



Simple, Sensitive, and easy to use, method for Determination of Palladium content in Palladium acetate using Flame Atomic Absorption Spectrophotometry

MELWIN DIEGO D'SOUZA^{1,2*}, POONAM DWIVEDI¹, RAMA LOKHANDE¹,
TUSHAR ANVEKAR² and ANDREW JOSEPH D'SOUZA²

¹Department of Chemistry, Jaipur National University, Jaipur, 302017, India.

²Department of Chemistry, St Xaviers College, Mapusa-Goa-403507, India.

*Corresponding author Email: melwindsouza3890@gmail.com

<http://dx.doi.org/10.13005/ojc/370415>

(Received: June 18, 2021; Accepted: August 12, 2021)

ABSTRACT

A simple, sensitive, and easy to use method for the determination of palladium content in palladium acetate was developed using homogeneous acid digestion of palladium acetate followed by atomic absorption spectrometry (AAS) analysis. Parameters affecting the extraction efficiency of palladium during digestion of palladium acetate were investigated and optimized. The palladium content was measured at 244.7 nm by atomic absorption (AA) spectrometers on PinAAcle™ 900 series with an air-acetylene flame. The linear calibration graph was observed in the range of 2.5-15ppm with a limit of detection of 8.33ppm and a correlation coefficient of 0.999970. For 5 replicate analyses of each palladium reference solution the relative standard deviation was within 2.00%. Analytical method validation for the method was carried out and obtained results were satisfactory. To verify, the accuracy parameter of the method validation, for the determination of Pd(II) from sample palladium acetate standard addition method was applied and satisfactory results were obtained. Optimization of analytical method variables during analytical method development is discussed.

Keywords: Palladium acetate, Air-acetylene flame, Atomic absorption spectrometry.

INTRODUCTION

There is an increasing demand for palladium elements in today's industries, and palladium is the widely used element of platinum group metals (PGM)¹. Furthermore, palladium is used in various areas of science and technology e.g. metallurgy and palladium is also used as a catalyst

especially in dehydrogenation and hydrogenation of some of the important organic compounds². High selectivity³⁻⁵, sensitivity, and the control effects of interference require analytical methods of palladium analysts⁶⁻⁸. Applications of palladium and its alloys, both in instrumentation and in the chemical industry were also studied before. A chemical compound of palladium acetate of palladium described by



the formula $[\text{Pd}(\text{O}_2\text{CCH}_3)_2]_n$. Determination of Pd content, spectrophotometry is one of the common methods, the main advantages of which is rapidity, accessibility, and simplicity. For the determination of palladium there exist many spectrophotometric methods, using inorganic or organic reagents, but they have some limitations. In environmental samples estimation of Pd contents, the most widely used methods include air flame atomic absorption spectrometry (AF-AAS)^{9,10} and inductively coupled plasma-mass spectrometry (ICP-MS)^{11,12}. Spectrophotometric determination of palladium by the coloration with 2-mercaptoethanol reported¹³ earlier and Hussainien reported¹⁴ FAAS determination of palladium after its selective recovery by silica modified with hydrazones. With the availability of a variety of atomic spectroscopy methods, we developed a simple, sensitive, and easy to use method for the determination of palladium content in palladium acetate using flame atomic absorption taking into consideration a variety of important criteria, including sample throughput, interferences, detection limits, data quality, cost, analytical working range and ease of use. The results obtained indicate that the proposed method is highly sensitive, selective, and easy to use for the determination of palladium in palladium acetate samples.

Table 1: Preparation of reference solutions using a stock solution

Sr. No.	Reference solution in ppm	The Volume of reference stock solution to be taken in mL	Volume to be diluted with diluent in mL
1	2.5	2.5	100
2	5.0	5.0	100
3	7.5	7.5	100
4	10.0	10.0	100
5	15.0	15.0	100

Instrumentation

For analysis, Perkin Elmer PinAAcle™ 900 series of atomic absorption (AA) spectrometer using air acetylene flame. A palladium hollow cathode lamp with a 247.6nm wavelength, a 9.0mA current, and a 0.4nm slit width was used as the radiation source.

Limit

The Palladium content in palladium acetate by analysis should be between (% w/w) 45.90–48.40%.

Validation of the method

To ensure that the analytical methodology

EXPERIMENTAL

Chemicals and reagents

Diluent: 5N Hydrochloric acid.

Dilute 425 mL of concentrated Hydrochloric acid to 1000ml with water.

Blank solution: Diluent: 5N Hydrochloric acid used as blank.

Test solution

Weigh accurately about 100 mg of palladium acetate in a 250 mL standard volumetric flask add 10 mL Conc. HCl and heat. Allow the flask to cool to room temperature and then make up the volume using 5 N Hydrochloric acid dilute up to the mark with diluent. Dilute 5.0mL of the solution to 100.0ml with 5 N Hydrochloric acids (about 10ppm of Palladium).

Reference stock solution: Dilute 10.0 mL of 1000ppm (palladium standard for AAS trace CERT®, 1000 mg/L Pd in hydrochloric acid) of Palladium to 100.0ml with diluent (100ppm).

Reference solution: Prepare 5 different reference solutions ranging from 2.5ppm to 15ppm from reference stock solution as per the Table 1 given below.

is valid and consistent for the determination of palladium content in palladium acetate by atomic absorption spectrometer (AAS). The method was validated various parameters such as LOD & LOQ, specificity, robustness, linearity, accuracy, and precision¹⁵. The above method has been fully developed and completely validated.

RESULTS AND DISCUSSION

System Suitability

The replicate injections of standard solution were injected. The system suitability parameters are

summarised in Table 3 and are well within the range of acceptance criteria (%RSD \leq 5).

Table 2: Optimal operating conditions for flame atomization of palladium

Element	Palladium
Wavelength	247.60nm
Read Time	10 sec
Lamp Current	9 mA
Recommended Flame	Air-Acetylene
Fuel Gas Flow	2.0
Support Gas Flow	17.0
Slit Width	0.4nm
Signal Type	Atomic Absorption
Atomization Site	Burner head
Equation	Linear Through Zero
Flame Type	Air-Acetylene
Pre Spray Time	3 sec
Integration Time	5 sec

Table 3: Readings of Absorption for System Suitability

Sr.No	Pd Concentration mg/mL	Absorption
1	9.419	0.3092
2	9.343	0.3070
3	9.336	0.3068
4	9.168	0.3021
5	9.113	0.3005
6	9.158	0.3018
Average	0.3046	
SD	0.0035	
% RSD	1.16	

Specificity

In this specificity aspirated blank (5N Hydrochloric acid used as blank), standard solution (six replicates), test solution, and spiked test solution were used. The results recorded the absorbance and responses of all the above-mentioned solutions. The palladium was not included in the blank as a result the blank showed no absorbance at the selected wavelength of palladium hence no interference from the blank. The analyst checked the interference of blank with standard and the data is summarized in Table 4. There is no interference of palladium in blank solution and hence the proposed method is specific for the determination of palladium from palladium acetate¹⁶.

Table 4: Average concentration for Specificity test

Palladium Concentration (ppm)	Wavelength	Average concentration n=3
Blank Solution	247.60	0.0007
Standard Solution	247.60	0.3077
Sample Solution	247.60	0.3015

Precision at LOQ Level

The following precision was reported as percentage relative standard deviation (%RSD) by aspirating the 8.33mg/L palladium standard 6 times for intraday and interday measurements. The results are presented in Table 5 and Table 6 respectively. The results were found to be within the range of acceptance criteria (%RSD \leq 5)¹⁷. Hence method meets the requirements of System Precision.

Table 5: Readings of absorbance of palladium standard for precision at LOQ Level(Intraday)

Sr. No.	Concentration (ppm)	Absorbance
1	8.33	0.2656
2	8.33	0.2655
3	8.33	0.2549
4	8.33	0.2555
5	8.33	0.2551
6	8.33	0.2656
Average	0.2604	
SD	0.0057	
% RSD	2.19	

Table 6: Readings of absorbance of palladium standard for precision at LOQ Level(Interday)

Sr. No.	Concentration (ppm)	Absorbance
1	8.33	0.2475
2	8.33	0.2534
3	8.33	0.2612
4	8.33	0.2562
5	8.33	0.2483
6	8.33	0.2545
Average	0.2535	
SD	0.0051	
% RSD	2.02	

Linearity and Range

The analyst prepared 5 different concentrations of reference solution from palladium standard solution. The results were recorded and calculated the mean area for each solution. The analyst further calculated the slope, Y-intercept, and correlation coefficient. A graph was plotted showing the correlation of concentration against peak area. The data obtained are summarized in Table 7. The calibration curve is shown in Fig. 1. The concentration of a standard solution is directly related and proportional to absorption in their lower and upper limits⁷⁻¹⁰. The calibration curve is shown in the regression equation. The ranges were plotted between palladium standard solutions 2.5-15.0ppm. The range plotted from LOQ level to 150% with respect to sample solution and was within range

of acceptance criteria¹¹⁻¹⁶ (Correlation Coefficient ≤ 0.99). The concentration range of palladium standard solutions was between 2.5-15.0ppm and the absorption results were recorded¹⁸.

Table 7: Absorption made by different concentrations of palladium standard solution

Concentration in ppm	Absorption
2.5	0.0916
5.0	0.1763
7.5	0.2519
10.0	0.3267
15.0	0.4534
Correlation coefficient	0.99997

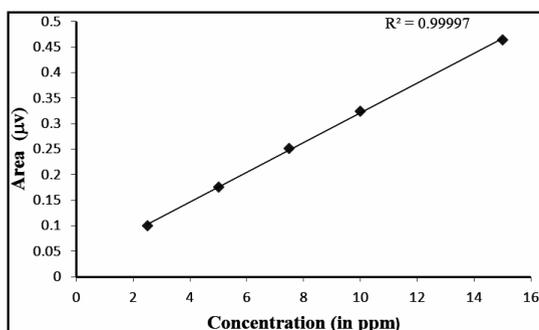


Fig. 1. Calibration Curve of different concentrations of palladium standard solution

Accuracy/Recovery

For the accuracy test, the palladium acetate sample was spiked with palladium standard at 3 levels each in triplicate, i.e. 3 x 150%, 3 x 100%, and 3 x 50%. Each sample was analyzed against a standard reference solution of palladium. From the amount added and the amount found, the percentage recovery was calculated in Table 8. The percent recovery of the added standard was found to be 98.34%. The method is free from either positive or negative interferences from the blank. From the

above result, it was found that the recovery data of the analyte is within the limit and hence the proposed method is accurate¹⁹.

Sample analysis

The sample was prepared and aspirated as per the above method and the palladium content was found in the given sample is 46.43% which is within acceptance criteria²⁰⁻²¹ (USP NF 40).

CONCLUSION

The above-validated method is specific for the determination of palladium content in palladium acetate. The method is linear, precise, and accurate across a suitable analytical range. The method was successfully applied to the determination of palladium content in palladium acetate samples and satisfied recoveries and suitable reproducibility were obtained. In this Flame AAS method, consumption of toxic solvents is minimum. The proposed method has reduced digestion time for the determination of palladium in palladium acetate samples²².

ACKNOWLEDGEMENT

The authors are highly thankful to Perkin Elmer Mumbai, for allowing us to use their PinAAcle 900 series AA spectrometer.

Conflict of interest

The authors declare that there is no conflict of interest regarding the publication of this paper titled Simple, sensitive, and easy to use method for determination of palladium content in palladium acetate using flame atomic absorption spectrophotometry.

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