

Determination of Palladium II in 5% Pd/BaSO₄ by ICP-MS with Microwave Digestion, and UV-VIS Spectrophotometer

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Abstract

Determination palladiums have been reported 5% (w/w) Pd/BaSO₄ known as Rosenmund Catalyst. The determination of palladium II known as Rosenmund Catalyst is always an expensive procedure usually involving procedures such as flame atomic absorption spectrophotometry, emission spectrometry, and many spectrophotometric methods. In this study, palladium II in 5% Pd/BaSO₄, was synthesized and employed to develop an extractive UV-Visible Spectrophotometric, and an inductively coupled plasma mass spectrometry ICP/MS methods for the determination of palladium II. Specification for Pd is 4.85% to 5.10%; the result was 4.97% for the UV-Visible spectrophotometer and 4.90% for the ICP/MS. Both results meet the requirements.

Keywords

Palladium Determination, 5% Palladium Barium Sulfate, Inductively Coupled Plasma Mass Spectrometry, UV-Visible Spectrophotometer, Microwave Digestion

1. Introduction

Palladium, platinum, rhodium, ruthenium, iridium and osmium form a group of elements referred to as the “platinum group elements” (PGMs). These have similar chemical properties, but palladium has the lowest melting point and is the least dense of them. Palladium founds in a variety of ores. It is found to some degree in all platinum ores and is present in a number gold, nickel and copper ore bodies [1]-[10]. Palladium is a broadly useful silver white, noble ductile metal [11] discovered in 1803 by William Hyde Wollaston. Palladium is a chemical element having an atomic weight of 106.4, atomic number of 46, and the symbol Pd. Palladium compounds are more stable unlike other platinum metals. Palla-

dium is soluble in concentrated HNO_3 . Palladium gives stable amine, nitrite, cyanide, chloride, bromide, and iodide complexes. Palladium group metals especially palladium is very important to industry [12]. Palladium is generally resistant to corrosion by most single acids, alkalis and aqueous solutions of simple salts. It is not attacked at room temperature by non-oxidizing acids such as sulfuric, hydrochloric, hydrofluoric, acetic and oxalic acids. Strongly oxidizing acids such as nitric acid and hot sulfuric acid attack palladium, as do ferric chloride and hypochlorite solutions.

Palladium is not tarnished by dry or moist air at ordinary temperatures [13] [14] [15]. Palladium is used in many applications because of its noble metal characteristics and often these can be provided most economically in the form of a coating. The catalyst stored indefinitely in well-sealed containers. The activation energy value for all Pd/BaSO_4 catalyst was around 49.1 kJ/mol.

Palladium on Barium Sulfate 5% Pd/BaSO_4 an appropriate form of carbon when used to catalyze the hydrogenation of acyl chlorides to aldehydes, the Rosenmund reduction [16], useful catalyst for many other hydrogenations. The palladium catalyzed hydrogenation of an acid chloride to an aldehyde is known as the Rosenmund reduction (Figure 1 and Figure 2).

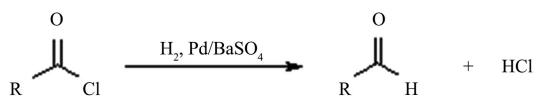


Figure 1. The catalytic hydrogenation of acid chlorides allows the formation of aldehydes.

Side products:

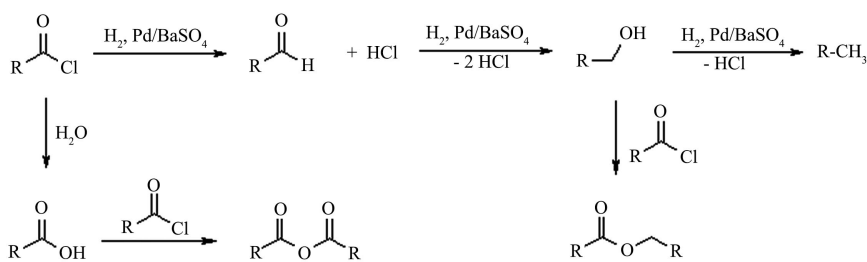


Figure 2. Mechanism of the rosenmund reduction.

The Pd catalyst must be poisoned, for example with BaSO_4 , because the untreated catalyst is too reactive and will give some over reduction. Some of the side products can be avoided if the reaction is conducted in strictly anhydrous solvents.

2. Material and Method

2.1. Determination of Palladium by ICP-MS

2.1.1. Instruments

- NexIon 300X ICP-MS, Inductively Coupled Plasma computer-controlled se-

quential emission spectrometer with interelement and background correction capabilities, and provisions for interfacing to a printer and an auto sampler [17].

- Ethos Plus Microwave
- ETHOS One Closed Vessel Microwave Digestion System, with temperature control and rotating turntable, well ventilated with corrosion-resistant cavity.
- Microwave digestion vessels for water samples, Teflon, capable of holding ~75 milliliters (mL), designed “for temperatures up to 260°C with self-regulating pressure control
- Digestion vessels for soil samples, capable of holding ~250 mL
- Watch glasses or vapor recovery device
- Glass dispensers, 2-liter (L), 1-L, or 1-gallon, checked quarterly for accuracy
- Graduated Cylinder, Class A, 50 mL
- Volumetric flasks, Class A, assorted volumes
- Balance, top-loading, capable of reading to 0.01 grams (g), for weighing digestion vessels before and after digestion
- Henke SASS plastic syringes
- Corning SCFA 0.45 microns (μm) filters
- Argon Plasma Support Gas in pressurized cylinders.

2.1.2. Reagents and Solutions

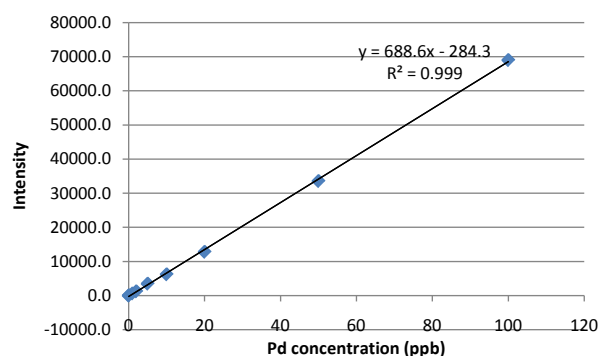
- Concentrated nitric acid, Seastar Chemicals. 67% - 70% (w/w HNO_3), purified by re-distilled, $\geq 99.999\%$ trace metals basis.
- Nitric acid, 2 percent(%) volume to volume (v/v), for the preparation of working standards, also to be used for the initial calibration blank.
- Deionized (DI) water, Type I Deionized water, for the preparation of all reagents and calibration standards and as dilution water.
- Hydrogen peroxide solution contains inhibitor, 30 wt% in H_2O , Sigma-Aldrich, ACS grade.
- Palladium, 5% Pd/ BaSO_4 (Palladium on Barium Sulfate) obtained from Sigma-Aldrich.

2.1.3. Microwave Digestion

200 mg of sample weighed and placed in each digestion vial. 8 mL of nitric acid (HNO_3) and 2 mL hydrogen peroxide (H_2O_2) have been added to each vial including a blank. Tighten the vials in the vessels, twist the screw on top by hand then use the teardrop racket to tighten further. No sample was added in a vessel for the blank preparation. For the blank, line up the holes and ensure that the tube goes in. Place them in microwave. After digestion, take out the vials from the ETHOS One Closed Vessel Microwave Digestion System. The teardrop racket was used to loosen the vials from the vessels. All the liquid from each digestion vial were transferred into 50 mL centrifuge tubes. About 10 mL deionized (DI) water, Type I Water was added to wash and rinse the vials to make the total volume 20 mL using a 5 mL pipet (Figure 3).

Table 1. Intensity of Palladium Standards.

Standard Palladium (Pd) conc (ppb)	intensity	intensity
	Pd-102	Pd-105
0	-1.8	58.0
0.1	52.5	1410.7
1	608.5	14,046.6
2	1231.1	28,240.2
5	3472.8	80,575.3
10	6215.0	147,069.6
20	12,807.3	299,821.6
50	33,563.0	779,584.4
100	69,026.7	1,627,390.4
Slope	688.6	16,201.7
Intercept	-284.3	-7704.5
R ²	0.99966026	0.999464345

**Figure 3.** Calibration curve of Palladium by ICP-MS.**Table 2.** Intensity of Palladium samples.

Sample	Weight (g)	Volume (L)	Dilution
Digested Blank #1	0	0.020	100.000
Digested Blank #2	0	0.020	100.000
5% Pd BaSO ₄ Sample 1	0.211	0.020	100.000
5% Pd BaSO ₄ Sample 1 dup.	0.211	0.020	100.000
5% Pd BaSO ₄ Sample 2	0.1994	0.020	100.000
5% Pd BaSO ₄ Sample 2 dup.	0.1994	0.020	100.000
5% Pd BaSO ₄ Sample 1 Spiked	0.1998	0.020	100.000
5% Pd BaSO ₄ Sample 1 Spiked dup.	0.1998	0.020	100.000
Sample	Weight (g)	Volume (L)	Dilution
Digested Blank #1	0	0.020	100.000
Digested Blank #2	0	0.020	100.000
5% Pd BaSO ₄ Sample 1	0.211	0.020	100.000
5% Pd BaSO ₄ Sample 1 dup.	0.211	0.020	100.000
5% Pd BaSO ₄ Sample 2	0.1994	0.020	100.000
5% Pd BaSO ₄ Sample 2 dup.	0.1994	0.020	100.000
5% Pd BaSO ₄ Sample 2 Spiked	0.1998	0.020	100.000
5% Pd BaSO ₄ Sample 2 Spiked dup.	0.1998	0.020	100.000

Table 3. Intensity of Palladium Samples (Cont.).

Pd-102 Intensity	Diluted Concentration (ug/L)	Undiluted Conc (ug/L)	Amount (ug)
23	0.4	44,625.3	892.5
15.6	0.4	43,550.7	871.0
3297.5	5.2	520,125.2	10,402.5
3273.1	5.2	516,582.0	10,331.6
3092.2	4.9	490,312.9	9806.3
3072.6	4.9	487,466.8	9749.3
3219	5.1	508,725.9	10,174.5
3222.7	5.1	509,263.2	10,185.3
Pd-105 Intensity	Diluted Concentration (ug/L)	Undiluted Conc (ug/L)	Amount (ug)
558.7	0.5	51,002.2	1020.0
408.0	0.5	50,072.0	1001.4
75,901.6	5.2	516,033.4	10,320.7
75,948.4	5.2	516,322.2	10,326.4
71,379.5	4.9	488,122.1	9762.4
71,567.0	4.9	489,279.4	9785.6
74,524.9	5.1	507,536.1	10,150.7
74,527.0	5.1	507,549.1	10,151.0

Table 4. Intensity of Palladium Samples (Cont.).

Amount (ug/g)	Amount (mg/g)	Amount (%)	Mean	STD	RSD
49,301.0	49.30	4.93			
48,965.1	48.97	4.90	4.91	0.02	0.3%
49,178.8	49.18	4.92			
48,893.4	48.89	4.89	4.90	0.01	0.3%
50,923.5	50.92	5.09			
50,977.3	50.98	5.10	5.10	0.00	0.1%
Amount (ug/g)	Amount (mg/g)	Amount (%)	Mean	STD	RSD
48,913.1	48.91	4.89			
48,940.5	48.94	4.89	4.89	0.00	0.0%
48,959.1	48.96	4.90			
49,075.2	49.08	4.91	4.90	0.01	0.1%
50,804.4	50.80	5.08			
50,805.7	50.81	5.08	5.08	0.00	0.0%

2.2. Determination of Palladium by UV-Vis Spectrophotometer Method

2.2.1. Instrument

UV/Visible spectrophotometers are widely used by many laboratories including those in academia and research as well as industrial quality assurance. The technique is mainly used quantitatively. The absorbance spectra for all measurements were carried out using a Shimadzu 1601 PC double beam UV-VIS Spectrophotometer, with 1 cm quartz cells and 2.0 nm fixed slit width. The spectrophotometer was connected to a computer, loaded with Shimadzu UVPC software, and equipped with an Epson LQ-850 printer. 1 [18] [19].

2.2.2. Reagents and Solutions

- 5% Pd basis BaSO₄ obtained from Sigma-Aldrich
- Deionized water, on the day of use. High-purity deionized water was obtained by Aries High Purity Water System, Aries Filter Works.
- Diluted hydrochloric acid TS (1:1, or 6 N)
- Palladium, 5% PdBaSO₄ (Palladium on Barium Sulfate) obtained from Sigma-Aldrich.
- Palladium standard stock solution for AA, Lot # BCBM7956V, c(HCl) = 5% (W/w)
- Palladium standard solutions: Serial palladium standards were prepared by 5.0 mL of 1000 mg/LPd AA Stock standard in a 100 mL VF, QF water (50 mg/L); 5.0 mL 1000 mg/L in 50 mL VF QF DI water (100 mg/L), 5 mL 1000 mg/L in 25 mL VF QF DI water (200 mg/L).

2.2.3. Sample Preparation

543.4 mg sample was leached and warmed with diluted HCl, dissolved PdSO₄; filtered, washed and brought to 200 mL in volumetric flask. A solution was in dilution also prepared 50 mL VF, pipette to 100 mL QFH₂O. DF = 2.

2.2.4. Procedure

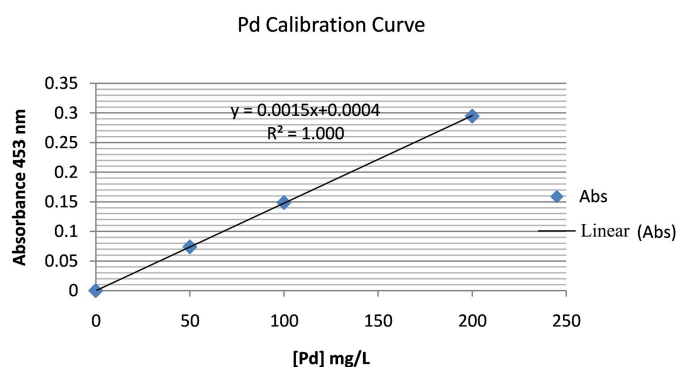
All absorption measurements were made in a Shimadzu 1601 PC double beam UV-VIS Spectrophotometer equipped with 1.0 cm quartz cells. The instrumental parameters were optimized and the best results were obtained in the wavelength at 453 nm (Figure 4).

Table 5. Calibration Curve Data.

[Pd] (mg/L)	Abs	Slope	0.00147
0	0.0000	Intercept	0.00040
50	0.0740	R²	1.0000
100	0.1488		
200	0.2948		

Table 6. Absorbance of Palladium 5% Samples.

Sample	DF	Absorbance	Sample weight (g)	[Pd] (mg/L)	Dilution Factor	Final volume (mL)	[Pd] (mg/L)
Air	1	0					
Water	1	0					
Blank	1	0					
LFB (50 mg/L)	1	0.0718		48.43			48.43
50 mg/L Check Std.		0.0738		49.52			49.52
Sample	1	0.1995	0.5434	135.05	1	200	135.05
Sample duplicate	1	0.0998	0.5434	67.42	2	100	134.84
Ave. sample result							134.95
Spike	1	0.2063	0.5434	139.66	1	200	139.66
Spike Duplicate	1	0.2064	0.5434	139.73	1	200	139.73

**Figure 4.** Calibration Curve of Palladium by UV-Vis.

3. Result and Discussion

QA/QC Study

Calibration Blank: A calibration blank is a sample of analyte-free media that can be used along with prepared standards to calibrate the instrument. A calibration blank may also be used to verify absence of instrument contamination [20].

Calibration Curve: A plot of instrument response to an analyte versus known concentrations or amounts of analyte standards. Calibration standards are prepared by successively diluting a standard solution to produce working standards which cover the working range of the instrument. Standards should be prepared at the frequency specified in the appropriate method. The calibration standards should be prepared using the same type of acid or solvent and at the same concentration as the samples following sample preparation [20].

Laboratory Control Sample (LCS): The Laboratory Control Sample (LCS) is analyzed to assess general method performance based on the ability of the laboratory to successfully recover target analytes from a control matrix. Aqueous and

solid LCSs is obtained from an independent source, and was prepared with each analytical batch of samples using the same preparation method as that employed for the samples. Percent recovery (%R) must be within 75% - 125% and calculated as:

$$\%R = \frac{(LCS - B)}{SA} \times 100$$

where: LCS = LCS result, B = Blank result, SA = spiked amount [20].

Laboratory Duplicate. The analysis or measurements of the variable of interest performed identically on two sub-samples of the same sample, usually taken from the same container. The results from duplicate analyses are used to evaluate analytical or measurement precision and include variability associated with sub-sampling and the matrix, but not the precision of field sampling, preservation, or storage internal to the laboratory [20].

Matrix Spike (MS)/Matrix Spike Duplicate (MSD): Matrix spikes are aliquots of samples to which known concentrations of certain target analytes have been added before sample preparation. Matrix spike-with compounds spiked into at a known level. Matrix spike duplicates are additional replicates of matrix spike samples that are subjected to the sample preparation and analytical scheme as the original sample. Analysis of spiked samples ensures a positive value, allowing for estimation of analytical precision [20]. Spiked sample percent recovery (%R) must be within 75% - 125% and calculated as [20]:

$$\%R = \frac{(SSR - SR)}{SA} \times 100$$

where; SSR = Spiked sample result, SR = Sample result, SA = Spiked amount

Relative Percent Difference (RPD): The Relative Percent Difference (RPD) and between matrix spike and matrix spike duplicates (MS/MSD) samples were $\pm 20\%$ and calculated as:

$$\%RPD = \frac{(S - D)}{(S + D)/2} \times 100$$

where: S = %R for matrix spike sample

After microwave digestion intensity of palladium (II) sample solutions and the intensity of palladium standards (0.0, 0.1, 1.0, 2.0, 5.0, 10.0, 20.0, 50.0, and 100.0 ppb) were measured by ICP/MS for the calibration curve (Table 1, Table 2, Table 3 and Table 4). Average results was 4.90% for the ICP/MS. The palladium (II) standard has been added into the sample for percent recovery. $\%R_{MS}$ and $\%R_{MSD}$ and $\%RSD$ have been shown in Table 7.

After extraction 5% Pd on $BaSO_4$ catalyst, $PdSO_4$ present in solution was measured at 453 nm. By UV-VIS Spectrophotometry. The absorbance readings plotted against the concentrations of palladium (II) to obtain the calibration curve. Table 5 and Table 6. Average results was 4.97% for the UV-Visible spectrophotometer. 5 ppm palladium (II) standards was added for the % recovery (MS/MSD), The results obtained are given in Table 7 and show that both instrument method can be successfully determined by UV-VIS and ICP/MS.

Table 7. Results of Palladium 5% by ICP/MS and UV-Vis.

Method	Specification	Results	Dup.	%RPD	%RMS	%RMS	Ave %R	Conforms
UV-Visible Spectrophotometer	4.85% - 5.1%	4.97%	4.96%	0.16	92.2	93.6	92.4	Passes
ICP-MS	4.85% - 5.1%	4.90%	4.90%	0.58	87.0	90.0	88.5	Passes

4. Conclusion

Inductively Coupled PlasmaMass Spectrometry ICP/MS and Direct Spectrophotometric method was developed for estimation of Palladium (II) and successfully used for quantitative extraction of Palladium in 5% Pd/BaSO₄ at acidic conditions. Since the equilibration time is very less; the method is quick and applicable for determination of Pd (II) from different synthetic mixtures and catalysts. The results obtained are given in **Table 7** and show that 5% (w/w) Pd (II) can be successfully determined by both methods.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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