Determining the Water Solubility of Platinum, Palladium and Rhodium Sponge by Modified Flask Method to Provide Guidance on the PGM Separation

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Abstract

Platinum Group Metals (PGM) is an active component in various catalyst formulations. The water solubility of platinum, palladium and rhodium sponges was evaluated. The solubility values can provide useful insight into probable separation/recovery strategies from spent catalysts. A simplified flask method from Organization for Economic Co-operation and Development (OECD) Guideline 105[2]was used in this case to determine the water solubility of these PGMsponges using ultra sonication followed by Inductively Coupled Plasma-Optical Emission Spectrometric (ICP-OES) analysis of the PGM content. The results provided reliable data on the solubility of these metal sponges previously unavailable in the literature[1,2].

Keyword

Platinum Group Metals, OECD, ICP-OES

Introduction

Vehicular exhaust emissions are one of the major sources of air pollution. To limit these pollutants e.g. CO, HC, NO_x, the emission standards, based on European regulations were first introduced in 2000. Progressively stringent norms have been laid out since then[3]. All the new vehicles manufactured after the implementation of the norms have to be compliant with the regulations. In 1996, there was a revision of the mass emission norms for petrol and diesel vehicles, and the fitment of a catalytic converter was mandatory. Currently BSVI norms are applicable all across India which demands a very high level of pollutant control in the after treated emission gases

A catalytic converter contains precious metals such as palladium, platinum, and rhodium in order to convert harmful gases emitted from vehicle engines to relatively harmless ones by reduction of nitrogen oxides (NO_x) into nitrogen N_2 and the oxidation of hydrocarbons and CO to CO2.Depending on the type of engine and application, the architecture of the catalyst with respect to concentrations of PGMs in the unit vary widely. In recent car catalytic converters, Pt, Pd and Rh concentration ranges from 300 to 3000 mg/L; In all cases, the percentage of total content of PGMs in the samples are less than 0.5%.

There is an increase in demand of these PGM out of the total general demand for these metals[4] (Figure 1, Table 1). While Palladium and Rhodium automotive catalyst demand is the biggest share of the overall demand (>80%), the Platinum automotive catalyst demand is 35% of the total demand

PGM	2018-2020		
	Pt	Pd	Rh
Total Demand (kOz)	23307	31663	3203
Automotive Demand (kOz)	8099	27045	2833
% of Total Demand	35	85	88
(Source: PGM Market Report 2021, Johnson Matthey)			

Table 1: Pt, Pd, Rh share of the automotive catalyst demand from 2018-2020.

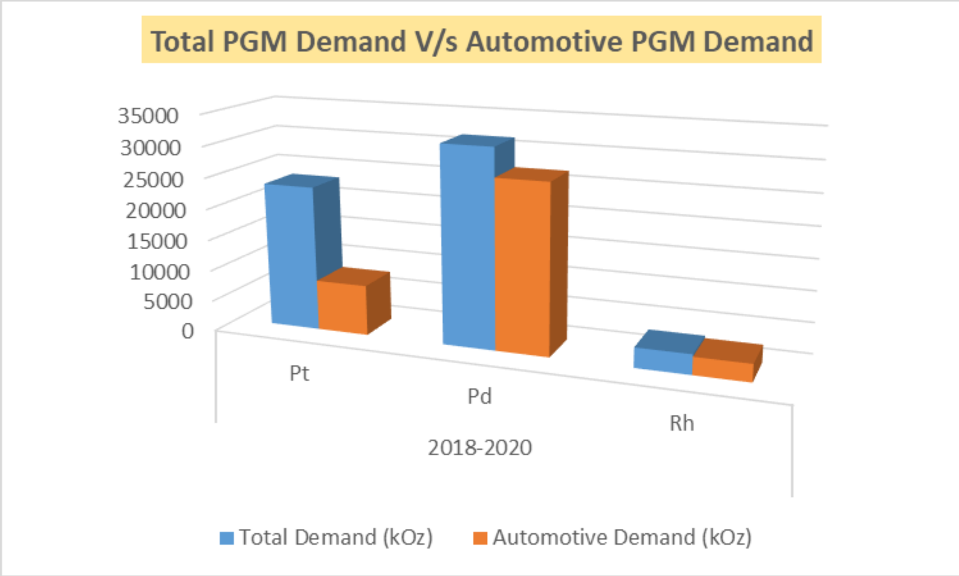


Figure 1: Comparison of the general demand of the PGM metals and its demand in the catalytic converter industry[4]

Thus, to cater to the general demand and low supply of the raw PGMs,there arises the need to recycle these precious metals to alleviate expensive and energy intensive mining and, in the process, avoiding negative environmental impact. Moreover, another motivation to recycle the spent catalytic converters is the high monetary values and quantitatively low availability and supply of the raw PGMs.

There are many separation processes available with respect to extraction of precious metals from spent catalysts. However, as the years are going by, we are moving towards electrical vehicles and greener ways of production. The most ideal way to separate the metals would be through specific precipitation using their solubility products because of its inherent simplicity and without the need for using expensive extracting agents and stripping procedure thereafter.

The solubility product constant, K_{sp} is the equilibrium constant for a solid substance dissolving in an aqueous solution. It represents the extent to which a solute dissolves in solution. The more soluble a substance is, the higher the K_{sp} value it has at a given temperature.

The water solubility's for 22 PGM salts and complexes were determined by Matt Gregory[1] as per the OECD Guideline 105. Our present work focuses on obtaining a comparative estimate of solubility product differences of all three PGM sponges– Platinum, Palladium and Rhodium using the OECD flask method[2] using a simple experimental setup. This will help us to further design an appropriate precipitation strategy to separate the PGM selectively to enable recovery from the spent catalyst.

Materials and Instruments

1. Furnace (850 °C)- Nebartherm Make Temperature Range up to 1100 °C with variable ramping options
2. Ultrasonicator–PEI make (40Hz)
3. MilliQ DI Water – Conductivity 1.27µS/cm (at 25 °C)
4. ICP OES- Agilent 5800 series

   Power: 1200kW

   Nebulizer gas: Argon

   Nebulizer flow: 0.5-0.7 L/min

   Auxiliary flow: 1.0L/min

   Pump Flow rate: 12 rpm

   Detector view: Dual

   Calibration Range:

Standard	Pt (ppm)	Pd (ppm)	Rh (ppm)
Blank	0	0	0
Std-1	1	1	1
Std-2	10	10	10
Std-3	20	20	20

Table 2: Calibration Mix

5. **NIST traceable standards** -1000ppm each for Platinum, Palladium and Rhodium for preparing the calibration mix (Table 2)
6. **pH Meter**: Analab make with ready to use traceable pH standards 4.0 /7.0 / 9.2
7. 10-15% w/w Platinum Nitrate, Palladium Nitrate and Rhodium Nitrate solutions – Heraus make- used without further purification

Experimental Details

2gm of each PGM solutions (Platinum Nitrate, Palladium Nitrate and Rhodium Nitrate) are weighed in a silica crucible and ignited at 850°C to yield corresponding PGM sponge (refer figure 2 showing palladium sponge).An approximate indicator of the solubility is provided by Test No. 105: Water Solubility;OECD[2]given in the table3 below

0.2 g of sponge was added to 20 ml of deionized water (MilliQ water -1.27µS/cm at 250°C) in three different conical flasks corresponding to sponges derived from Platinum nitrate, Palladium nitrate and Rhodium nitrate respectively. The flasks were stoppered tightly and ultra-sonicated at 40Hz frequency for 1 min at 30°C. After 24 hours the solutions were filtered using 0.1 µm membrane filters and the PGM content was determined by ICP-OES. The pH of the solution was also measured (Table 3). The analysis was repeated for each material to provide duplicate data.

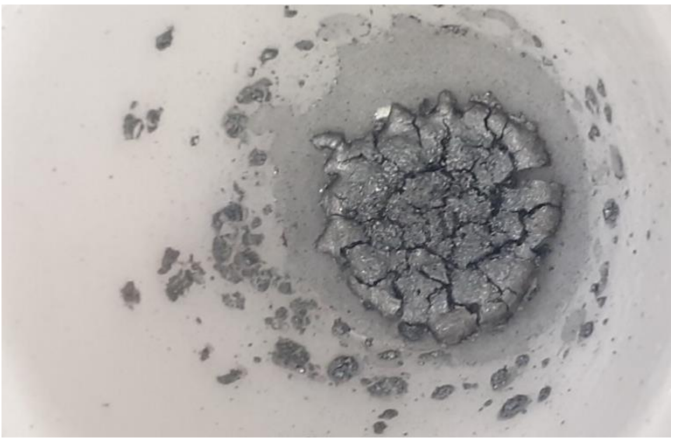


Figure 2: Palladium Sponge

Results and Discussion

The water solubility reported by Matt Gregory[1] using the shake flask method as per the OECD Guideline 105 for a variety of PGM containing salts, but the comparative solubility for a similar salt /moiety of the PGM is not available. The present experimental setup is designed to compare the water solubility's for PGM metal sponges. Here to ensure uniform shaking ultrasonic frequency and sonication time was kept same for all three sponge samples to ensure less variability as compared to manual shaking.

The Linearity of the ICP calibration with the calibration mix (Table 2) was verified first prior to analyzing the filtered samples. The correlation coefficient of calibration in each of Platinum, Palladium and Rhodium was >0.9999 which is adequate.

The filtered samples were analyzed and the ppm of the metal content obtained in the filtrate was converted to g/L (water solubility). The pH of these filtrate solutions was also measured by a pH meter calibrated by pH Buffer 4.0/7.0/9.2

The results of the analysis are tabulated in Table 3

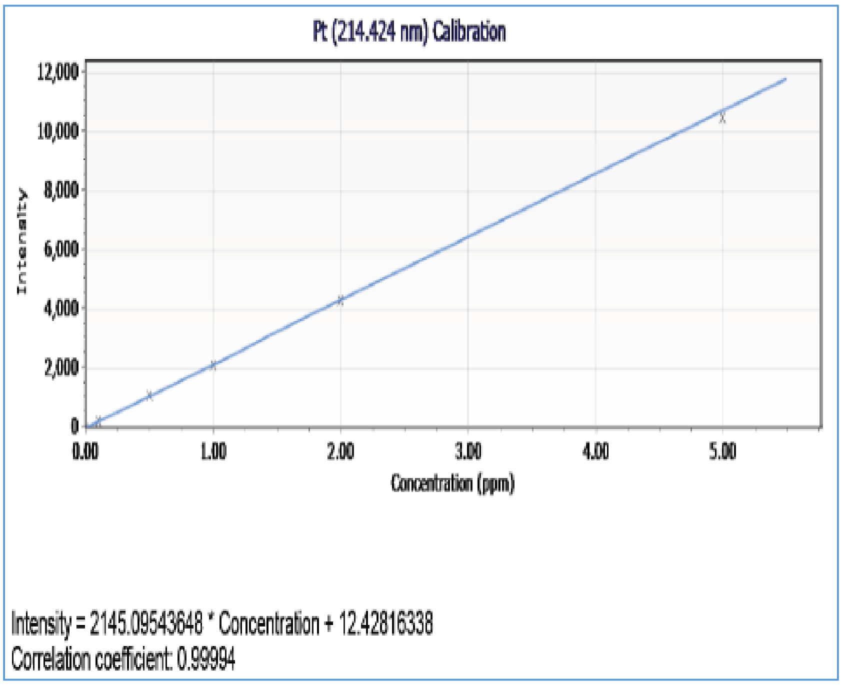
Compounds	CAS No	ppm in filtered sample	Water Solubility g/L	pH
Palladium Sponge	1314-08-5	0.06	$6X10^{-5}$	5.03
Platinum Sponge	1314-15-4	1.1	$1.1X10^{-3}$	3.38
Rhodium Sponge	12036-35-0	6	$6X10^{-3}$	3.93

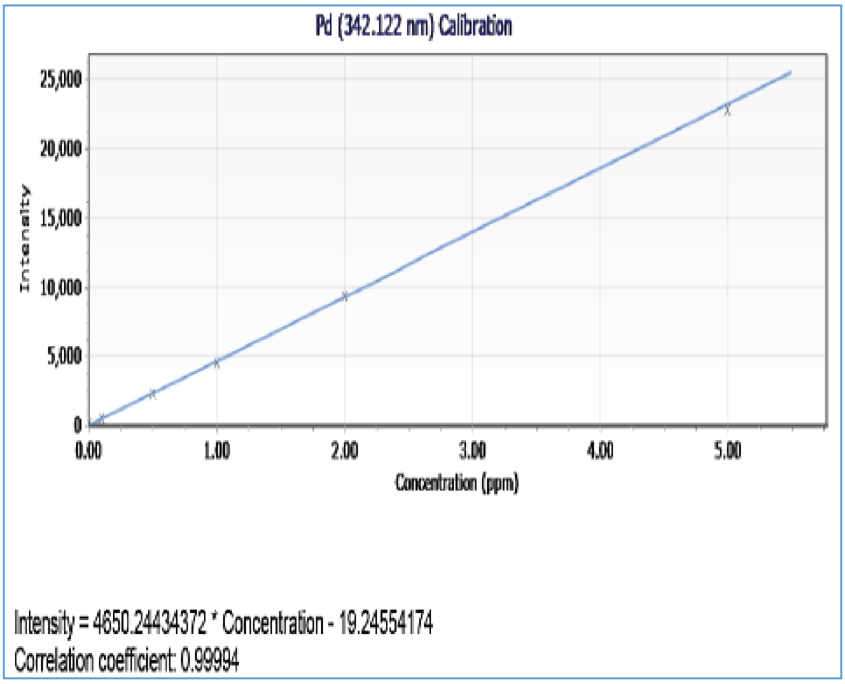
Table 3: Analyzed water solubility and pH of PGM sponge in DI water

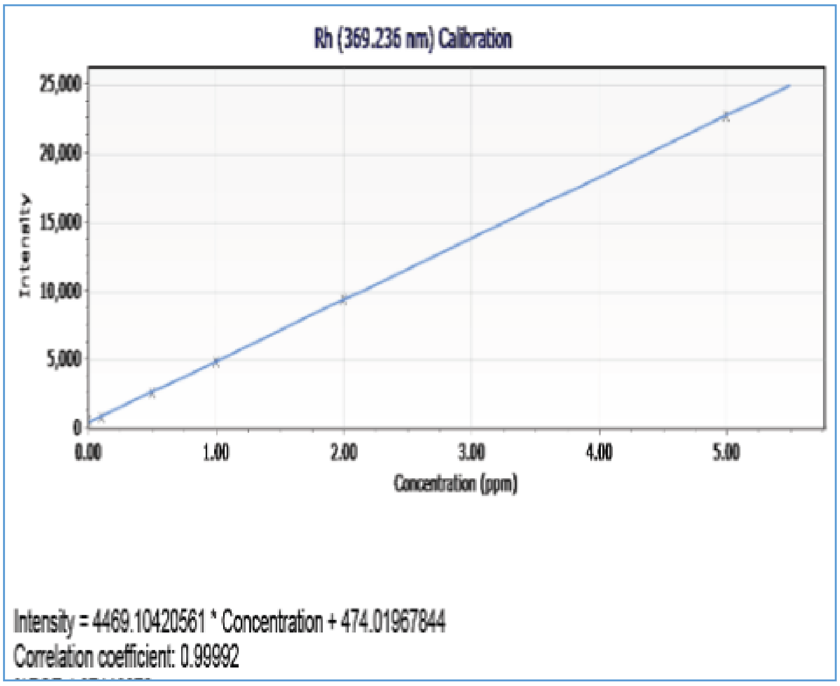
A distinct trend in the water solubility's of these metals could be obtained where Platinum sponge has the highest water solubility while Palladium sponge has the least water solubility. The pH of these filtrate solutions was analyzed to check for differences due to the various PGE's and shows a distinct relative basicity of the Palladium sponge in comparison to the Platinum and Rhodium sponges (Table3).In the actual catalytic converter, however, the PGM metals are anchored on a solid support material on the honeycomb structure after calcination and converts emission gases based on solid state chemical reactions between solid and gaseous interaction, hence will not leach out. The leaching out process may require strongly oxidizing conditions such as aqua regia[5], attrition scrubbing[6] and does not simulate the situation at the gas-liquid interface of the engine exhaust. The extraction of PGM sponge in acidic solution (DI water after acidifying) was therefore not in the current scope of the work.

As observed above, the calibration range was very broad compared to the water solubility's (concentration of platinum, palladium and rhodium analyzed) in the samples, hence a narrower calibration range from 0 to 5ppm was made to enhance the detection accuracy and reduce the errors (% RSD).

With the narrower calibration range the % RSD was found to be reduced to about 2 -2.7% which was earlier nearly 5% (for Palladium and Rhodium). Also, the correlation coefficient was also consistent (Figure 3)







%RSD: 2.72% %RSD: 2.02% %RSD: 1.97%

Figure 3: Linearity plot of Intensity v/s Concentration–Pt, Pd and Rh – narrower range with correlation coefficient & error

A second set of water solubility trial was undertaken with fresh sponge samples and the results are tabulated in Table 4

Compounds	CAS No	ppm in filtered sample	Water Solubility g/L	pH
Palladium Sponge	1314-08-5	0.09	$9X10^{-5}$	5.06
Platinum Sponge	1314-15-4	1.79	$1.8X10^{-3}$	2.82
Rhodium Sponge	12036-35-0	4.89	$4.9X10^{-3}$	2.97

Table 4: Analyzed water solubility of PGM sponge in DI water with narrower calibration range and pH of the filtrate

The same trend of water solubility's could be obtained where Platinum sponge has the highest water solubility while Palladium sponge has the least water solubility. Also, similar trend of pH observed as in the first trial.

Conclusions

This investigation has provided reliable water solubility data for a range of PGM sponge previously unavailable in the literature and is required to convert PGM sponge into the solution form before it is being used in manufacturing of Catalytic converter. A range of PGM sponges were analyzed for water solubility. Each substance was measured in duplicate and compared. The flask method according to OECD 105 guideline was used for the oxide samples. From the experiment it is clear the water solubility of the sponge is of the order Pt >Rh>Pd.

This investigation has provided reliable water solubility data for a range of PGM sponge previously unavailable in the literature. Measurement of solubility is of paramount importance as losses in PGM due to inadequate solubility or less recovery will not only lead to resource as well as economic loss. In addition, this can form the basis for selective precipitation strategies for PGM recovery from waste catalysts especially Pd (due to two orders difference in solubility) from Pt and Rh without resorting to the use of expensive extracting agent.

Acknowledgement

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