

## Flame Atomic Absorption Spectrometric Determination of Gold, Palladium and Platinum in Catalytic Converters

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A simple procedure for the flame atomic absorption spectrometric determination of gold, palladium and platinum contents of the catalytic converters of the automobiles was proposed in the present work. The procedure includes the combination of solid phase extraction of gold, palladium, platinum on amberlite XAD-7 adsorption resin and flame atomic absorption spectrometric determination. The procedure was also applied to the determination of analyte contents of natural waters with satisfactory results.

**Key Words:** Determination, Gold, Palladium, Platinum, Catalytic converter, Atomic absorption spectrometry.

### INTRODUCTION

The determination of the trace heavy metal ions by atomic absorption spectrometry is problematic due to low levels of the analytes and the interference effects of the main components of the samples. In order to solve these problems, separation and enrichment procedures including cloud point extraction, liquid-liquid extraction, coprecipitation, ion-exchange, electrodeposition, etc.<sup>1-7</sup> have been proposed by the researchers. Solid phase extraction based on adsorption is also one of the important enrichment and separation techniques for trace heavy metal ions. Various materials<sup>8-13</sup> like synthetic resins including amberlite XAD, chromosorb, amborsorb, diaion resins and natural adsorbents including activated carbon, alumina, and wool have been used in solid phase extraction of trace metal ions.

Because the levels of platinum, gold and palladium in the environmental samples are generally lower concentration levels than the detectable levels of these elements by flame atomic absorption spectrometry, separation and pre-concentration procedures including solid phase extraction have been applied for the determination of these elements<sup>14-19</sup>. Palladium and platinum play a decisive role in the performance of exhaust systems, worldwide applied in vehicles and in some household utensils, to reduce the emission of carbon monoxide, nitrogen

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oxides and hydrocarbons<sup>20</sup>. Emission of palladium and platinum from the abrasion of automotive catalytic converters into the environment has significantly increased. The concentration of these elements is still relatively low in environmental compartments, thus their analysis requires analytical methods of high sensitivity, selectivity and the control of interference effects<sup>20</sup>. Various procedures have been proposed for the determination of these elements<sup>21-28</sup>.

In the present work, a simple procedure has been proposed for the flame atomic absorption spectrometric determination of gold, platinum and palladium contents of catalytic converters and natural waters.

## EXPERIMENTAL

### Instruments

All metals were determined with a Perkin-Elmer Model 3110 atomic absorption spectrometer. For analytical quality assurance, the result of each metal was corrected by subtracting the value from the blank. Also, after every sample reading, standards were run to make sure that the obtained results were within range. A 10 cm long slot-burner head, a lamp and air-acetylene flame were used. No background corrections were made.

### Reagents and solutions

All chemicals used were the same as previously described in Elci *et al.*<sup>29</sup> Analytical reagent-grade chemicals were employed for the preparation of all solutions. Freshly prepared double distilled water, from a quartz still, was used in all experiments. Standard solutions (1000 mg/L) of the metal ions were prepared by dissolution of pure metals or their salts (E. Merck, Darmstadt) and further diluted prior to preparation of standard solutions of the metal ions. Extra pure acetone, hydrochloric acid and nitric acid from Merck, Darmstadt were used for the preparation of acid solutions and buffer solution used throughout these work and digestion of samples. Potassium iodide of analytical reagent grade was purchased from Merck, Darmstadt.

A 500 mg sample of amberlite XAD-7 (particle size 0.3–0.9 mm) resin suspended in water was slurry-packed in a glass column (10 mm i.d.) fitted with porous disk filter and a glass stopcock. The adsorption column is given in Fig. 1. After completing each experiment, the column was rinsed with very large volume of water and stored for the next use.

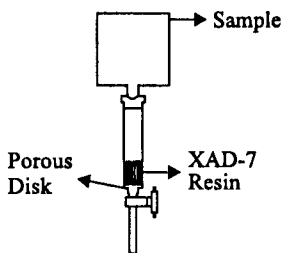


Fig. 1. Adsorption column for pre-concentration

### Procedure for catalytic converter

Used catalytic converter samples after the washing of their surfaces, were dried at 110°C for 2 h. A 50–200 mg amount of sample was decomposed with 5–10 mL of aqua regia and the solution was evaporated to dryness. The digestion process was repeated twice. Ten millilitres of 2 M HCl was added to the residue. The suspension was filtered through a blue band filter paper and the insoluble part was washed with a solution containing 2 M HCl and 0.1 M KI. The final solution was diluted to 25 mL with the mixture solution of 2 M HCl and 0.1 M KI. The solutions were gravitationally passed through the column, at a flow rate of 5 mL/min. The retained analytes were eluted by 8–10 mL of acetone at a flow rate of 1–2 mL/min. The flow rates were controlled in the range of 1.0–25 mL/min, by the stopcock of the column. The effluent was collected in a small glass beaker and carefully evaporated to 0.5–1 mL on a hot plate adjusted to *ca.* 30–40°C. The residue was diluted to 2 or 5 mL using 1 M HCl solution. Gold, palladium and platinum in the final solution were determined by flame atomic absorption spectrometry (FAAS).

## RESULTS AND DISCUSSION

The optimized conditions for the preconcentration/separation were established using 50 mL of de-ionized water containing 2–10 µg of palladium, gold and platinum and submitting these solutions to the procedure. The percentage of metal adsorbed on the column was calculated from the amounts of metal in the starting sample and the amounts of metal eluted from the XAD-7 column. The optimal conditions for preconcentration and separation were previously examined in detail<sup>29</sup>. In order to obtain the quantitative recovery values for analyte ions, the effect of iodide concentration on the recoveries of gold, palladium and platinum was also investigated using the test solution prepared with varying concentration of iodide in 2 M HCl. Gold, palladium and platinum were quantitatively (95%) recovered together from 0.5 M KI solution prepared in 2 M HCl. Recoveries for palladium and gold were found quantitative up to a sample volume of 300 mL and 400 mL, respectively. Platinum was completely (95%) recovered up to a sample volume of 100 mL. The amount of amberlite XAD-7 on the glass mini column was 500 mg. In the light of our previous works on the solid phase extraction<sup>5, 14, 13</sup>, acetone was chosen as an eluent. The minimum volume of acetone required for the quantitative elution of the retained complexes of gold, platinum and palladium was experimentally found to be 8–9 mL. The maximum flow rates for sample solutions, the quantitative retentions obtained for gold, palladium and platinum, were found to be as 25, 11 and 4 mL/min, respectively. The flow rate of acetone as eluent was chosen as 2.0 mL/min for gold, platinum and palladium.

The effects of some metal ions for the preconcentration of analytes are at tolerable levels. As pointed in literature<sup>29</sup>, Sb<sup>3+</sup>, As<sup>3+</sup>, Na<sup>+</sup>, Zn<sup>2+</sup>, Cr<sup>3+</sup>, Mg<sup>2+</sup>, Pb<sup>2+</sup>, Ca<sup>2+</sup>, Ni<sup>2+</sup>, Fe<sup>2+</sup> and Cu<sup>2+</sup> ions at 6000 mg/L levels did not influence, the separation and determination of gold, palladium and platinum.

The relative standard deviations (RSD) for flame atomic absorption spectrometric determinations were lower than 9%. The recoveries obtained for gold and palladium with the model solutions were higher than 95%. The detection limits, based on three times the standard deviation of the blank ( $3\sigma$ ,  $n = 20$ ) for gold, palladium and platinum, were found to be 0.032, 0.025 and 0.103 mg/L, respectively.

Gold, platinum and palladium contents of tap water samples from Erciyes University were measured by the proposed method. Table-1 shows the results of analysis of the drinking water sample in which known amounts of gold, palladium and platinum were spiked. The recoveries of gold and palladium were greater than 95%. For this reason, the relative errors are 5% or lower than 5%. The recovery of platinum was lower than 90% from water sample.

TABLE-1  
RECOVERIES OF GOLD, PALLADIUM AND PLATINUM IN A TAP WATER SAMPLE  
BY THE SOLID PHASE EXTRACTION PROCEDURE ( $n = 3$ )

Analyte	Added, $\mu\text{g}$	Found, $\mu\text{g}$	Recovery, %
Gold	—	n.d.	—
	5	4.9	98
	10	9.7	97
Palladium	—	n.d.	—
	5	4.8	96
	10	10.0	100
Platinum	—	n.d.	—
	5	4.4	88
	10	8.5	85

n.d.: not detected

A used catalytic converter sample removed from an automobile was also analyzed. In order to determine some metals in the catalytic converter, 200 mg of the catalytic converter was dissolved by aqua regia and then analyzed directly using flame atomic absorption spectrometry for Cu, Fe, Ni and Pb levels. As a result, the concentrations of copper, iron, nickel and lead with triplicate measurements were found to be 39, 91, 30 and 613  $\mu\text{g/g}$ , respectively. The content of palladium was found to be  $1781 \pm 251 \mu\text{g/g}$  ( $n = 4$ , with confidence limits at 95% confidence level). The relative standard deviation (RSD) for palladium determinations is 8.9%.

According to the tolerable levels of copper, iron, nickel and lead for the presented method, the low concentrations of copper, iron, nickel and lead in the sample are not important for interference on the determination of gold and palladium by the proposed column procedure.

Thus the proposed separation/preconcentration procedure given in the experimental section was successfully applied to the solution obtained by dissolving 200 mg of the catalytic converter sample. The result for palladium was found to be 1692.43  $\mu\text{g/g}$  ( $n = 4$ , with confidence limits at 95% confidence level). RSD is 1.6%. At the 95% confidence level, there is no significant difference between the two concentration values of palladium obtained with the direct flame atomic absorption spectrometric measurement and the proposed column procedure.

The concentrations of gold and platinum were not detected with direct flame atomic absorption spectrometric determination and the proposed preconcentration-separation procedure.

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