S.; Mojski, M. Talanta **1984**, *31*, 959.

7. Rollins, O.W.; Oldham, M.M. Anal. Chem. **1974**, *43*, 146.
8. Shijo, Y.; Nakaji, K.; Shimizu, T. Analyst **1988**, *113*, 519.
9. Wasey, A.; Bansal, R.K.; Stake, M.; Puri, B.K. Bull. Chem. Soc. Jpn. **1983**, *56*, 3603.
10. Brajter, K.; Kozicka, U. Anal. Chim. Acta **1984**, *156*, 323.
11. Kalinowski, K.; Marczenko, Z. Mikrochim. Acta **1985**, *I*, 167.
12. Shravah, K.; Sindhwani, S.K. Bull. Chim. Soc. Jpn. **1985**, *58*, 3560.
13. Taher, M.A. Anal. Chim. Acta **2000**, *408*, 153.
14. Wang, N.; Ren, X.; X. Si X.; Jiang W.; Liu C.; Liu X. Talanta **2000**, *51*, 595.
15. Godlewska-Zylkiewicz, B.; Lesniewska, B.J. Trace Microprob. Techniq. **2001**, *19*, 345.
16. Mori, I.; Toyoda, M.; Fujita, Y.; Matsuo, T.; Taguchi, K. Talanta **1994**, *41*, 251.
17. El-Sayed, A.Y.; Abu-Shanab, A.A. Mikrochim. Acta **1998**, *129*, 225.
18. Mori I.; Fujita Y.; Toyoda M.; Maekubo S. Bull. Chem. Soc. Jpn. **1991**, *64*, 1689.
19. Blacerzak, M.; Swiecicka, E.; Balukiewicz, E. Talanta **1999**, *48*, 39.
20. El-Sayed, A.Y.; Abdl-Rahem, M.; Omran, A.A. Anal. Sci. **1998**, *14*, 577.
21. Seco-Lago, H.; Perez-Iglesias, J.; Fernandez-Solis, J.M.; Castro-Romero, J.M.; Gonzalez-Rodriguze, V. Fresenius J. Anal. Chem. **1997**, *357*, 464.
22. El-Sayed, A.Y. Mikrochim. Acta **1995**, *117*, 161.
23. El-Sayed, A.Y. Chem. Soc. Jpn. **1994**, *67*, 3216.
24. Savittzky, A.; Golay, M.J.E. Anal. Chem. **1964**, *36*, 1627.
25. Jeffery, P.G.; Hutchison, D. *Chemical Method of Rock Analysis*, 3Edn.; Pergamon Press: Oxford, 1981; 74.
26. Miller, J.C.; Miller, J.N. *Statistics for Analytical Chemistry*, 3Edn.; Ellis Horwood: New York, 1993; 110–120.
27. Broissova, R.; Koeva, M.; Topalova, E. Talanta **1975**, *22*, 791.
28. Propistsova, R.F.; Savvin, S.B. Zh. Analit. Khim. **1973**, *28*, 1769.
29. Inczedy, J. *Analytical Applications of Complex Equilibria*; Ellis Horwood: Chichester, 1979; 173.
30. Rosales, D.; Ariza, J.L.G. Analyst **1986**, *111*, 449.

Received January 21, 2002
Accepted August 3, 2002