Determination of Platinum Levels in Environmental Samples by ICP-MS and Optimization Conditions for Preconcentration

Uyan Yuksel

Department of Chemistry, Vocational School of Technical Sciences, Siirt University, Siirt 56100, Turkey

Abstract: In this study, the platinum (Pt) levels in environmental samples (soil, water, dust) collected from heavily trafficked streets in the city center of Siirt were determined using ICP-MS (Inductively Coupled Plasma Mass Spectrometry). The results obtained were compared with the platinum levels in environmental samples collected from rural areas. A total of 20 samples (10 soil and 10 dust) were collected from streets with heavy traffic in the center of Siirt. These samples were digested using microwave-assisted digestion and then analyzed for platinum content by ICP-MS. For determining platinum concentrations at very low levels in environmental samples, ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy) or GF-AAS (Graphite Furnace Atomic Absorption Spectroscopy) could be used; however, prior enrichment is recommended in these cases due to the higher detection limits of these instruments compared to ICP-MS. To facilitate enrichment, a SPE (Solid-Phase Extraction) method was studied. For this purpose, a column was prepared using Amberlite XAD-4 as the adsorbent and the bacterium *Aneurinibacillus thermoaerophilus* VO-12 as a biosorbent, which was then used for the pre-concentration of platinum from environmental samples. Optimization of certain parameters, such as pH and flow rate, for the SPE process was carried out, and the most suitable conditions were identified. Platinum levels in samples collected from both the city center and rural areas were determined using the developed method. The accuracy of the method was validated by using the BCR-723 certified reference material.

Key words: Platinum, ICP-MS, Siirt, SPE, pre-concentration.

1. Introduction

Platinum (Pt) is a rare, valuable, and chemically inert metal, known for its remarkable resistance to corrosion, high melting point, and exceptional catalytic properties. Its importance spans across various industrial sectors, including electronics, jewelry, and particularly in automotive applications where it is used in catalytic converters. Platinum's ability to withstand harsh environmental conditions while facilitating crucial chemical reactions makes it indispensable in reducing harmful emissions from vehicles, especially in converting toxic gases such as carbon monoxide (CO), nitrogen oxides (NO_x), and hydrocarbons (HC) into less harmful substances like carbon dioxide (CO_2) and nitrogen (N_2) [1].

In addition to platinum, the PGEs (Platinum Group Elements) include palladium (Pd), rhodium (Rh), osmium (Os), iridium (Ir), and ruthenium (Ru). These metals share similar physical and chemical properties, such as high catalytic efficiency, resistance to oxidation, and stability at high temperatures [2]. Due to these characteristics, PGEs are widely utilized in various industrial applications, but their use in catalytic converters is perhaps the most critical in terms of environmental impact. Since their introduction in the 1970s, catalytic converters have significantly reduced vehicle emissions worldwide. However, the use of PGEs in these converters has led to their gradual accumulation in the environment, particularly in areas with high traffic density [3, 4]. Despite the benefits of using PGEs in reducing air pollution, their release into

Corresponding author: Uyan Yuksel, Assistant Professor, research fields: analytical chemistry, chromatography, ICP.

the environment, particularly from vehicle exhaust systems, has raised concerns over long-term environmental and health impacts. PGEs are emitted as fine particles and can accumulate in roadside soils, plants, and sediments. They can also enter aquatic systems via runoff, potentially infiltrating the food chain [5, 6]. Although PGEs in their metallic form are generally considered biologically inert, their soluble compounds, especially chloride-containing ones, can be cytotoxic and allergenic, posing risks to human health. Platinum, in particular, has been linked to conditions such as asthma, dermatitis, and reproductive issues such as spontaneous abortion [7]. Given the increasing concentrations of PGEs in urban environments, particularly in high-traffic areas, there is growing concern about their environmental persistence and bioavailability. The accurate determination of trace amounts of these elements in environmental samples, such as soil, sediment, and water, is crucial for monitoring their environmental impact and for assessing potential risks to human health. PGEs, which include platinum (Pt), palladium (Pd), rhodium (Rh), osmium (Os), iridium (Ir), and ruthenium (Ru), are highly valued due to their unique chemical and physical properties, such as resistance to corrosion, high melting and boiling points, and superior catalytic performance [1, 2]. These characteristics have led to their extensive use in industrial applications, particularly in catalytic converters, where they play a critical role in reducing harmful emissions from vehicle exhausts [3, 4].

Catalytic converters, first introduced in the mid-1970s in the USA, and later in Germany and the EU, were developed to decrease the emission of hazardous gases such as nitrogen oxides (NO_x), carbon monoxide (CO), and hydrocarbons (HC) by converting them into less harmful substances like nitrogen (N_2), carbon dioxide (CO_2), and water vapor (H_2O) [3]. However, as the number of vehicles equipped with these catalytic converters has grown, so too has the unintended release of PGEs into the environment. Vehicle exhausts have become a significant source of PGE contamination in urban areas, where high traffic density accelerates their emission into the atmosphere [5]. Once released, PGEs can settle into road dust, soil, and water bodies, where they accumulate and pose potential environmental and health risks. Platinum and other PGEs have been detected in airborne particulate matter, roadside soils, and vegetation, indicating that these metals can become bioavailable and enter the food chain [8-10]. Notably, platinum in its metallic form is considered relatively inert; however, its soluble compounds, especially those containing chloride, are known to be cytotoxic and allergenic, posing serious health risks such as asthma, dermatitis, and reproductive issues, including increased rates of spontaneous abortion [7].

The growing concern over the environmental and human health risks associated with long-term exposure to PGEs necessitates accurate and reliable methods for their detection and quantification in environmental matrices. This is particularly challenging due to the extremely low concentrations of PGEs in soils, sediments, and water, combined with the complex nature of these matrices. ICP-MS (Inductively Coupled Plasma Mass Spectrometry) has emerged as one of the most effective techniques for trace-level detection of PGEs, due to its high sensitivity and multi-element capability [11-13]. However, ICP-MS is often hindered by spectral and non-spectral interferences, especially when analyzing complex environmental samples, such as seawater and road dust, where monoatomic and polyatomic ions from the matrix can overlap with the signals of interest [14, 15]. To overcome these challenges, various pre-treatment techniques have been developed, with SPE (Solid-Phase Extraction) being among the most effective for isolating and concentrating PGEs prior to ICP-MS analysis [12, 14, 16]. SPE involves the use of sorbents such as Amberlite XAD-16, Dowex resins, and modified silica gels, which have been shown to effectively separate and pre-concentrate PGEs from environmental samples [17, 18].

Additionally, advancements in ICP-MS technology, such as the DRC (Dynamic Reaction Cell), have further

enhanced the accuracy of PGE determination by minimizing spectral interferences during analysis [19]. This study aims to develop and optimize a reliable method for the simultaneous determination of platinum in environmental samples using an automated flow analysis system coupled with ICP-MS. The method utilizes an on-line pre-concentration technique based on a chelating resin, which selectively retains PGEs, followed by elution with a nitric acid-thiourea solution. This approach ensures effective separation and concentration of PGEs from complex environmental matrices, enabling precise and sensitive detection of these elements in road dust, water, and biological samples. The accuracy of the method will be validated using CRMs (Certified Reference Materials), and its application will be demonstrated on environmental samples collected from various locations.

2. Experimental

2.1 Instruments

Platinum levels in the collected samples were determined using a Thermo Scientific iCAP Q ICP-MS. The ICP-MS operational conditions are provided in Table 1. Sample digestion was performed using a Berghof Microwave Digestion System, with Teflon vessels (100 mL volume) that can withstand up to 60 bar pressure and 250 ℃ temperature. The digestion parameters are listed in Table 2.

2.2 Reagents

For calibration, a 1,000 mg/L platinum standard stock solution (Merck) was used. Chemicals for the digestion process included concentrated nitric acid (HNO_3, 65%, Merck, Germany), hydrogen peroxide (H_2O_2, 30%, J.T. Baker), hydrochloric acid (HCl, 37%, Merck), and hydrofluoric acid (HF, 40%, Merck). CRMs used in the study were NIST SRM 2557 (Recycled monolith autocatalyst) and BCR-723 (road dust) [4, 20].

2.3 Sample Collection

Soil, roadside dust, and plant samples were collected from high-traffic areas in Siirt city center. As a control, plant samples were also collected from rural areas with minimal vehicular activity. Plant samples were dried at 36 ℃, weighed, and ground into powder before undergoing the digestion process. Roadside dust samples were dried at 105 ℃, ground, and homogenized before

Table 1   ICP-MS operating conditions.

Instrument	Thermo Scientific and ICAP Q
RF power (W)	0.95
Nebulizer gas flow (L/min)	1.12
Auxiliary gas flow (L/min)	0.80
Cooling gas flow (L/min)	14.00
Acquisition mode	Peak jumping, simultaneous pulse count/analog detector system
Dwell time/isotope	30 ms for ^{195}Pt
Channels per mass	3 for ^{195}Pt
Number of repetitions	3

Table 2   Microwave digestion conditions for Programs A and B.

Program A	Step 1	Step 2	Step 3	Step 4
Temperature (℃)	100	160	180	100
Time (min)	10	10	10	10
Ramp time (min)	5	3	3	3
Program B	Step 1	Step 2	Step 3	Step 4
Temperature (℃)	100	170	180	100
Time (min)	3	5	5	3
Ramp time (min)	3	2	2	3

digestion. Platinum levels in all samples were then determined using ICP-MS. The same digestion process applied to the roadside dust samples was also used for the CRMs BCR-723 and NIST SRM 2557 [5, 8].

2.4 Preparation of Biosorbent for SPE

The biosorbent was prepared using *Aneurinibacillus thermoaerophilus* VO-12, which was isolated from the Billoris Hot Springs in Siirt. After drying and grinding 250 mg of dead bacterial biomass, it was mixed with 750 mg of Amberlite XAD-4 resin and 10 mL of deionized water. The mixture was stirred using a heated magnetic stirrer until homogeneity was achieved. The material was then packed into a polypropylene column (1.0 cm × 10.0 cm), and used for SPE. A 50.0 μg/L platinum solution was prepared, adjusted to the desired pH, and passed through the column using a peristaltic pump at an optimal flow rate. After the solution had passed through, the retained platinum was eluted using 1.0 M HCl and analyzed via ICP-OES [9, 17].

2.5 Microwave Digestion Procedure for Samples and CRMs

For plant samples, 500 mg of sample and 50 mg of the 2,557 SRM were placed in Teflon digestion vessels. To each vessel, 5 mL of concentrated HNO_3 and 3 mL of H_2O_2 were added, and digestion was performed using Program A conditions listed in Table 2. Once the digestion was complete, the vessels were cooled to room temperature, and 0.2 mL of HF and 4 mL of HCl were added, followed by Program B. After digestion, the samples were transferred to 50 mL Falcon tubes and diluted with deionized water to a final volume of 50 mL. For roadside dust and soil samples, approximately 1 g of each sample was digested using the same Programs A and B. After digestion, the samples were evaporated to dryness and treated with 3 mL of concentrated HCl. This heating process was repeated twice. Finally, 25 mL of 0.25 M HCl was added, and the samples were filtered through membrane filters, then diluted to 50 mL and stored for ICP-MS analysis. The same

digestion procedure was applied to the CRMs BCR-723 [14, 20].

3. Results and Discussion

3.1 Optimization for SPE

3.1.1 Effect of pH

The effect of different pH values (2.0-8.0) on the biosorption of metals by immobilized *Aneurinibacillus thermoaerophilus* VO-12 is shown in Fig. 1. According to Fig. 1, the optimum biosorption pH value for platinum was found to be 3. It has been reported that pH is a crucial factor in biosorption efficiency for various microorganisms. In metal-microorganism interactions, the pH of the medium is a significant parameter in biosorption processes because it affects the form of the metal and the functional groups on the cell surface that have an affinity for metals, as well as the negative network of the cell wall chemistry. The pH-dependent metal uptake is related to the competition between protons and metal cations at the surface of the biosorption medium. As a result of these different chemical interactionsns between the metal and the cell surface, the retention capacity for metal ions can vary across different pH levels. The relationship between metal uptake and pH depends on the functional groups present on the bacterial cell wall. pH is the most critical parameter affecting the biosorption of metal ions onto the surface of microorganisms.
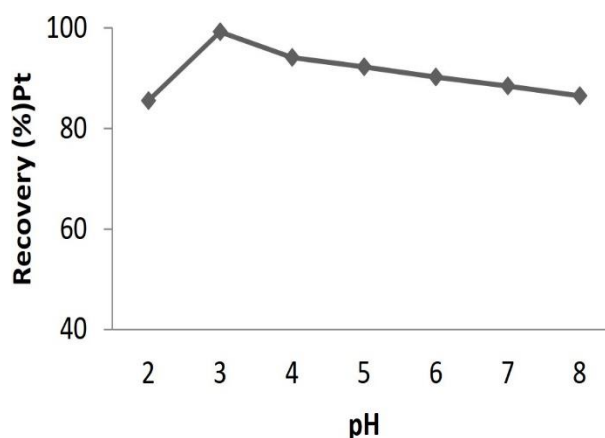

Fig. 1   Effect of different pH values on platinum biosorption.

Determination of Platinum Levels in Environmental Samples by ICP-MS and
Optimization Conditions for Preconcentration

259

3.1.2 Effect of Flow Rate

The flow rate of metal solutions through the column is one of the important parameters in SPE studies, as it is crucial for the recovery of analytes and time management. The effect of flow rate on the biosorption of platinum was studied at flow rates between 1.0 and 5.0 mL/min. The experimental results are presented in Fig. 2. According to these results, the recovery for platinum was found to be over 95% at a flow rate of 1.0 mL/min, whichwas selected as the optimal flow rate for subsequent studies.

3.2 Accuracy of the Digestion System with SRM 2557 and BCR 723

The results of the platinum determinations by ICP-MS in the solutions obtained after microwave-assisted digestion of the SRM materials used for method validation are given in Table 3. The data indicate that there was no loss of material from the microwave digestion system, and platinum was recovered from the SRM materials with high efficiency. The digestion system was found to be accurate and reliable.

3.3 Platinum Levels in Plant Samples

The results of the platinum analyses performed by

ICP-MS on plant samples collected after microwave digestion are presented in Table 4. It was observed that platinum levels in the plant samples decreased as the distance from the city center increased, and that platinum levels in the samples collected from areas with high traffic density in the city center were elevated.

3.4 Platinum Levels in Roadside Dust Samples

The platinum levels in roadside dust samples are presented in Table 5. It was observed that platinum levels in the dust samples collected from roadsides with heavy traffic were higher compared to other samples (plants, soil).
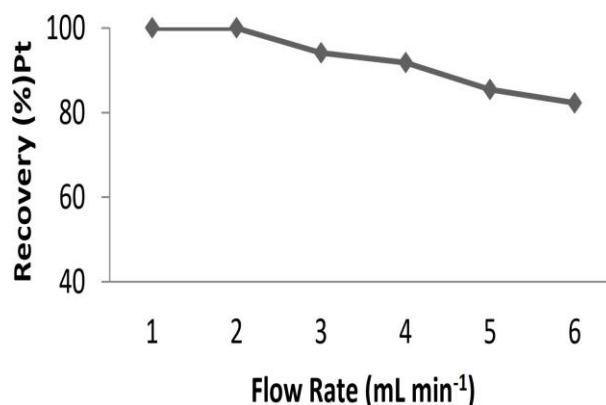

Fig. 2   Effect of flow rate on platinum biosorbent.

Table 3   Platinum recoveries from SRM 2557 and BCR-723.

Sample	Element	Certified amount (g/kg)	Measured (g/kg)
BCR-723	^{195}Pt	81.3 ± 3.3	83.1 ± 3.4
SRM 2557	^{195}Pt	$1,131 \pm 16$	$1,139 \pm 45$

Table 4   Platinum levels in plant and soil samples collected from rural and urban areas.

Sample	Element	Measured (g/kg)
Rural soil	^{195}Pt	0.93 ± 0.02 to 0.36 ± 0.007
Rural plant	^{195}Pt	1.50 ± 0.04 to 3.25 ± 0.09
Urban soil	^{195}Pt	7.50 ± 0.30 to 10.25 ± 0.42
Urban plant	^{195}Pt	15.40 ± 0.62 to 32.25 ± 1.10

Table 5   Platinum levels in roadside dust samples.

Sample	Element	Measured (g/kg)
Roadside dust	^{195}Pt	45.50 ± 2.70 to 65.80 ± 4.50

4. Conclusion and Recommendations

The method for the determination of platinum by ICP-MS, following microwave-assisted digestion of samples, was found to be a suitable method for detecting platinum in very low concentrations (μg/kg) from different sources (plants, dust, soil). Signal ratio measurements were performed to eliminate interference in ICP-MS analyses, and these interferences were successfully mitigated. The accuracy and precision of the microwave digestion procedures and ICP-MS and optimization conditions for preconcentration interference elimination techniques were tested with certified standards (SRM 2557 and BCR-723), and the results demonstrated the reliability of these methods. For the determination of trace platinum in environmental samples, if ICP-OES or GF-AAS are to be used, a pre-concentration step should be applied after digestion, due to the higher detection limits of these instruments compared to ICP-MS. In this study, SPE was employed as the pre-concentration method, with *Aneurinibacillus thermoaerophilus* VO-12 bacteria immobilized on Amberlite XAD-4 resin being used as the biosorbent in a column for platinum pre-concentration from environmental samples. Specific parameters such as pH and flow rate were optimized for the SPE method. Further studies could focus on the optimization of other parameters such as eluent volume and type, column packing material quantity, and column life for platinum analyses. The platinum levels in plant samples collected from rural areas were significantly lower than those in samples collected from high-traffic urban areas. These findings suggest that the primary source of platinum pollution is the release of platinum from catalytic converters in exhaust gases, as indicated in previous studies [20]. The platinum levels observed in the roadside dust samples collected in the city of Siirt were found to be lower than those detected in urban areas in European Union countries [20]. This result is expected, as the traffic density in Siirt is lower than that in European cities. Since platinum levels in roadside dust samples from any city in Turkey have not been previously studied, comparisons were made with European Union countries. Further studies in metropolitan cities of Turkey would be beneficial for assessing the level and control of platinum pollution.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

References

[1] Bond, G. 1991. "General İntroduction to Catalysis by Platinum-Group Metals." İn *Chemistry of the Platinum Group Metals: Recent Developments*, edited by F. R. Hartley. New York: Elsevier.

[2] McDonald, A. 1987. "Ore Deposites Models: Pt Group Element Deposites: Classification and Genesis." *Geosci. Can.* 14: 155-66.

[3] Ek, K., Morrison, G., and Rauch, S. 2004. "Platinum Group Elements in the Environment." *Science of the Total Environment* 334: 21-32.

[4] Castillo, M., Torres, A., Alonso, E., Cordero, T., and Pavon, J. 2012. "Multi-element Determination of Pt, Pd and İr Traces in Environmental Samples by İCP-MS after Preconcentration." *Talanta* 99: 853-8.

[5] Ravindra, K., Bencs, L., and Grieken, R. V. 2004. "Platinum Group Elements in the Environment and Their Health." *Science of the Total Environment* 318: 1-43.

[6] Ni, W., Wang, T., Mao, X., Zhang, L., Guo, X., Fan, L., and Xiao, F. 2025. "Isotopic Spike [190]Os as İnternal Standard and Empirical Coefficient LA-ICP-MS Combined with Sb Fire Assay for the Determination of Ultra-trace Platinum Group Elements in Geochemical Samples." *Talanta* 281: 126932.

[7] Cristaudo, A., Sera, F., Severino, V., and de Rocco, M. 2005. "Occupational Hypersensitivity to Metal Salts

Determination of Platinum Levels in Environmental Samples by ICP-MS and Optimization Conditions for Preconcentration

261

İncluding Platinum in the Secondary İndustry." *Allergy* 60: 159-64.

[8] Motelica-Heino, M., Rauch, S., Morrison, G., and Donard, O. 2001. "Determination of Platinum, Palladium and Rhodium Concentrations in Urban Road Sediments by İCP-MS." *Analytica Chimica Acta* 436: 233-41.

[9] Anthemidis, A., Themelis, D., and Stratis, J. 2001. "Stopped-Flow İnjection Liquid-Liquid Extraction Spectrophotometric Determination of Palladium in Airborne Particulate Matter and Automobile Catalysis." *Talanta* 54: 37-43.

[10] Bencs, L., Ravindra, K., and Grieken, R. 2003. "Platinum Group Elements in the Environment and Their Health Risk." *Spectrochimica Acta Part B* 58: 1723-55.

[11] Barefoot, R., and Loon, J. V. 1999. "Recent Advances in Determination of Platinum Group Elements and Gold." *Talanta* 49: 1-14.

[12] Font ás, C., Salvado, V., and Hidalgo, M. 2002. "Separation and Concentration of Pd, Pt and Rh from Automotive Catalytic Converters by Combining Two Hollow-Fiber Liquid Membrane Systems." *Industrial Engineering and Chemistry Research* 41: 1616-20.

[13] Fornieles, A. C., de Torres, A. G., Alonso, E. V., and Pavón, J. C. 2016. "Simultaneous Determination of Traces of Pt, Pd, and Ir by SPE-ICP-OES. Test for Chemical Vapor Generation." *Microchemical Journal* 124: 82-9.

[14] Lesniewska, B., Godlewska-Zylkiewicz, B., Ruszczynska, A., Bulska, E., and Hulanicki, A. 2006. "Elimination of İnterferences in Determination of Platinum and Palladium in Environmental Samples by İCP-MS." *Analytica*

Chimica Acta 564: 236-42.

[15] Alonso, M. C., Rigoldi, A., Ibba, A., Zicca, L., Deplano, P., Mercuri, M. L., ... and Serpe, A. (2015). "A Simple, Sensitive Analytical Method for Platinum Trace Determination in Human Urine." *Microchemical Journal* 122: 1-4.

[16] Abdulbur-Alfakhoury, E., and Leermakers, M. 2021. "Elimination of İnterferences in the Determination of Platinum, Palladium and Rhodium by Diffusive Gradients in Thin Films (DGT) and İnductively Coupled Plasma Mass Spectrometry (ICP MS) Using Selective Elution." *Talanta* 223: 121771.

[17] Ojeda, C. B., Rojas, F. S., and Pavon, J. C. 2003. "Preconcentration of Palladium, Platinum and Rhodium on Modified Silica Gel for Their Determination by İCP-MS." *Analytica Bioanalytica Chemica* 375: 1229-35.

[18] Tunceli, A., and Turker, A. 2000. "Determination of Heavy Metals in Environmental Samples Using Solid-Phase Extraction and İCP-MS." *Analytical Sciences* 16: 81-7.

[19] Resano, M., Garcia-Ruiz, E., McIntosh, K., and Vanhaecke, F. 2008. "Dynamic Reaction Cells Pressurized with nh3 for the Reduction of İnterferences in İCP-MS Analysis of Rhodium." *Journal of Analytical Atomic Spectrometry* 23: 1599-605.

[20] Niemel ä, M., Per äm äki, P., Piispanen, J., and Poikolainen, J. 2004. "Determination of Platinum and Rhodium in Dust and Plant Samples Using Microwave-Assisted Sample Digestion and İCP-MS." *Analytica Chimica Acta* 521: 137-43.