ICP-OES Determination of Palladium in Palladium Jewellery Alloys Using Yttrium Internal Standard

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INTRODUCTION

Methods for measuring the palladium (Pd) concentrations in palladium jewellery alloys (1) generally include the gravimetric method with dimethylglyoxime (2,3), complexometric titration (4), inductively coupled plasma optical emission spectroscopy (ICP-OES), internal standardization (5), and the difference method (6). Using internal standardization (7-11) of ICP-OES can improve precision, reduce matrix effects and drift. The direct determination of palladium by internal standardization with ICP-OES (5) is feasible for routine applications, requires no tedious filtration separation, and is accurate, simple, and fast.

The ISO 11495:2008 regulation (5) recommends measuring the ratio of the intensity of Pd at 340.45 nm to the intensity of yttrium (Y) at 371.03 nm, and using this ratio to calculate the concentration. The analytical line pair of Pd 342.124 nm vs. Y 371.030 nm is more commonly used for the determination of Pd (12). However, Pd at 340.45 nm is not available on an IRIS Intrepid II emission spectrometer. The charge-injection device detector of the spectrometer is CID38 (13) (Thermo CIDTEC, Liverpool, NY, USA) with a 512×512 array. Less than 10 or greater than 502 are in the edge of the array, which is an area that does not permit spectral analysis. The Pd 340.45-nm line, located in (4.30, 154.40) of the

ABSTRACT

A different analytical line pair is required when the Pd 340.45-nm line, as recommended by ISO regulation 11495:2008, is not available on an inductively coupled plasma optical emission spectrometer (ICP-OES) for the determination of Pd in palladium jewellery alloys. This work selected Pd 342.124 nm and Y 371.030 nm as the optimal analytical line pair from 21 spectral lines of palladium and 7 spectral lines of yttrium based on recoveries, relative standard deviations (RSD), spectral interferences, simultaneous detection principle of the analyte and the internal standard signals. The recoveries of the line pair were in the range of 101.6~101.9% and the RSD was 0.2% (n=10). This method is complementary to the ISO 11495:2008 regulation.

array is just in the edge. Consequently, a new analytical line pair needs to be selected.

The aim of this work was to compare 147 analytical line pairs, composed of 21 spectral lines of palladium and 7 spectral lines of yttrium, and to select the optimal pair for the ICP-OES determination of Pd in palladium jewellery alloys.

EXPERIMENTAL

Instrumentation

The ICP-OES measurements were carried out using a radial IRIS Intrepid II XSP (Thermo Fisher Scientific, USA) with Echelle optics and a charge injection device (CID) detector for the simultaneous recording of the selected emission lines. The sample introduction system consisted of a cyclonic spray chamber and a Meinhard® concentric nebulizer. The system is controlled with TEVA™ software (Thermo Fisher Scientific, USA).

Table I lists the instrumental operating parameters. The chosen settings fulfill the robust plasma conditions (14) checked by the Mg(II)/Mg(I) ratio.

TABLE I
ICP-OES Instrumental Operating Parameters

Instrument	IRIS Intrepid II XSP ICP-OES
RF power	1150 W
Ar nebulizer gas pressure	179 kPa
Ar plasma gas flow rate	15 L min ⁻¹
Ar auxiliary gas flow rate	1.0 L min ⁻¹
Solution uptake rate	2.40 mL min ⁻¹
Maximum integration times (low wavelength range)	30 s
Maximum integration times (high wavelength range)	30 s

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Reagents and Samples

Pd and Y reference solutions used for calibration were prepared by diluting a stock solution of 1000 mg L⁻¹ of the given element (supplied by the National Analysis Center for Iron and Steel of China) and stored in polyethylene bottles. HCl and HNO₃ solutions were of analytical reagent grade. Deionized water with a specific resistivity of 18.2 MΩ·cm (Milli-Q® gradient A10, Millipore Corporation, Bedford, MA, USA) was used to prepare the samples and standards.

Approximately 100 mg of palladium jewelry alloy (Pd950) with a palladium content of 95% was weighed to at least 0.01 mg and dissolved in 40 mL *aqua regia* in a 100-mL volumetric flask. Then, 5 mL of the solution was placed into a 50-mL volumetric flask, brought to volume with deionized water, and mixed thoroughly. A 1 mg L⁻¹ amount of yttrium solution was used as the internal standard solution. The sample and internal standard solutions were mixed on-line.

RESULTS AND DISCUSSION

Available Spectral Lines of Pd and Y

The available 21 spectral lines of palladium and 20 spectral lines of yttrium are listed in Tables II and III, arranged by signal-to-background ratio (SBR). The net signal was the spectral line intensity of a single element of 10 mg L⁻¹ after background subtraction. The diffraction order is listed in braces.

147 Analytical Line Pairs

Twenty-one spectral lines of Pd in Table II and seven strong spectral lines of Y in Table III were used in this research project. They compose 147 analytical line pairs. Among them, the wavelengths of Y at 324.228 nm and Pd at 324.270 nm are too close to each other, and

the backgrounds need to be subtracted.

Using the 147 line pairs, the recovery and relative standard deviation (RSD) values for 10 replicate determinations from the palladium solution of 95 mg L⁻¹ are shown in Figure 1. Table IV lists the 11 analytical line pairs which satisfies the following conditions: recoveries obtained between 95% and 105% with an RSD of <1.00%. The 11 line pairs in Table IV are composed of 9 Pd spectral lines and 3 Y spectral lines, arranged by recovery.

TABLE II
21 Spectral Lines of Pd

Wavelength (nm)	Net Signal	SBR
Pd 229.651 {146}	16.48	2.19
Pd 363.470 { 92}	67.37	1.85
Pd 351.694 { 95}	24.60	1.05
Pd 223.159 {151}	6.52	1.03
Pd 223.159 {150}	4.03	0.90
Pd 324.270 {103}	11.37	0.88
Pd 248.892 {134}	0.85	0.82
Pd 360.955 { 93}	31.14	0.71
Pd 342.124 { 98}	18.49	0.59
Pd 248.892 {135}	0.86	0.54
Pd 244.618 {137}	0.91	0.43
Pd 355.308 { 94}	8.27	0.35
Pd 348.115 { 96}	7.64	0.35
Pd 346.077 { 97}	11.16	0.32
Pd 248.653 {135}	0.63	0.30
Pd 244.791 {137}	0.53	0.29
Pd 236.796 {141}	0.30	0.24
Pd 247.642 {135}	0.40	0.23
Pd 235.134 {142}	0.16	0.14
Pd 276.309 {121}	0.58	0.11
Pd 330.213 {102}	1.48	0.10

Seven Analytical Line Pairs

The IRIS emission spectrometer uses a low wavelength slit and a high wavelength slit around the 234-nm line, respectively. There are four line pairs in Table IV (in bold font) on the use of the two slits; their analytical line and internal standard line were not determined simultaneously. The four line pairs were Pd 223.159 nm {151} vs. Y 371.030 nm {90}, Pd 223.159 nm {150} vs. Y 437.494 Y 361.105 nm {93}, and Pd 223.159 nm {150} vs. Y 371.030 nm {90}. Except for these four line pairs, the remaining seven line pairs are as follows: Y 371.030 nm {90} and

TABLE III
20 Spectral Lines of Y

Wavelength (nm)	Net Signal	SBR
Y 324.228 {103}	483.1	50.32
Y 371.030 { 90}	1320	49.58
Y 224.306 {150}	351.8	45.28
Y 360.073 { 93}	1362	27.00
Y 377.433 { 89}	1590	23.01
Y 361.105 { 93}	793.2	20.15
Y 437.494 { 77}	1177	16.34
Y 320.332 {105}	164.7	13.81
Y 319.562 {105}	187.2	12.86
Y 320.027 {105}	163.5	11.05
Y 242.220 {138}	13.76	10.35
Y 358.452 { 94}	166.6	9.43
Y 349.609 { 96}	144.3	5.86
Y 488.369 { 69}	1025	5.82
Y 423.594 { 79}	269.5	3.55
Y 508.742 { 66}	794.0	3.50
Y 485.487 { 69}	460.2	2.47
Y 360.192 { 93}	44.92	1.61
Y 439.802 { 76}	34.40	0.34
Y 408.371 { 82}	2.19	0.05

seven spectral lines (in regular font) of Pd [276.309 nm {121}, 324.270 nm {103}, 330.213 nm {102}, 342.124 nm {98}, 348.115 nm {96}, 351.694 nm {95}, and 360.955 nm {93}]. The ionization and excitation energies of the seven line pairs are shown in bold font in Table V.

Of the seven line pairs, Pd 330.213 nm {102} vs. Y 371.030 nm {90} and Pd 342.124 nm {98} vs. Y 371.030 nm {90} were the line pairs with recoveries closest to 100% and of smaller %RSD values.

Spectral Interference

Palladium jewellery alloys, in addition to Pd and Y, may also contain elements such as Cu, Ni, Zn, Fe, Co, Ru, Ag, In, Ga, and Sn (2, 5, 15). The sum of any other trace elements present never exceeds 0.1% (15). The spectral interference of the nine spectral lines of Pd in Table IV with these elements was determined and found to be as follows: Pd 95 mg L⁻¹, Cu 5 mg L⁻¹, Ni 5 mg L⁻¹, Zn 5 mg L⁻¹, Fe 5 mg L⁻¹, Co 5 mg L⁻¹, Ru 5 mg L⁻¹, Ag 5 mg L⁻¹, In 10 mg L⁻¹, Ga 5 mg L⁻¹, Sn 5 mg L⁻¹, and Y 10 mg L⁻¹. The presence of Zn at the 330.259-nm line to the left of Pd at 330.213 nm is shown

in Figure 2. All other lines showed no interference.

Optimal Analytical Line Pair

The optimal analytical line pair of the 147 line pairs was Pd 342.124 {98} vs. Y 371.030 {90}, based on the evaluation of the recoveries, RSD values, spectral

interferences, and simultaneous detection principle of the analyte and the internal standard signals.

The ionization and excitation energies (16) of the spectral lines as listed in Table V are arranged according to excitation energy. The letters I and II represent the atomic and ionic lines, respectively.

TABLE IV
11 Analytical Line Pairs* (Arranged by Recovery)

Analytical Line (nm)	Internal Standard Line (nm)	Recovery (%)	RSD (%)
Pd 223.159 {151}	Y 371.030 { 90}	95.1	0.80
Pd 223.159 {150}	Y 437.494 { 77}	95.8	0.92
Pd 324.270 {103}	Y 371.030 { 90}	96.7	0.80
Pd 351.694 { 95}	Y 371.030 { 90}	97.0	0.92
Pd 348.115 { 96}	Y 371.030 { 90}	97.3	0.97
Pd 360.955 { 93}	Y 371.030 { 90}	98.2	0.92
Pd 223.159 {150}	Y 361.105 { 93}	98.5	1.00
Pd 330.213 {102}	Y 371.030 { 90}	99.1	0.91
Pd 342.124 { 98}	Y 371.030 { 90}	101.7	0.88
Pd 276.309 {121}	Y 371.030 { 90}	102.3	0.92
Pd 223.159 {150}	Y 371.030 { 90}	102.4	0.84

*: The four line pairs are shown in bold font, which are exposed non-simultaneously from the two different slits.

Fig.1. Recoveries and RSDs of 147 analytical line pairs.

Fig.2. Spectral coincidence profiles of Pd at 330.213 nm (95 mg L⁻¹) and Zn at 330.259 nm (5 mg L⁻¹).

TABLE V
Ionization and Excitation Energies of Spectral Lines*

Wavelength (nm)	Atomic/Ionic	Ionization Energy (eV)	Excitation Energy (eV)	Energy Sum (eV) (at 10 mg L ⁻¹)	SBR
Y 437.494 {77}	II	6.22	3.24	9.46	16.34
Y 377.433 {89}	II	6.22	3.41	9.63	23.01
Y 371.030 {90}	II	6.22	3.52	9.74	49.58
Y 361.105 {93}	II	6.22	3.56	9.78	20.15
Y 360.073 {93}	II	6.22	3.62	9.84	27.00
Y 324.228 {103}	II	6.22	4.00	10.22	50.32
Pd 363.470 {92}	I		4.22	4.22	1.85
Pd 346.077 {97}	I		4.40	4.40	0.32
Pd 360.955 {93}	I		4.40	4.40	0.71
Pd 276.309 {121}	I		4.49	4.49	0.11
Pd 351.694 {95}	I		4.49	4.49	1.05
Pd 342.124 {98}	I		4.58	4.58	0.59
Pd 324.270 {103}	I		4.64	4.64	0.88
Pd 348.115 {96}	I		4.81	4.81	0.35
Pd 355.308 {94}	I		4.94	4.94	0.35
Pd 247.642 {135}	I		5.01	5.01	0.23
Pd 330.213 {102}	I		5.01	5.01	0.10
Pd 244.791 {137}	I		5.06	5.06	0.29
Y 224.306 {150}	II	6.22	5.53	11.74	45.28
Pd 248.892 {134}	II	8.33	8.09	16.43	0.82
Pd 248.892 {135}	II	8.33	8.09	16.43	0.54
Pd 236.796 {141}	II	8.33	8.34	16.68	0.24
Pd 248.653 {135}	II	8.33	8.34	16.68	0.30
Pd 244.618 {137}	II	8.33	8.43	16.76	0.43
Pd 229.651 {146}	II	8.33	8.51	16.84	2.19
Pd 235.134 {142}	II	8.33	8.63	16.97	0.14
Pd 223.159 {150}	II	8.33	8.66	17.00	0.90
Pd 223.159 {151}	II	8.33	8.66	17.00	1.0

*: The seven line pairs, composed by seven Pd spectral lines and one Y spectral line, are shown in bold font, which satisfy the following conditions: recoveries obtained between 95% and 105%, an RSD of <1.00%, and the simultaneous detection principle.

The data in Table V can be interpreted as follows:

(a) An analytical line pair is not necessarily a combination of two atomic lines or two ionic lines. The optimal analytical line pair in this paper consists of one atomic line and one ionic line. The line pair of Al I 396.153 nm vs. Y II 371.029 nm adopted by Roberta Eliane dos Santos Froes et al. (17) in their study is also a combination of one atomic line and one ionic line.

(b) To determine major elements, the best analytical line is often not the most sensitive line. The minimum SBR of the 21 spectral lines of Pd in Table V was 0.10, maximum 2.19. The SBR of Pd 342.124 nm {98} was 0.59, which was a weak line.

(c) Both the internal standard and the analytical lines should have similar excitation energies. The seven line pairs shown in bold font in Table V have closer excitation energies (3.52 eV, 4.40~5.01 eV); and their energy sum showed no regularity (9.74 eV, 4.40~5.01 eV).

(d) Accuracy and precision are the final screening indicators for the analytical line pair.

Application to Commercial Pd950 Alloys

The calibration curve was prepared with reference solutions of 50, 70, 80, 90 and 100 mg L⁻¹ Pd. The linear regression equation was $Y = -0.25021 + 0.12461 \cdot X$, where X was the concentration of Pd (mg L⁻¹) and Y was the intensity ratio of the analytical line and the internal standard line. The correlation coefficient was 0.99976. The precision of the method, expressed as %RSD values for 10 replicate determinations from the palladium solution of 95 mg L⁻¹, was 0.21%. The accuracy of the method was verified by performing the recovery test. A 2-mL sample solution of ~950 mg L⁻¹ Pd was placed into a 50-mL volumetric

flask, then spiked with 2 mg and 3 mg of Pd, and made up to volume with 10% (v/v) HCl. The spike recoveries obtained were 101.6% and 101.9%, respectively.

CONCLUSION

A new optimal analytical line pair (Pd 342.124 nm vs. Y 371.030 nm) is recommended for the ICP-OES determination of palladium in palladium jewellery alloys when Pd 340.45 nm is not available, as for instance, when using the radial IRIS Intrepid II XSP spectrometer. The recoveries of the new line pair were in the range of 101.6~101.9%. The RSD was 0.2% (n=10). This method is complementary to the ISO 11495:2008 regulation.

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