

SIMULTANEOUS DETERMINATION OF Pt, Pd, Rh AND Ir TRACES IN ENVIRONMENTAL SAMPLES BY FLOW INJECTION SOLID PHASE EXTRACTION COUPLED WITH ONLINE INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROSCOPY (ICP-AES).



A. Calvo Fornieles, E. Vereda Alonso, A. García de Torres and J.M. Cano Pavón

Department of Analytical Chemistry, Faculty of Sciences, University of Málaga

UNIVERSIDAD
DE MÁLAGA

Abstract

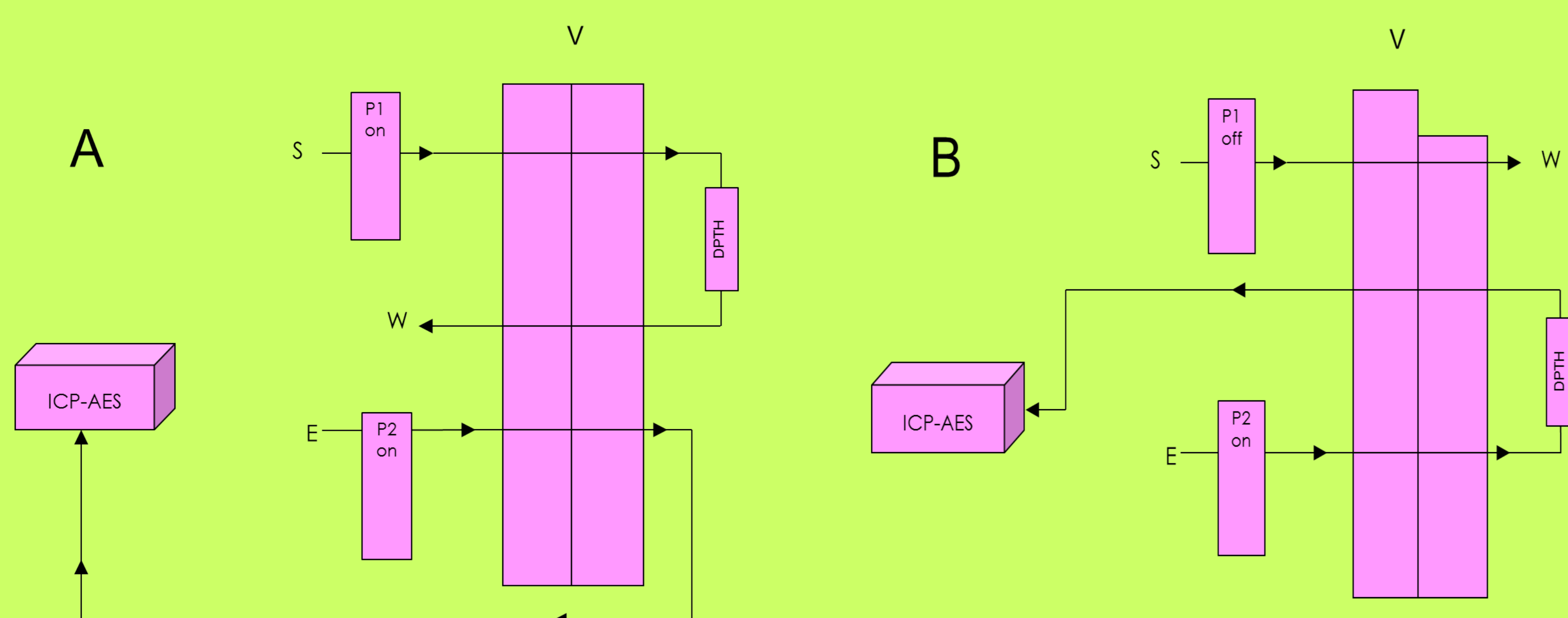
An increased worldwide usage of platinum group elements (PGEs) has been observed during the last twenty years due to their applications in areas such as chemical industry, metallurgy, jewelry production, dental devices, anti-cancer drug and automobile catalytic converter systems. These applications were found to be anthropogenic sources of pollution of these elements nowadays. The presence of PGEs in different environmental and biological materials is a risk to ecological and human health because they may be easily mobilized and solubilized in several matrices. The determination of Pt, Pd, Rh and Ir presents difficulties because of the low concentrations of these metals in environmental samples and the numerous interactions between the analytes and the matrix constituents, which can significantly influence both the limit of detection and the accuracy of determination in complex samples. Initial sample pretreatment such as pre-concentration of these elements and matrix separation are often necessary. Numerous reviews devoted to PGEs determination have been published; however, they deal mainly with techniques used for analytical signal formation and less with pre-concentration and separation procedures which usually precede the quantification of the analyte by spectrometric techniques [1]. In this work, Pt, Pd, Rh and Ir have been simultaneously determined by flow injection solid phase extraction coupled online with ICP-AES. The system is based on the retention of the analytes onto a minicolumn filled with a chelating exchange resin placed in the injection valve of a simple flow manifold. This configuration offers several advantages, including (a) elimination of the matrix effect, (b) increase the sensitivity by the preconcentration and, (c) automatization of the different steps. The effects of chemicals and flow variables were investigated. The optimized operating conditions selected were: sample pH 7.5, sample flow rate 2.2 mL min⁻¹, eluent flow rate 0.9 mL min⁻¹, eluent 0.07% thiourea in 2M HCl. With these conditions, the enrichment factors obtained were 6.3, 6.7, 3.7 and 6.3 for Pt, Pd, Rh and Ir respectively. Detection limits (3 min sample loading time) were 1.4 µg L⁻¹ for Pt, 0.5 µg L⁻¹ for Pd, 256 µg L⁻¹ for Rh and 0.6 µg L⁻¹ for Ir. The accuracy of the proposed method was checked with the certified reference material NIST-2557 autocatalyst. The results obtained using this method were in good agreement with the certified values of the standard reference material. The method was applied to the determination of Pt, Pd, Rh and Ir in different sea-water samples collected in Málaga, Spain.

Experimental

The on-line column preconcentration/ICP-AES procedures

Step	Solución	Valve position	Flow rate/ mL min ⁻¹	Time/ s	Direction
Prefill	HCl 2M	1	2.2	45	Waste
	MQ water	1	2.2	30	Waste
Sample loading	Sample	1	2.2	180	Waste
Wash period	MQ water	1	2.2	60	Waste
Elution (Pump 1 off)	0,07% Thiourea in HCl 2M	2	0.9	85	ICP-AES

Schematic diagrams of the on-line pre-concentrating and eluting procedure. P1: peristaltic pump 1; P2: peristaltic pump 2; V: five port valve 1; DPTH: DPTH-gel minicolumn; S: sample; E: eluent; W: waste; (A) preconcentration step; (B) elution step.



Results

Determination of Pt, Pd, Rh and Ir in a certified reference material NIST-2557 autocatalyst also two water samples collected from different points of Málaga Bay were analyzed. The concentrations were in µg g⁻¹ for solid sample and µg L⁻¹ for water samples.

Sample	Element	Certified value	Added	Found	Recovery (%)
NIST-2557	Pt	1131±11	-	1142±8	100.9
	Pd	233.2±1.9	-	232.9±3.9	99.8
	Rh	135.1±1.9	-	137.5±2.9	101.7
	Ir	-	-	54.5±2.8	-
Seawater Zone1	Pt	-	-	-	-
		10	10.58±0.02	105.8	
	20	19.19±0.01	95.9		
	Pd	-	-	-	-
		10	10.09±0.03	100.9	
	20	19.98±0.01	99.9		
Rh	-	-	-	-	
	1000	956±3	95.6		
3000	2893±2	96.4			
Ir	-	-	-	-	
	10	9.45±0.01	94.5		
20	19.84±0.03	99.2			
Seawater Zone 2	Pt	-	-	-	-
		10	10.22±0.01	102.2	
	30	29.48±0.01	98.2		
	Pd	-	-	-	-
		10	10.06±0.01	100.6	
	30	30.52±0.01	101.7		
Rh	-	-	-	-	
	1000	962 ± 1	96.2		
3000	2991±2	99.7			
Ir	-	-	-	-	
	10	9.5±0.02	95.0		
30	30.32±0.01	101.0			

Conclusions

The FI on-line preconcentration and separation system using DPTH-gel as a sorbent material was evaluated and demonstrated to be promising for routine determination of the trace amounts of Pt, Pd, Rh and Ir in sea-waters and it was found to be rapid, easy, automatic, selective with good sensitivity and low consumption of sample and reagents. The sorbent has a practically unlimited lifetime without the demand of regeneration.

References

- [1] B. Godlewska-Zylkiewicz, Microchim. Acta 147 (2004) 189.