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RESEARCH ARTICLE

Internal Standard Method for the Determination of Au and some Platinum Group Metals Using Inductively Coupled Plasma Optical Emission Spectrometry

Ntebogeng S. Mokgalaka, Robert I. McCrindle*, Barend M. Botha
and Ljiljana Marjanovic

Department of Chemistry and Physics, Technikon Pretoria, Private Bag X680,
Pretoria, 0001, Republic of South Africa

* To whom correspondence should be addressed; e-mail: McCrindle@techpta.ac.za

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Abstract

A method is described for the determination of Au, Pt, Pd, Ru and Rh in a converter matte sample, using inductively coupled plasma optical emission spectrometry (ICP-OES), with Y or Sc as internal standard. The results obtained by this method are discussed and compared with values obtained by an independent laboratory. The efficiency of internal standardization was evaluated by varying the operating conditions of the ICP-OES. Changes in the amount of energy transferred from the plasma to analyte, the amount of aerosol reaching the plasma and analyte residence time, were studied in terms of their effect on the emission intensity of the analyte and the internal standard. It was found that changes in the emission signals of the PGMs due to power variations could be effectively compensated for, using either Sc, Y or Ar lines as internal standards. For variations in aerosol gas flow rate, both Sc and Y could only compensate for Pd and Au between flow rates of 0.60 and 0.80 l min^{-1} and for Pt, Ru and Rh at 0.80 l min^{-1}. The effect of sodium on the determination of Au and the PGMs, and the use of Sc and Y as internal standards, to compensate for

Na matrix effects on accuracy were also studied. It was found that emission intensities of the analytes decreased with increasing Na concentration. Furthermore, Sc as an internal standard could compensate for Pt, Ru and Rh up to 5 g l^{-1} *Na, while Y could only compensate for the same elements up to 1 g* l^{-1} *Na.*

Keywords ICP-OES; internal standardization; platinum group metals.

1. Introduction

Due to their unique applications in new technologies,[1-9] there is an increasing demand the world over for gold (Au) and the platinum group metals (PGMs) consisting of Pt, Pd, Ru, Rh, Ir and Os. Inductively coupled plasma optical emission spectrometry (ICP-OES) is widely used for the quantitative analysis of the PGMs using the internal standardization method.[2,9] Although interferences are less of a problem in ICP-OES than in other spectroscopic techniques,[5,14] matrix effects, thermal drift, effects of change in the energy transfer and effects of change in the aerosol formation and transport may be present. These can affect the analytical results in terms of accuracy and precision.[10-21]

The isolation of PGMs sometimes requires an alkali fusion. During the fusion, which is normally carried out using sodium peroxide, easily ionizable elements (EIEs) like sodium are introduced into the sample solution. The presence of EIEs in the plasma may result either in an enhancement or a depression of the analyte emission intensity, as well as a shift in its spatial distribution. The effects of EIEs in ICP-OES have been widely recognized and studied,[10-15] but owing to various factors that affect the overall behaviour of the analyte, the mechanism involved in the effect of EIEs on the analyte emission intensity is still not completely understood.

Internal standardization can be used in ICP-OES to compensate for degradation in accuracy and precision.[11,14,16-21] This is accomplished by adding one or more elements, at the same concentration, to the samples and standards, in order to correct for variations in the analyte response. Variations may arise from the adverse effects associated with instrumental factors. Internal standardization will be most effective if the behavioural characteristics of the internal standard and the analyte elements are very similar with respect to plasma conditions[18,19,20] and interference effects.[11,14] Previously published work shows that the use of internal standardization is complex,[11,14,16-21] not necessarily efficient and depends strongly on the operating conditions.[18-20] In some cases,[19,20] the use of a combination of several standards was recommended, because the use of a single standard was insufficient to compensate for the variation in each analyte emission intensity. Computations resulting from the above can be complex and time consuming.

Considerable disagreement exists within the PGM industry relating to the use of an internal standard for the determination of Au and the PGMs. There are several alternatives used in industry, for example In, B, Sc and Y. Concentrations as high as 500 µg ml^{-1} of an expensive internal standard such as Sc (1000 ZAR, 2001 price) are often added. Of the above possibilities, Y would be a cost effective substitute, providing it was as effective or better than Sc.

The aim of this work was to investigate the possible selection of Y rather than Sc as internal standard, during the analysis of Au and the PGMs in a converter matte sample. The efficiency of the method was therefore evaluated under various operating conditions. Possible variations, that may have occurred during analytical procedures, were simulated. Modifying the aerosol carrier gas flow rate was used as one variation. Modifying the forward power simulated a change in the amount of energy transferred from the plasma to the analyte. The effect of Na on the determination of Au and the PGMs in samples containing 1, 5 and 10 g l^{-1} Na was also studied. The method was evaluated with water-based calibration standards and internal standardization was applied during the analysis of various Na matrix samples. Included was an evaluation of the concentration required, as lower concentrations of the internal standard would obviously be more cost effective and consequently more beneficial to the industry.

2. Experimental

Instrumentation

A simultaneous Perkin-Elmer Optima 4300DV ICP-OES, which allows either axial or radial mode of viewing, was used. Instrumental operating conditions are summarized in Table 1. This system was equipped with a 40 MHz free running solid-state generator and an Echelle grating, associated with a segmented array charge coupled device (SCD) detector. A Fassel-type demountable quartz torch was used with a 2.0 mm i.d. injector tube. A cross flow gem tip nebulizer, capable of handling solutions containing high concentrations of salt was used with a double pass (Scott type) spray chamber made of Ryton.

Table 1 Instrumental operating conditions.

Forward power/W	1400
Outer plasma gas flow rate/l min^{-1}	15
Intermediate plasma gas flow rate/l min^{-1}	0.3
Aerosol carrier gas flow rate/l min^{-1}	0.8
Sample uptake rate/ml min^{-1}	2.0

Wavelength Selection

As a method was required which needed minimum mathematical computation, it was important to find lines that were free from interferences. In preliminary investigations spectra were recorded of elements of interest, and intense, interference free lines were selected, and are listed in Table 2.

Table 2 Analytical wavelengths selected.

Element	Wavelength (nm)
Pt I	265.945
Pt II	214.423
Pd I	340.458
Rh I	343.489
Ru II	240.272
Au I	242.795
Au I	267.595
Y II	371.030
Sc II	361.384
Ar I	363.268
Ar I	420.069

Reagents

All reagents and standards used were prepared from analytical-reagent grade and Specpure chemicals (Johnson Matthey). The spectrometer was calibrated for Au, Pt, Pd, Ru and Rh using six standard solutions prepared from 1000 µg ml^{-1} standard stock solutions (Specpure, Johnson Matthey) in a concentration range selected to cover the full range of Au, Pt, Pd, Ru and Rh in the converter matte sample. Y or Sc standard stock solutions (Specpure, Johnson Matthey) were added as internal standard to obtain a selected concentration of 5 µg ml^{-1}. To study the effect of EIEs on the determination of Au, Pt, Pd, Ru and Rh, a series of working standard solutions containing 1, 5 and 10 g l^{-1} Na was prepared. UnivAR® sodium chloride (Saarchem,SA) was used for all sodium additions. All solutions were prepared in pure water (distilled and passed through a Milli-Q water purification system from Millipore, Milford, MA, USA).

Sample preparation

A 10 g portion of a converter matte sample (material obtained after PGM sulphides are mostly converted to oxides) and 30 g of NH_4Cl were accurately measured into a 600 ml beaker. The mixture was dissolved in 300 ml HCl and then heated until the reaction was completed. The PGMs were precipitated by the addition of 25 ml $SnCl_2$ and 200 ml boiled distilled water. They were separated from the mother liquor, containing base metals, by filtration. After washing, the PGMs were dissolved in 40 ml *aqua regia*. The final volume was adjusted to 100 ml with pure water. The internal standard (Y or Sc) was added to the sample to obtain a final concentration of 5 µg ml^{-1}.

3. Results and Discussion

3.1. Determination of Au and some PGMs

Platinum, palladium, ruthenium, rhodium, and gold were determined in a converter matte sample. A suitable certified reference material is not available, therefore, the same converter matte sample was analyzed by an independent laboratory, Lakefield Research Laboratories, Johannesburg, RSA. The independent laboratory used a lead fusion fire assay sample preparation method for Au, Pt and Pd; and a nickel sulphide fusion fire assay method for Ru and Rh with ICP-OES. The results of this work obtained without internal standardization are compared with values obtained by an independent laboratory (Table 3). The results in Table 3 represent the mean of three readings of samples, however, the RSDs reported are those for triplicate measurements of the instrument precision. The concentration of Au, when no internal standard was used, was 16.5% lower than that obtained by an independent laboratory. Using the students' *t*-test this was found to be significantly different ($P>0.5$). This difference may be attributed to 'instrumental' differences, or the different sample preparation method (lead fusion fire assay) used by the independent laboratory.

Table 3 Comparison of analytical results (µg ml^{-1}) for Au and the PGMs in a converter matte sample.

	Independent Laboratory		This Work	
Element	Mean	RSD	Mean	RSD
Pt	110	0.75	111	0.22
Pd	49.6	1.0	50.1	0.48
Ru	26.7	2.5	25.6	0.53
Rh	15.7	2.8	16.0	0.43
Au	3.33	0.34	2.78	0.50

The results obtained from the analysis of Au, Pt, Pd, Ru and Rh in a converter matte sample with and without using Y and Sc as internal standards are given in Table 4 together with the results obtained using the method of standard additions. No suitable certified reference material is available for the converter matte, therefore, the results obtained using the standard additions method were assumed to be 'true' concentrations of Au, Pt, Pd, Ru and Rh in a converter matte sample. Both methods, i.e. when no internal standard used and when using Y and Sc as internal standards, were validated for accuracy using the student *t*-test. The results obtained when no internal standard was used, were lower by 5% for Pt, 7% for Ru, 11% for Rh and 5% for Au when compared to results obtained using the standard additions method, as well as when using Y and Sc as internal standards. The last two methods mentioned yielded comparable results ($P>0.5$). The tendency to overcompensate for Pd was observed with both Y and Sc as internal standards.

The results reported using Y and Sc as internal standards in Table 4 were obtained at a concentration of 5 µg ml^{-1}. The concentration was found to be sufficient for adequate improvement of accuracy during the analysis of Au and the PGMs in a converter matte sample. The fact that no improvement in precision was found with the use of an internal standard, and which have been expected, may not be significant. The RSDs reported in all cases are those given by the instrument and reflect the computations of the software. The stable plasmas supplied by modern instruments yield RSD values which are not easily improved by internal standardization.

Table 4 Comparison of analytical results (µg ml^{-1}) for Au and PGMs in a converter matte sample using Y or Sc as internal standard.

	Standard Addition		No Internal standard		Y(II) 371.030 nm		Sc(II) 361.384 nm	
Element	Mean	RSD	Mean	RSD	Mean	RSD	Mean	RSD
Pt	116	0.84	110	0.87	116	0.87	115	0.86
Pd	50.8	0.11	50.1	0.11	51.2	0.14	51.3	0.11
Ru	27.6	0.83	25.6	0.53	27.7	0.70	27.5	0.75
Rh	18.3	0.41	16.0	0.43	17.8	0.68	17.8	0.60
Au	2.86	0.24	2.73	0.50	2.85	0.31	2.88	0.33

3.2. Change in the Efficiency of Aerosol Formation and Transport

Changes in the amount of aerosol reaching the plasma and analyte residence time were studied to verify the effect they have on the behaviour of the PGMs and the element used as internal standard in the plasma. This was achieved by calibrating the instrument at conditions given in Table 1 and then varying the aerosol carrier gas flow rate from 0.50 to 0.90 l min^{-1}, while keeping other operating parameters constant. It can be seen (Fig. 1) that with axial viewing of the plasma, the use of neither Y(II) 371.030 nm or Sc(II) 361.384 nm lines were necessarily adequate for efficient compensation of changes in the amount of aerosol formed and analyte residence time within the range of flow rates studied. This was particularly true for Pt(I) 265.945 nm, Pt(II) 214.423 nm, Ru(II) 240.272 nm and Rh(I) 343.489 nm lines. Both Y and Sc could be applied as internal standards to compensate for Pd(I) 340.458 nm at aerosol carrier gas flow rates between 0.60 and 0.80 l min^{-1}, 0.70 and 0.80 l min^{-1} for Au(I) 267.595 and Au(I) 242.795 nm respectively.

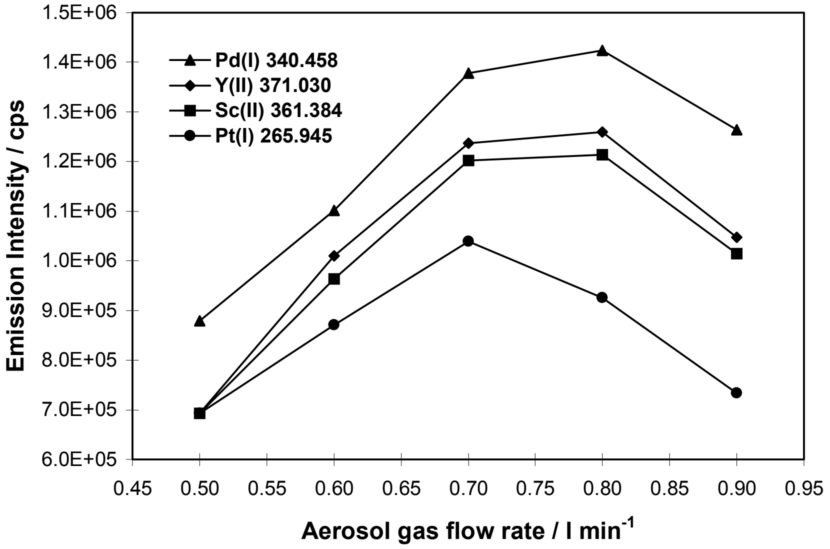

Figure 1 Effect of aerosol gas flow rate on emission intensities: Axial viewing.

Similar observations were obtained when viewing the plasma radially (Fig. 2): both Y and Sc could only be applied as internal standards to compensate for Pt(I) 265.945, Pt(II) 214.423 and Ru(II) 240.272 at flow rates below 0.70 l min^{-1}. In contrast, Rh(I) 343.489 nm could be compensated for at flow rates between 0.70 and 0.80 l min^{-1}, while the internal standardization using either Y or Sc couldn't be applied to the Au(I) 267.595 and Au(I) 242.795 nm lines.

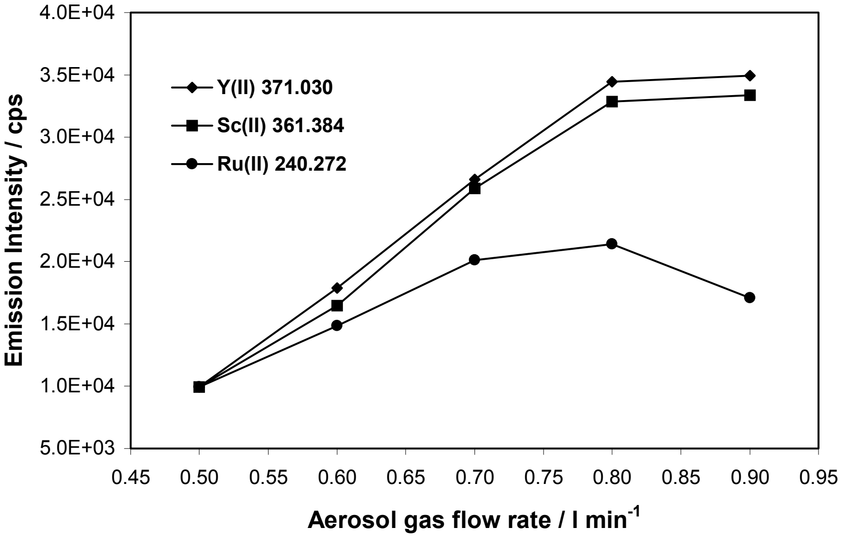

Figure 2 Effect of aerosol gas flow rate on emission intensities: Radial viewing.

Since an increase in the aerosol carrier gas flow rate corresponds not only to changes in the amount of aerosol and analyte residence time,[19,20] but also to a shift in the spatial distribution in the plasma,[19] the behaviour of some of the PGMs lines depends on the observation height used for the experiment. When the plasma was viewed radially (Fig. 2), the observation height of 15 mm above the load coil was selected as a compromise between the various atomic and ionic lines.

3.3. Change in Forward Power

In order to study the effect of possible energy transfer variation during analysis, the forward power was varied from 1100 to 1500 W, while keeping other operating parameters constant.

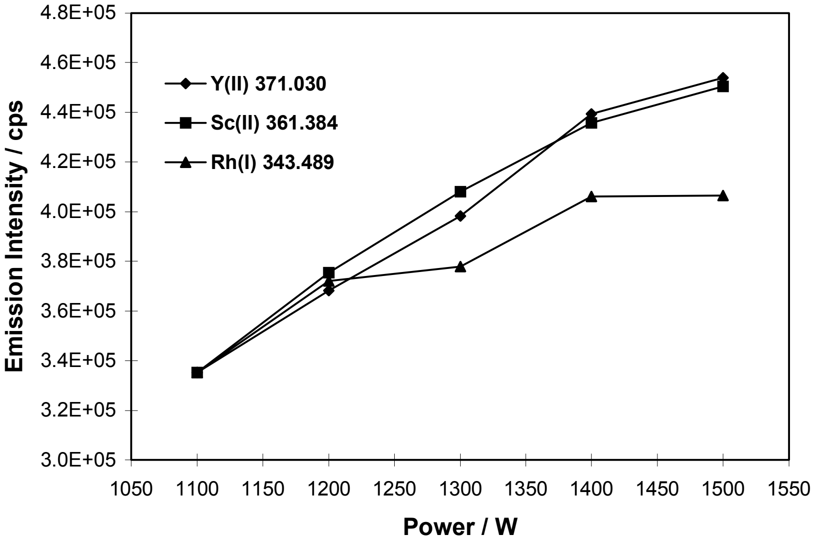

Figure 3 Effect of power on emission intensities: Axial viewing.

When the plasma was viewed both axially and radially (Figs. 3 to 6), an increase in the power led to a corresponding increase in the emission intensities of the PGMs and the internal standards lines. The overall change (of the intensity ratio of the analyte to the internal standard) was between 0.93 and 1.20, when Y(II) 371.030 nm, Sc(II) 361.384 nm, Ar(I) 363.268 nm and Ar(I) 420.069 nm were used as internal standards.

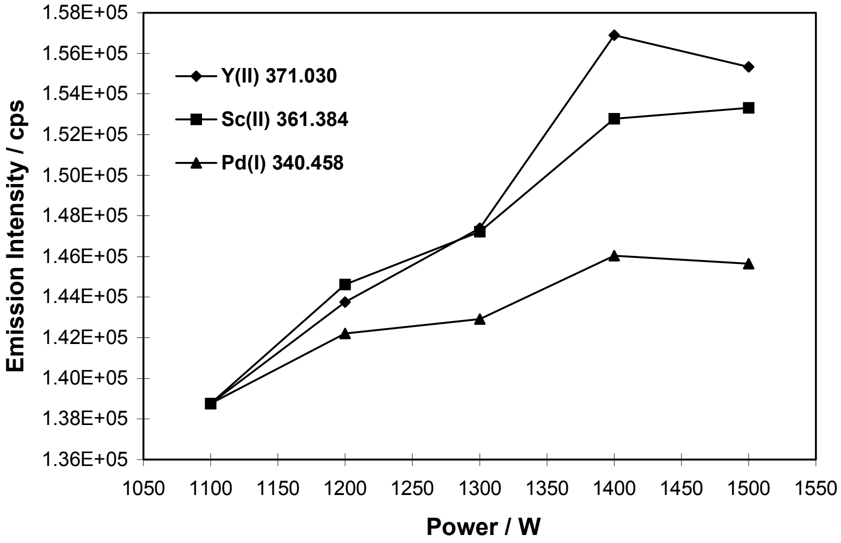

Figure 4 Effect of power on emission intensities: Radial viewing.

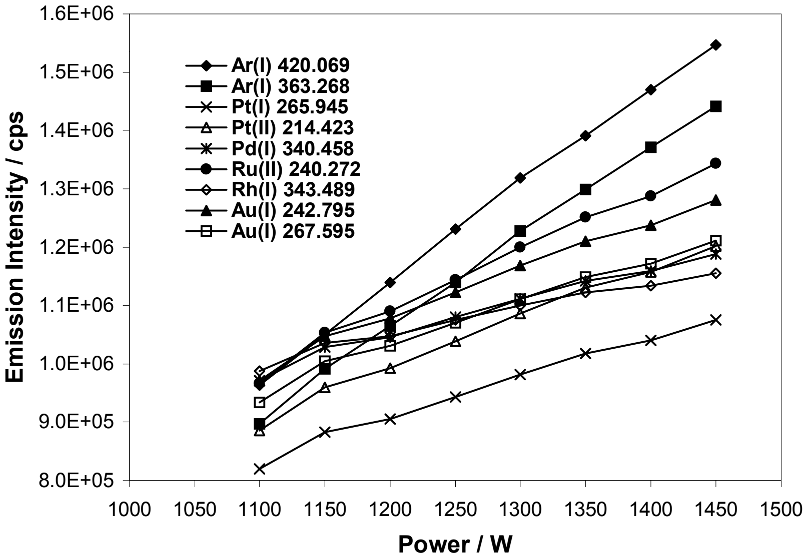

Figure 5 Effect of power on emission intensities: Axial viewing.

In contrast, both Ar lines could not be used as internal standards in the radial mode of viewing (Fig. 6) to compensate for variations in the forward power. Since small variations of the intensity ratio were observed over the whole range of atomic and ionic PGMs lines, a single internal standard, i.e. either Y(II) 371.030 nm or Sc(II) 361.384 nm in both axial and radial plasmas, Ar(I) 363.268 nm or Ar(I) 420.069 nm only with axial viewing, may be used to compensate for variations in energy transfer during analysis.

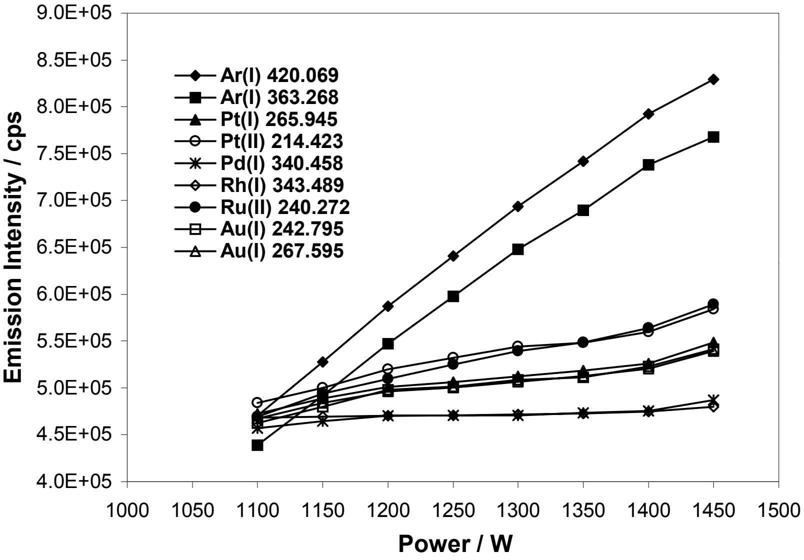

Figure 6 Effect of power on emission intensities: Radial viewing.

3.4. Effect of Sodium

The effect of increasing the Na concentration, on the emission intensities of Au and the PGMs is illustrated for the axial view in Fig. 7 and for the radial observation in Fig. 8. Relative intensities (expressed as the ratio of the emission intensities obtained from a solution with no sodium to those obtained from a solution containing sodium)[11] can be used as a measure of the Na interference. It can be seen in Fig. 7 and Fig. 8 that increasing Na concentration suppressed the emission signals of the analytes, with the exception of Au, which was initially suppressed and thereafter showed an enhancement in emission intensity. Initial enhancement of emission intensity was observed in Pd (Fig. 7) and Pt (Fig. 8) at low Na concentrations, further signal depression was observed with increasing Na concentration of up to 10 g l^{-1}. This apparent signal enhancement was found to be statistically insignificant (P>0.1). The magnitude of the initial signal enhancement can be related to the ionization potential of the elements and a possibility of a shift in the ionization equilibrium.[15] Increased vaporization effect or possible shifts in ionization equilibrium may be responsible for the decrease in emission intensities of the PGMs in both axial and radial viewed plasmas.

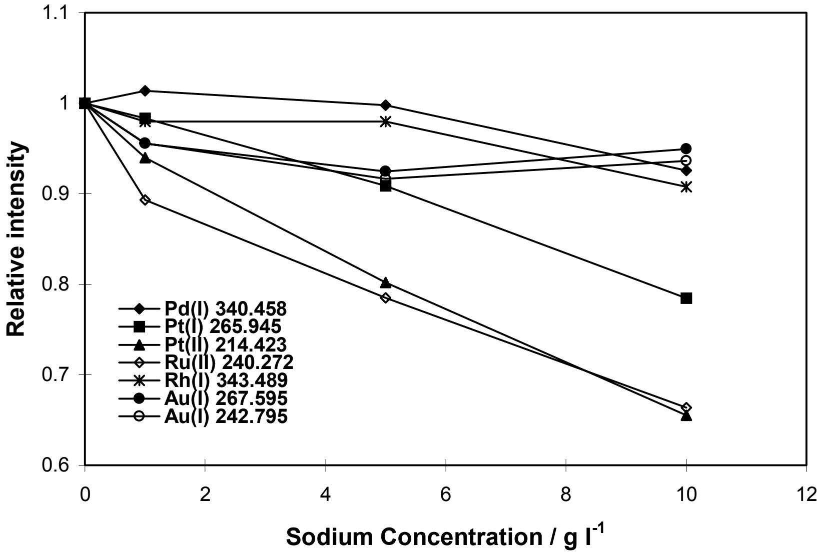

Figure 7 Effect of Na on emission intensities: Axial viewing.

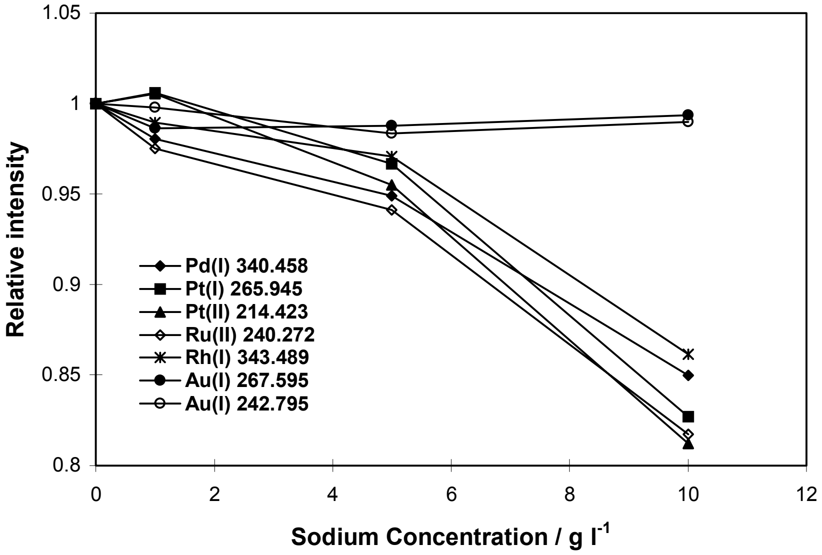

Figure 8 Effect of Na on emission intensities: Radial viewing.

The potential of Sc(II) 361.384 and Y(II) 371.030 nm as internal standard to compensate for Na matrix effects on accuracy was evaluated. Sample solutions containing 1, 5 and 10 g l^{-1} Na and 5 µg l^{-1} Sc or Y were analyzed using water based standard solutions as calibration standards. The extent of compensation, using internal standard concentration of 5 µg ml^{-1}, is illustrated in Tables 5 and 6 for axial and radial modes of viewing, respectively. When no internal standard was used, the addition of Na resulted in a depressive effect of the analyte concentrations. The effect was more pronounced at 5 and 10 g l^{-1} than at 1 g l^{-1} Na. The use of Sc as an internal standard with radial viewing was more effective, because Sc was able to compensate for Pt, Ru and Rh up to 5 g l^{-1} Na. Y could, however, only compensate for Pt, Ru and Rh up to 1 g l^{-1} Na for both modes of viewing. Over compensation for Pd and Au was observed in both modes of viewing when using either Y or Sc as internal standard.

Table 5 Compensation of interference effects on the concentrations (μg ml^{-1}) of Au and the PGMs due to 1, 5 and 10 g l^{-1} Na using Y or Sc as internal standard. Axial viewing.

Element		No Internal standard			Y(II) 371.030 nm			Sc(II) 361.384 nm		
	True Conc (μg ml^{-1})	Na (1 g l^{-1})	Na (5 g l^{-1})	Na (10 g l^{-1})	Na (1 g l^{-1})	Na (5 g l^{-1})	Na (10 g l^{-1})	Na (1 g l^{-1})	Na (5 g l^{-1})	Na (10 g l^{-1})
Pt	110	110	102	87.9	115	132	94.5	117	111	93.4
Pd	50.1	51.4	50.6	47.0	57.4	73.4	47.0	59.6	63.1	58.1
Ru	25.6	23.4	20.5	17.3	26.8	30.2	21.4	28.1	26.2	22.0
Rh	16.5	17.2	17.6	16.0	19.9	25.8	19.6	20.6	22.4	20.3
Au	2.73	2.67	2.56	2.62	3.07	3.75	3.21	3.07	3.14	3.24

Table 6 Compensation of interference effects on the concentrations (μg ml^{-1}) of Au and the PGMs due to 1, 5 and 10 g l^{-1} Na using Y or Sc as internal standard. Radial viewing.

Element		No Internal standard			Y(II) 371.030 nm			Sc(II) 361.384 nm		
	True Conc (μg ml^{-1})	Na (1 g l^{-1})	Na (5 g l^{-1})	Na (10 g l^{-1})	Na (1 g l^{-1})	Na (5 g l^{-1})	Na (10 g l^{-1})	Na (1 g l^{-1})	Na (5 g l^{-1})	Na (10 g l^{-1})
Pt	111	115	111	94.6	117	142	102	119	120	106
Pd	49.6	49.0	47.5	42.7	51.5	59.0	44.4	53.7	52.7	46.8
Ru	25.9	26.5	25.6	22.1	26.9	32.1	22.9	29.0	27.8	23.1
Rh	16.0	16.6	16.3	14.5	17.2	20.7	15.1	18.2	17.9	15.3
Au	2.78	2.97	2.93	2.95	3.03	3.60	2.90	3.06	3.02	2.94

4. Conclusions

Conditions for effective use of Sc, Y and Ar lines as internal standards in the determination of Pt, Pd, Ru, Rh and Au were established. The internal standards, Y, Sc and Ar lines compensated for changes in forward power of the instrument. The best compensation, (using Y and Sc as internal standards), for variations in aerosol gas flow rate was obtained at flow rates of the aerosol carrier gas of 0.80 l min^{-1} and below. Since statistically improved results were obtained for this work using the internal standardization method (Table 4), Sc(II) 361.384 and Y(II) 371.030 nm can be used to improve accuracy during the analysis of the Pt, Ru, Rh and Au in a converter matte sample. Due to the over compensation for Pd, internal standardization seems to be inadequate in this case. It can be concluded that, the variable effects of EIE-induced processes in the plasma were only partly compensated using Sc(II) 361.384 and Y(II) 371.030 nm as internal standards. Sc was the better internal standard for samples containing up to 5 g l^{-1} Na, and for radial viewing of the plasma (Tables 5 and 6). Y can only be used to correct for low sodium matrices below 1 g l^{-1} in both modes of viewing. It would seem that the use of an internal standard is limited in compensating for very high sodium matrices.

To adequately improve accuracy during the analysis of Au and the PGMs the concentration of the internal standard need not exceed 10 µg ml^{-1}. The concentration of 10 µg ml^{-1} (and even lower) of the internal standard is sufficient for computing the ratio of the emission intensity of the analyte to the internal standard, which is incorporated during compensation calculations. It was found that in most cases it is not necessary to use high concentrations of an expensive internal standard such as Sc.

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