J. Iran. Chem. Soc., Vol. 5, No. 2, June 2008, pp. 336-341.

JOURNAL OF THE
Iranian
Chemical Society

Development of Inductively Coupled Plasma Atomic Emission Spectrometry for Palladium and Rhodium Determination in Platinum-Based Alloy

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(Received 12 July 2005, Accepted 30 September 2007)

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) with internal standardization was applied for the analysis of an in-house reference platinum alloy containing palladium and rhodium (approximately 5% by weight). In order to compensate for variations in signal recovery due to matrix interferences, and therefore to improve the precision, platinum, the major component, was chosen as an internal standard. Quantitative analysis was based on calibration using a set of matrix-matched calibration standards with and without employing the internal standard. These results were compared with those obtained by X-ray fluorescence (XRF) spectroscopy. The results for both techniques were in a good agreement, although the precision was slightly better in the ICP-AES technique, with or without the internal standard.

Keywords: ICP-AES technique, X-ray fluorescence spectroscopy, Ternary $PtPd_5Rh_5$ alloy, Internal standard

INTRODUCTION

Platinum group elements have attracted enormous interest due to increased demands in the jewelry, pharmaceutical, telecommunications and automotive industries. Platinum alloys with palladium and rhodium are widely used as catalysts for ammonia oxidation. Furthermore, platinum-rhodium alloys are also used in platinum resistance thermometers, thermocouples and strain gauges.

The determination of palladium and rhodium in platinum-based alloys is important in order to characterize their physical properties when used in industrial applications. The analysis has several challenges, such as high levels of major components as well as demand for high precision and accuracy. Due to the complex chemistry of the precious metal elements and the high intrinsic value of the materials, an extensive range of analytical methods are used in order to obtain the required precision and accuracy. The determination of these major elements is a very important task as even small errors in the determination of the major elements in precious metal alloys may result in significant expense. Gravimetric and volumetric methods are mostly applied for the determination of higher-content precious metals [1-4]. Additionally, atomic absorption spectrometry has been applied to the determination of platinum content [5].

Several ISO-approved methods for inductively coupled plasma atomic emission spectroscopy (ICP-AES) have been described for the determination of precious metal in their alloys [6,7]. Those ISO methods use yttrium as an internal standard for the determination of the higher-content precious metals in jewelry alloys. Marucco *et al.* [8] determined concentrations of gold and other alloying elements in gold alloys in jewelry by ICP-AES using yttrium or indium as the internal standard.

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X-ray fluorescence (XRF) seems to be a very promising technique for the analysis of precious metal alloys. Cernohorsky *et al*. [9] applied "combined" field portable (FP) XRF for the analysis of binary (Ir-Pt, Rh-Pt) and ternary (Rh-Pd-Pt, Rh-Ir-Pt) alloys and Pt-Rh thermocouple wire. Although there are many advantages with XRF, a large set of calibration standards is usually necessary for the calculation of coefficients to correct for matrix effects. In addition, the accuracy of this method is strongly dependent on matching the samples and standards in size and surface quality [10,11]. Internal standardization has often been used to improve the precision in quantitative analytical emission spectroscopy. Internal standardization is used in order to correct the non-spectroscopic matrix effect. Dubuisson *et al*. [12] reported that internal standards can be efficiently used to compensate for matrix effects using radially-viewed ICP under robust conditions. Robustness is usually obtained by selecting a high power and a low carrier gas flow rate [13].

In this study, under optimized experimental conditions, an ICP analysis of the palladium and rhodium content in an in-house reference platinum ternary alloy ($PtPd_5Rh_5$) was performed both sequentially and simultaneously. An internal standard was applied by comparing the intensity of the spectral lines of the analytes with those of the major matrix element (platinum), which had known and reasonably constant concentration (90% by weight) for all the specimens tested. The ICP results were compared with those obtained by XRF.

EXPERIMENTAL

Instrumentation and Apparatus

All measurements were performed by both sequential ICP-AES, using an ARL model 3410 + spectrometer with Plasma Vision software, and simultaneous ICP-AES using a Spectro Ciros Vision spectrometer. The ARL 3410 + spectrometer with radial plasma viewing had a Czerny-Turner optical design and a photomultiplier detector, with a spectral range of 165-800 nm. The Spectro Ciros^{CCD} with radial plasma viewing was a double-grating spectrometer, with 22 linear CCDs as detectors, arranged on a Rowland circle, enabling a spectral range of 125-770 nm. Energy for the plasma was achieved with a free-running 27.12 MHz generator. The operating parameters for both instruments are given in Table 1.

The XRF measurements were carried out using a portable spectroscope (NITON XLt 797 X, Thermo) with X-ray tube technology and an internal color video camera.

Sample Preparations

For the XRF analysis, sample preparation was not necessary. The sample was tested in the portable test stand (photo), placing the sample directly on the instrument window.

For the ICP analysis, the ternary $PtPd_5Rh_5$ alloy (0.0500 g) was dissolved in 20 ml of a mixture of concentrated hydrochloric acid and nitric acid (aqua regia). After complete dissolution, the solution was cooled to room temperature, transferred to a 50-ml volumetric flask and diluted to final volume with deionized water. The same series of standard solutions and sample replicates were measured with both devices.

Preparation of Calibration Solutions

Five standard solutions of palladium and rhodium were used to obtain calibration curves, with concentrations of 0, 10, 20, 50 and 100 mg l^{-1} prepared from a 1000 mg l^{-1} stock solution (SPEX, Metuchen, USA). All the reagents were of analytical grade.

Two sets of calibration solutions were prepared, the first set without matrix matching and the second set with matrix matching. In the second set, five standards were matched with previously dissolved platinum wire (0.045 g, purity 99.99%) in aqua regia. In this way, the concentration of platinum in the calibration solutions was the same as in the sample solutions. These two sets of calibration solutions were used for the six analytical programs mentioned in Table 2. An additional calibration for precious metals was used for the XRF measurements.

Spectral Lines for Analytes and Internal Standard

In this study, recommended spectral lines for palladium and rhodium for certain noble metal alloys were chosen from the literature [14] and are shown in Table 2.

RESULTS AND DISCUSSION

In order to improve precision and overcome the problems in the determination of higher contents of precious metals by

Table 1. Operating Parameters for Sequential and Simultaneous ICP Spectrometers

	Sequential ICP-OES	Simultaneous ICP-OES
Power	700 W	1400 W
Coolant flow rate	7.5 l min^{-1}	12 l min^{-1}
Auxiliary flow rate	0.8 l min^{-1}	0.9 l min^{-1}
Nebulizer flow rate	0.7 l min^{-1}	0.9 l min^{-1}

Table 2. Analytical Programs and Wavelengths Used for Determination of Palladium and Rhodium in Ternary $PtPd_5Rh_5$ Alloys

Analytical program	Wavelength (nm)		
	Pd	Rh	Pt
NoISNoMm	Pd I 340.458	Rh I 343.489	-
NoISMm	Pd I 340.458	Rh I 343.489	-
ISMm1	Pd I 340.458	Rh I 343.489	Pt I 214.423
ISMm2	Pd II 229.651	Rh II 233.477	Pt I 214.423
ISMm3	Pd I 340.458	Rh I 343.489	Pt I 265.945
ISMm4	Pd II 229.651	Rh II 233.477	Pt I 265.945

classical analytical methods, which are time-consuming and expensive, quick and accurate sequential and simultaneous ICP techniques were employed in this study. It appears that there is no general consensus regarding the selection of an adequate and versatile internal standard, which is typically absent from the samples. However, with alloys of a narrow composition range and a matrix element of almost constant concentration, matrix element lines can be used as internal standards [15]. In this study, platinum is a convenient internal standard because it is already present in the analyte and has a similar ionization potential as the analytes (Pt: 9.02 eV; Pd: 8.34 eV; Rh: 7.46 eV). Furthermore, using platinum eliminates the need for extreme precision in adding exactly the same amount of internal standard to each calibration solution, which is very time-consuming work.

The results for the determination of palladium and rhodium in the ternary alloy are shown in Table 3, with the average means calculated from five replicates for sequential ICP-AES (data set A) and ten replicates for simultaneous ICP-AES measurements (data set B). By XRF, the in-house reference platinum alloy has palladium and rhodium contents of 5.22 ± 0.13% and 4.68 ± 0.13%, respectively. Ten repetitions of the reading were taken for 60 seconds for each sample to determine the repeatability of this method. Before the start of every reading, the sample was moved from the spot and placed again.

Using the recommended procedure, the recoveries of spiked palladium and rhodium from the $PtPd_5Rh_5$ alloy were calculated through all analytical programs. The results show that 98.7-102.0% and 93.6-98.4% of the spiked palladium and rhodium, respectively, were recovered within RSD ranges of 0.18-0.34% and of 0.31-0.81%, respectively. These results suggest that the proposed methods are applicable to the analysis of this sample.

The F-test for the two data sets (A and B) for the determination of palladium and rhodium shows that the ratios of variances, F_{calc}, are smaller than $F_{tabular}$, which confirms that there is no significant difference in precision between the two experimental data sets at a 95% confidence level. Both ICP-AES techniques are equally suitable for this application. The

Table 3. Palladium and Rhodium Content in Ternary $PtPd_5Rh_5$ Alloys

		%Pd		%Rh	
Analytical program		Data set A	Data set B	Data set A	Data set B
NoISNoMm	<x> ± s	5.18 ± 0.03	5.23 ± 0.05	4.79 ± 0.05	4.77 ± 0.04
	%RSD	0.58	0.96	1.04	0.84
	F test	2.78		1.56	
NoISMm	<x> ± s	5.21 ± 0.04	5.18 ± 0.07	4.80 ± 0.07	4.73 ± 0.08
	% RSD	0.77	1.35	1.46	1.69
	F test	3.06		1.31	
ISMm1	<x> ± s	5.22 ± 0.03	5.19 ± 0.04	4.72 ± 0.05	4.78 ± 0.04
	% RSD	0.57	0.77	1.06	0.84
	F test	1.78		1.56	
ISMm2	<x> ± s	5.22 ± 0.06	5.20 ± 0.07	4.74 ± 0.04	4.79 ± 0.06
	%RSD	1.15	1.35	0.84	1.25
	F test	1.36		2.25	
ISMm3	<x> ± s	5.17 ± 0.04	5.21 ± 0.04	4.78 ± 0.06	4.75 ± 0.06
	%RSD	0.77	0.77	1.26	1.26
	F test	1.00		1.00	
ISMm4	<x> ± s	5.18 ± 0.03	5.19 ± 0.03	4.73 ± 0.06	4.79 ± 0.06
	%RSD	0.58	0.58	1.27	1.25
	F test	1.00		1.00	

Table 4. Comparison of XRF and ICP-AES Results for Palladium and Rhodium Content[a]

Sample	XRF	ICP-AES
Sample 1	%Pd 5.23 ± 0.13 %Rh 4.58 ± 0.13	%Pd 5.20 ± 0.03 %Rh 4.68 ± 0.07
Sample 2	%Rh 6.34 ± 0.04	%Rh 6.30 ± 0.05
Sample 3	%Rh 12.81± 0.10	%Rh 12.89 ± 0.06

[a] n = 6.

determinations of palladium and rhodium in this Pt-based alloy are not affected by varying the operating conditions from non-robust to robust.

Furthermore, the t-test was used to compare the two experimental averages. All average means for palladium determination were compared in data set A. In all cases, the $t_{tabular}$ is greater than t_{calc}, confirming that there is no significant difference between the two experimental averages at a 95% confidence level. No matter which program is used, with or without matrix matching or the use of platinum as the internal standard, the same results are obtained. Additionally, the results for matrix matching are in a good agreement, even with those obtained for instrument calibration with aqueous standards (program NoISNoMm). Platinum, as major component of the ternary alloy, does not affect the determination of palladium and rhodium, but its use as an internal standard does not substantially improve the precision, either. The conclusion of the t-test is the same for the determination of palladium in data set B.

Based on the results given in Table 3 for rhodium determination, the t-test performed for data sets A and B shows that, in all cases, the $t_{tabular}$ is greater than t_{calc}, confirming that there is no significant difference between the two experimental averages at a 95% confidence level. It appears that, with platinum as an internal standard, matrix matching has no influence on the determination of rhodium in this platinum-based alloy. Additionally, there is no significant difference between the experimental results and the content of palladium and rhodium in the in-house reference platinum alloy (“true value”).

The validity of the method was tested by comparing the results obtained by ICP-AES (with and without an internal standard with a certified value) and those by XRF, as shown in Table 4. The precision, expressed as RSDs, for data sets A and B is, for palladium, 0.57-1.15% and 0.58-1.35%, respectively, and for rhodium 0.84-1.46% and 0.84-1.69%, respectively. For the results of the XRF analysis, the precision (RSD, $n = 10$) for palladium and rhodium is 2.49% and 2.78%, respectively. Regardless of which program was used, whether or not matrix matching or an internal standard was employed, the precision was improved by a factor of 2-4 for palladium and 2-3 for rhodium by ICP-AES.

It should also be noted that, for both ICP techniques, there is no significant difference between those results obtained by rationing the ionic lines of palladium and rhodium to two different atomic platinum lines and those obtained by rationing the atomic lines of palladium and rhodium to the same atomic platinum line.

CONCLUSIONS

ICP-AES is an advantageous alternative to the traditional methods for the determination of palladium and rhodium in platinum-based alloys. Despite the fact that it is a destructive method, ICP-AES allows for quick simultaneous determination of all the constituents with very high precision and accuracy, comparable to those of XRF spectrometry analysis, and even better than XRF in the case of the $PtPd_5Rh_5$ alloy. Generally, however, the gains in precision for both elements were modest, as a factor of approximately two was typical.

All measured values for palladium and rhodium content with both ICP-AES techniques were in a good agreement with XRF and certified values, thus confirming the suitability of both ICP-AES techniques and validating their precision for platinum-based alloys.

The internal standard made no difference in precision and the matrix matching had no affect on the accuracy of the technique in this determination. It remains to be elucidated if any element in the internal standard would improve precision in the determination of palladium and rhodium in platinum-based alloys.

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