CHAPTER 3

THE QUANTITATIVE DETERMINATION OF THE PLATINUM GROUP ELEMENTS AND GOLD BY ICP-MS

3.1 Introduction

Non-spectroscopic interferences, matrix effects and drift of calibration curves and analyte sensitivities are well known problems in ICP-MS and if not properly compensated for can lead to a degradation in analytical precision and accuracy *[5, 20, 22, 35 - 41]*. These interference effects are generally believed to be due to the physical and chemical behaviour of the matrix elements (and analytes) in the sample introduction system, the interface region and the ion optics. These include transport effects, ionisation equilibrium effects and ion sampling effects *[25, 42, 43]*. Moderate amounts (0.1 - 1%) of a matrix ion can change analyte signals significantly *[5, 21, 25, 41]*. Standard addition and isotope dilution methods have been tried to minimise matrix effects in ICP-MS *[44]*. However, standard addition is time consuming and isotope dilution is not applicable to mono-isotopic elements *[22, 45]*. In this study the feasibility of using an internal standard as a possible solution to the above-mentioned problems was investigated.

Some investigations into trends in non-spectroscopic interferences and signal drift in ICP-MS have appeared in literature *[5, 25, 46]*. The general consensus is that internal standardisation is most effective when the internal standards and analytes are closely matched in terms of mass and first stage ionisation potential. Some caution has been suggested even when these selection criteria are used *[22]*. In this study the different isotopes of Sc, Y and La were considered as possible internal standards in the quantitative determination of the platinum group elements and gold.

A variety of internal standards that span the *m/z* range are often employed *[47, 48]*. This procedure requires spikes and usually precludes determination of the spike elements in the original sample. As an alternative, ions that are already present in the spectrum can be used. Several researchers *[25, 48, 49]* have published results where polyatomic ions have successfully been employed as internal standards. In this study the use of the ^{36}Ar isotope, which is always present in the spectrum, was investigated as a possible internal standard.

Table 3.1: Relevant data of the platinum group elements, gold and the internal standards investigated *[50]*.

Atomic no.	Element	Mass no.	Relative abundance	Atomic mass (g mol^{-1})	First ionisation potential (eV)	Second ionisation potential (eV)
18	Argon	36 38 40	0.337 0.063 99.600	39.948	15.76	27.63
21	Scandium	45	100.0	44.956	6.56	12.80
39	Yttrium	89	100.0	88.905	6.53	12.23
57	Lanthanum	138 139	0.089 99.911	138.91	5.61	11.06
44	Ruthenium	96 98 99 100 101 102 104	5.51 1.87 12.72 12.62 17.07 31.63 18.58	101.07	7.36	16.76
45	Rhodium	103	100.0	102.905	7.45	18.07
46	Palladium	102 104 105 106 108 110	0.96 10.97 22.23 27.33 26.71 11.81	106.4	8.33	19.42
77	Iridium	191 193	37.3 62.7	192.2	9.1	
78	Platinum	190 192 194 195 196 198	0.013 0.78 32.9 33.8 25.3 7.21	195.09	8.96	18.56
79	Gold	197	100.0	196.967	9.23	20.5

One of the dissolution methods employed in the analysis of the platinum group metals and gold involves an aqua regia (3:1 mixture of concentrated HCl and concentrated HNO_3) leaching procedure *[51, 52]*. This has the effect that the matrix of the final sample solution is mainly diluted aqua regia. The standard solutions from which the calibration curves are constructed however is in a 1.0% v/v HCl matrix. The effect of matrices consisting of different concentrations of aqua regia on the quantitative analysis of sample solutions was investigated.

Table 3.1 shows the relative abundances of the naturally occurring isotopes of the platinum group elements, gold and the internal standards investigated, as well as the first and second ionisation potentials of the various elements. From this table it can be seen that the mass of the isotope of Y is relatively well matched to those of the isotopes of Ru, Pd and Rh. The masses of the isotopes of La are relatively well matched to those of Ir, Pt and Au. The first ionisation potentials of Sc, Y and La are relatively close to those of the platinum group elements and gold. Some elements have overlapping isotopes, e.g. ^{102}Ru and ^{102}Pd, as well as ^{104}Ru and ^{104}Pd. The feasibility of using isotopes of very low abundance, e.g. ^{138}La and ^{192}Pt was also investigated.

3.2 Experimental

3.2.1 Preparation of solutions

Tables 3.2 and 3.3 show the results of calculations performed in order to prepare stock solutions of the platinum group elements, gold, the internal standards, as well as standard solutions for the preparation of calibration curves in the range 0 to 150 μg dm^{-3} and 50 μg dm^{-3} sample solutions in matrices containing aqua regia from 0.35 to 2.50% v/v. Higher acid concentrations were not considered as this would shorten the lifetime of the nickel sampler and skimmer cones considerably.

Certified solutions of the platinum group elements and gold each containing 1000 mg dm^{-3} of the element in 4.9% HCl were employed for the preparation of the calibration and sample solutions (Spectrascan, Teknolab A/S, Dröbak, Norway). Certified solutions of Sc and Y each containing 1000 mg dm^{-3} of the element in 2.5% HCl were used (Spectrascan, Teknolab A/S, Dröbak, Norway). A certified solution of La containing 5000 mg dm^{-3} of the element in 2.5% HNO_3 was used for the preparation of a stock solution (Spectrascan, Teknolab A/S, Dröbak, Norway). High purity hydrochloric acid (> 32%) and nitric acid (> 65%) (Fluka) were used for the preparation of acidic solutions. High purity water with resistivity 18.2 MΩ cm (Millipore Corporation, United States of America) was used for dilutions.

All solutions were prepared in pre-conditioned plastic laboratory ware. A-grade pipettes and volume adjustable pipettes were used for the transfer of solutions. The calibration standard solutions as well as the sample solutions were transferred to clean PTFE holders which were placed on the sample rack of the autosampler of the instrument.

3.2.2 Optimisation of the ICP-MS

The instrument was optimised as described in chapter 2. A warm-up time of one hour was allowed before any analyses were performed in order for instrumental conditions to equilibrate.

3.2.3 Mass scans of the platinum group elements and gold

Mass scans of a 100 μg dm^{-3} solution of the platinum group elements and gold in 1.00% v/v HCl were performed in order to verify the validity of 1) the isotopic ratios used and 2) the mass calibration of the instrument.

3.2.4 Data acquisition

The intensities of the various isotopes of the internal standards, ^{36}Ar, the platinum group elements and gold were measured. The operating conditions of the inductively coupled plasma mass spectrometer and settings for data acquisition are listed in table 3.4. The data was then used to construct calibration curves and perform quantitative analysis of the platinum group elements and gold.

3.3 Results and discussion

3.3.1 Mass scans of a solution of the platinum group elements and gold

Figures 3.1 and 3.2 show the mass scans of the platinum group elements and gold. The heights of the bars, indicating the isotopic ratios, were calculated using the relative abundances of the isotopes (see table 3.1). From both figures it can be seen that the isotopic patterns fit the scan indicating the validity of the mass calibration of the instrument. The intensities at masses 102 and 104 (for Ru and Pd) also fit the theoretical patterns reasonably well. From figure 3.2 it can be seen that the peak shape at mass 192 (for ^{192}Pt) could lead to imprecise and inaccurate readings due to the low abundance of this isotope.

Table 3.2: Preparation of stock solutions of Au, Ir, Pd, Pt, Rh, Ru, Sc, Y and La.

Solution to prepare	**[Element] (mg dm^{-3})**	**[HCl] (% v/v)**	**[HNO$_3$] (% v/v)**	**Dilution factor**	**Volume of certified solution to transfer (10^{-3} dm^3)**	**Volume of flask (10^{-3} dm^3)**	**Volume of HCl to add (10^{-3} dm^3)**	**Volume of HNO$_3$ to add (10^{-3} dm^3)**
Certified platinum group element solution	1000	4.9	0.0	0	0.00	0	0.000	0.000
Stock platinum group element solution	10	5.0	0.0	100	5.00	500	23.530	0.000
Certified Sc solution	1000	2.5	0.0	0	0.00	0	0.000	0.000
Certified Y solution	1000	2.5	0.0	0	0.00	0	0.000	0.000
Certified La solution	5000	0.0	2.5	0	0.00	0	0.000	0.000
Stock La solution	1000	0.0	2.5	5	10.00	50	0.000	1.000

Table 3.3: Preparation of A.: Platinum group elements and gold calibration standards with internal standards in 1% v/v HCl and
B.: Sample solutions to study the effect of aqua regia concentration on the quantitative analysis of the platinum group elements and gold.

	[platinum group element] (μg dm^{-3})	[HCl] (% v/v)	[HNO$_3$] (% v/v)	[aqua regia] (% v/v)	Dilution factor	Volume of platinum group element stock solution to transfer (10^{-3} dm^3)	Volume of flask (10^{-3} dm^3)	Volume of HCl to add (10^{-3} dm^3)	Volume of HNO$_3$ to add (10^{-3} dm^3)	[internal standard] (mg dm^{-3})	Dilution factor	Volume of each internal standard solution to transfer (10^{-3} dm^3)
A.	Blank	1.00	0.00	0.00	-	0.000	1000	9.950	-	1.00	1000	1.000
	10	1.00	0.00	0.00	1000	1.000	1000	9.900	-	1.00	1000	1.000
	50	1.00	0.00	0.00	200	5.000	1000	9.700	-	1.00	1000	1.000
	100	1.00	0.00	0.00	100	10.000	1000	9.450	-	1.00	1000	1.000
	150	1.00	0.00	0.00	67	15.000	1000	9.200	-	1.00	1000	1.000
B.	50	0.26	0.09	0.35	200	5.000	1000	2.325	0.850	1.00	1000	1.000
	50	0.38	0.13	0.50	200	5.000	1000	3.450	1.225	1.00	1000	1.000
	50	0.75	0.25	1.00	200	5.000	1000	7.200	2.475	1.00	1000	1.000
	50	1.13	0.38	1.50	200	5.000	1000	10.950	3.725	1.00	1000	1.000
	50	1.50	0.50	2.00	200	5.000	1000	14.700	4.975	1.00	1000	1.000
	50	1.88	0.63	2.50	200	5.000	1000	18.450	6.225	1.00	1000	1.000

Table 3.4: Operating conditions of the inductively coupled plasma mass spectrometer and settings for data acquisition.

Instrument	Spectromass-ICP
Torch	Fassel
Spray chamber	Scott-type double-pass
Nebuliser	Meinhard
Sampler cone	Ni with diameter approximately 1 mm
Skimmer cone	Ni with diameter approximately 1 mm
RF power	1350 W
Coolant argon gas flow rate	16 dm^3 min^{-1}
Auxiliary argon gas flow rate	1.5 dm^3 min^{-1}
Aerosol carrier argon gas flow rate	0.96 dm^3 min^{-1}
Sample introduction	1.0×10^{-3} dm^3 min^{-1}
Dwell time	2 s
Resolution	Normal
Readings per measurement	5
Rinse time with water between samples to avoid contamination	120 s
Total pre-flush time with sample before measurement	120 s (of which the first 20 s was set at an uptake rate of approximately 3×10^{-3} dm^3 min^{-1})
Isotopes monitored	^{36}Ar, ^{45}Sc, ^{89}Y, ^{138}La, ^{139}La, ^{96}Ru, ^{98}Ru, ^{99}Ru, ^{100}Ru, ^{101}Ru, ^{102}Ru, ^{104}Ru, ^{103}Rh, ^{102}Pd, ^{104}Pd, ^{105}Pd, ^{106}Pd, ^{108}Pd, ^{110}Pd, ^{191}Ir, ^{193}Ir, ^{192}Pt, ^{194}Pt, ^{195}Pt, ^{196}Pt, ^{198}Pt, ^{197}Au

3.3.2 *Intensities as measured*

Tables 3.5 to 3.7 (Addendum A) show the averages of the intensities measured for the isotopes of the internal standards, the platinum group elements and gold.

3.3.3 *The effect of aqua regia concentration on the ratios of the isotopes of the platinum group elements and gold to the isotopes of the internal standards*

The values from tables 3.5 to 3.7 (Addendum A) were used to calculate the effect of the aqua regia concentration in the solution on the ratios of the isotopes of the platinum group elements and gold to those of the internal standards. This was done in order to see whether the isotopes of the platinum group elements and gold and those of the internal standards behave in a similar manner in aqua regia matrix.

Effect of aqua regia concentration on the ratios of the isotopes of the platinum group elements and gold to ^{36}Ar

From figures 3.3 to 3.8 it can be seen that the analyte to internal standard isotope ratios generally decrease with an increase in aqua regia concentration. The decreases in the isotope ratios are about 20%. The relative standard deviations for the various isotopes are about 10%. The isotopes of the platinum group elements and gold are thus not affected in the same way as the ^{36}Ar isotope. These preliminary results are an indication that ^{36}Ar would possibly not serve as a good internal standard for the platinum group elements and gold.

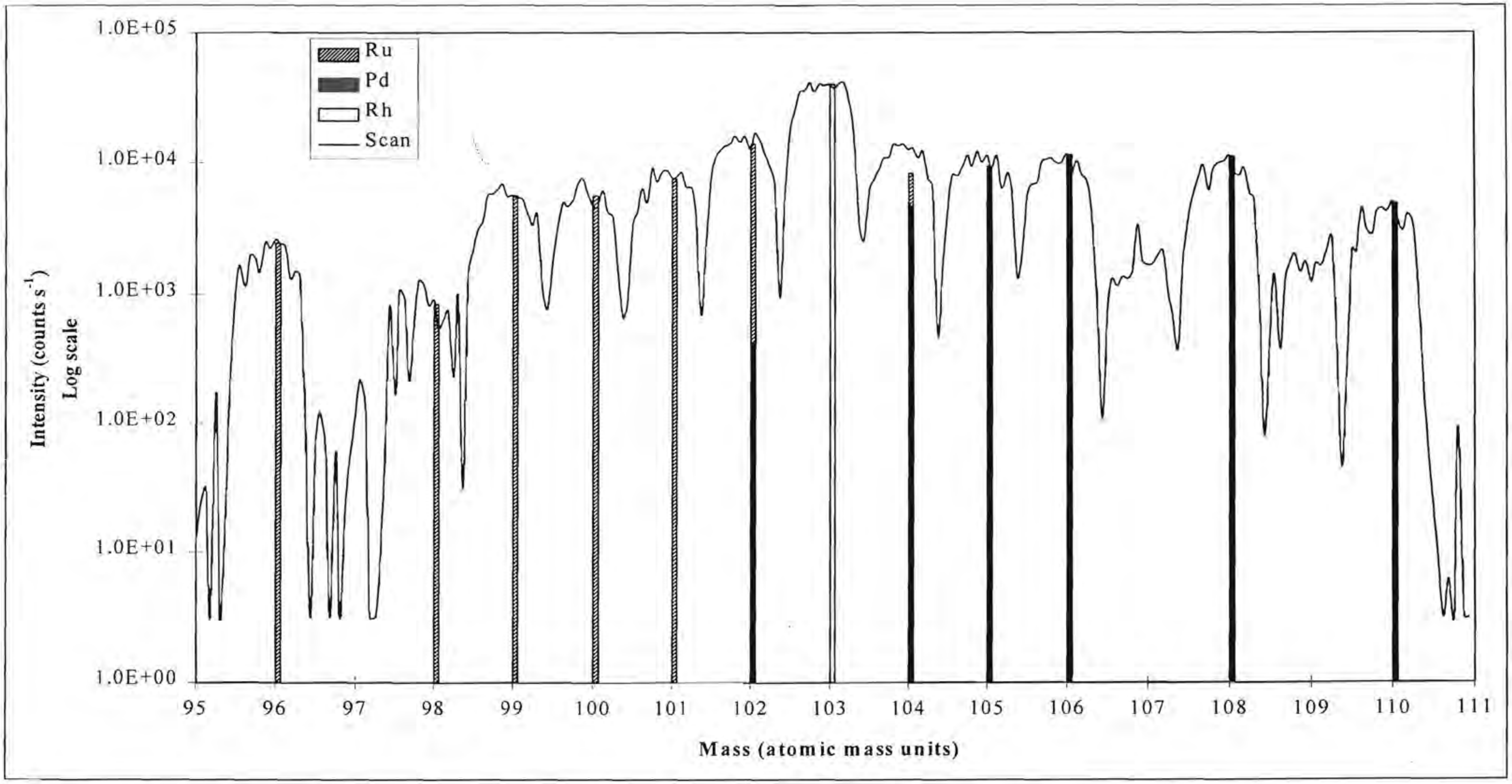

Figure 3.1: Mass scan (at normal resolution) of a solution containing 100 μg dm^{-3} platinum group elements and gold in 1.00% v/v HCl. The theoretical relative abundances of the isotopes of Ru, Pd and Rh are shown.

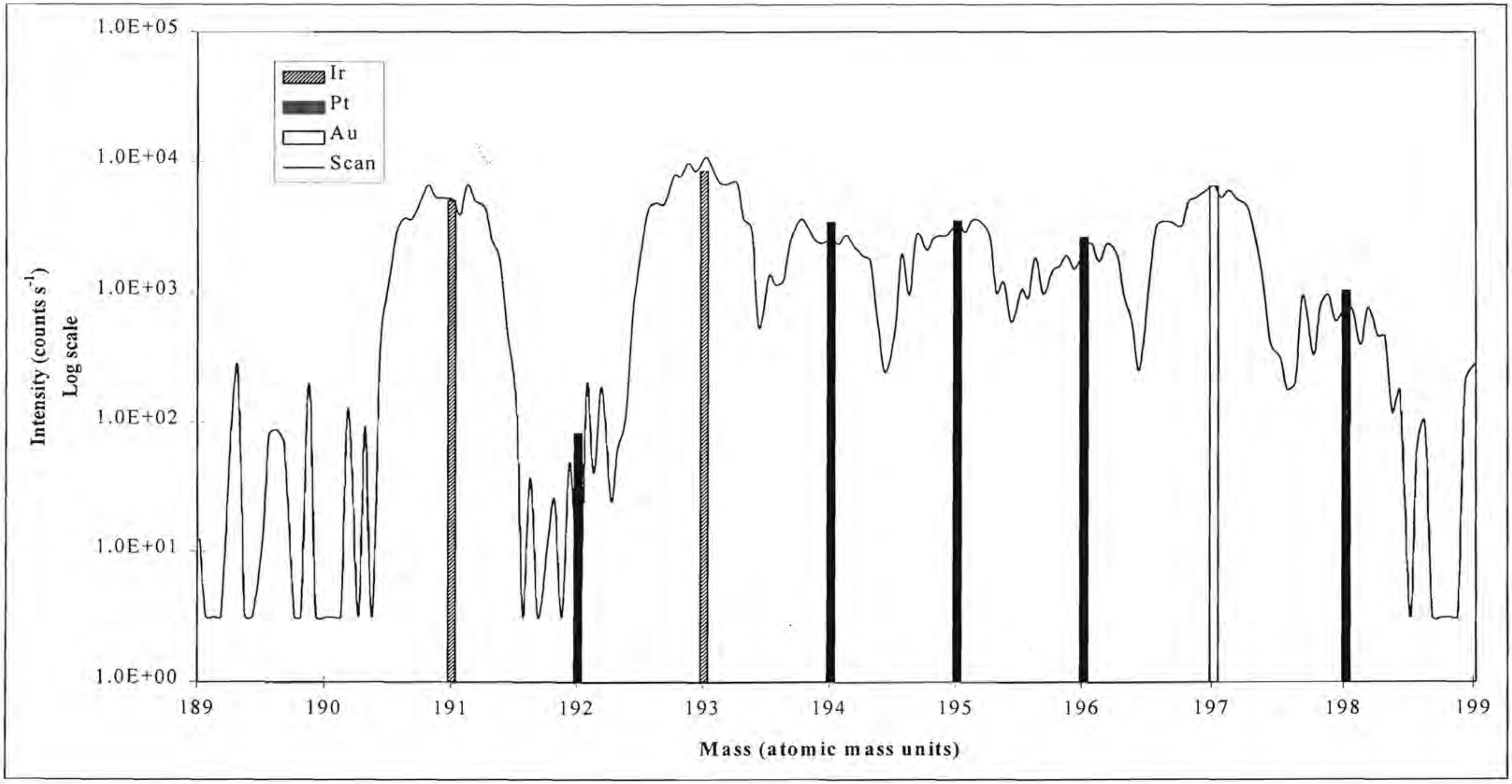

Figure 3.2: Mass scan (at normal resolution) of a solution containing 100 μg dm^{-3} platinum group elements and gold in 1.00% v/v HCl. The theoretical relative abundances of the isotopes of Ir, Pt and Au are shown.

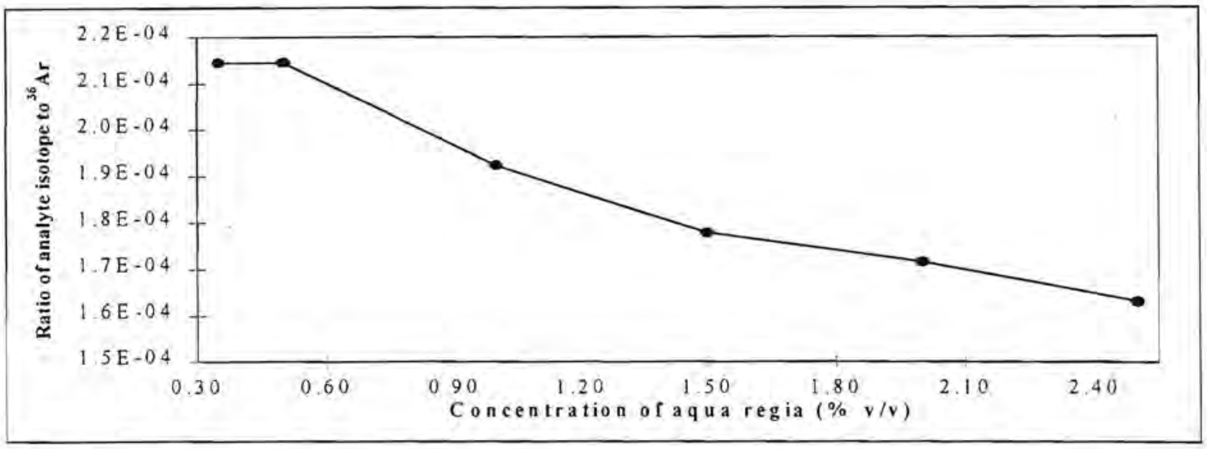

Figure 3.3: Effect of aqua regia concentration on the ratio of the gold isotope to the ^{36}Ar isotope. RSD for ^{197}Au to ^{36}Ar ratio is 12%.

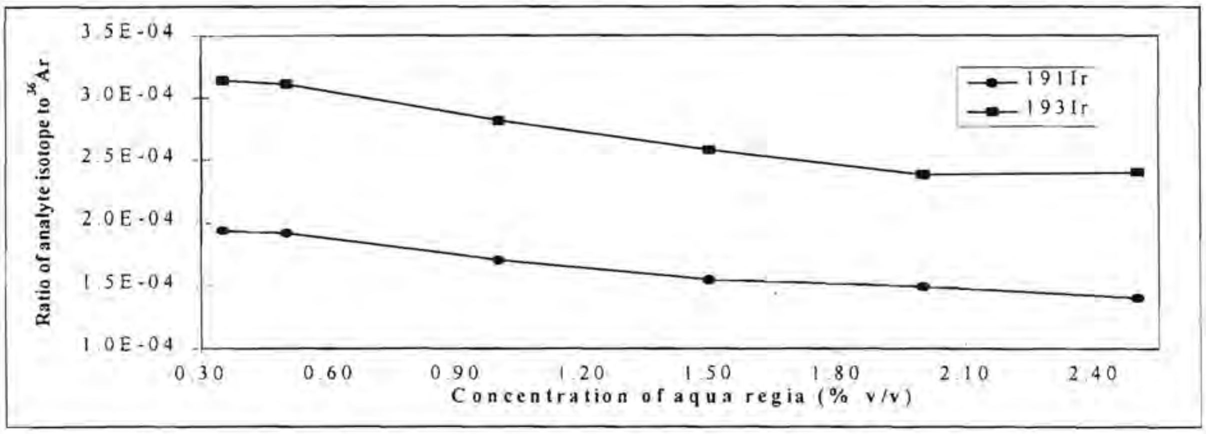

Figure 3.4: Effect of aqua regia concentration on the ratios of the iridium isotopes to the ^{36}Ar isotope. RSD for analytes to ^{36}Ar ratios is ^{191}Ir: 13% and ^{193}Ir: 12%.

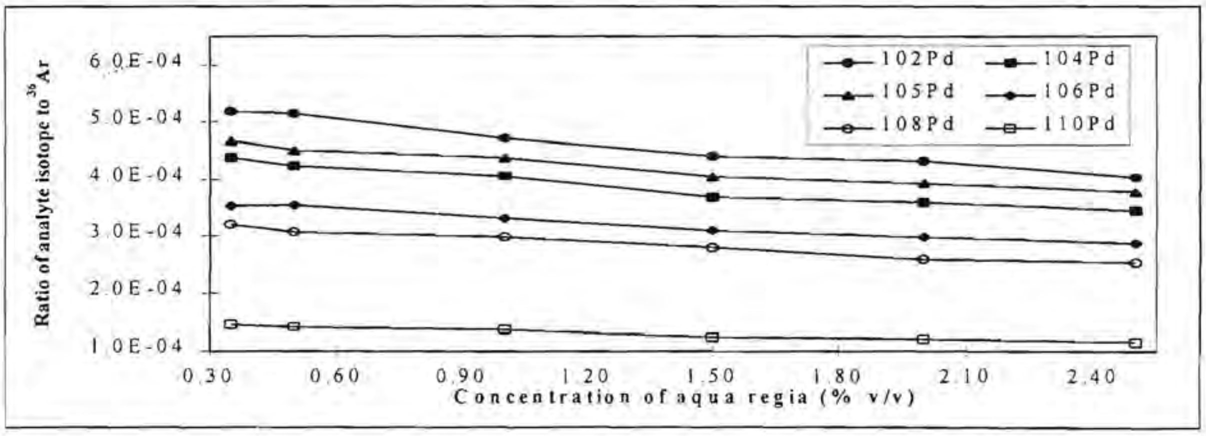

Figure 3.5: Effect of aqua regia concentration on the ratios of the palladium isotopes to the ^{36}Ar isotope. RSD for analytes to ^{36}Ar ratios is ^{102}Pd: 10%, ^{104}Pd: 10%, ^{105}Pd: 8%, ^{106}Pd: 9%, ^{108}Pd: 9% and ^{110}Pd: 9%.

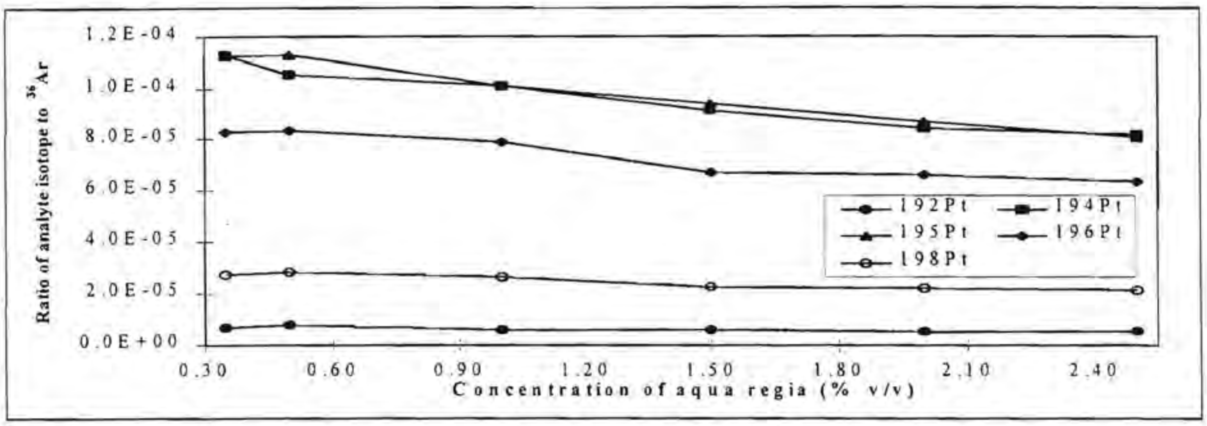

Figure 3.6: Effect of aqua regia concentration on the ratios of the platinum isotopes to the ^{36}Ar isotope. RSD for analytes to ^{36}Ar ratios is ^{192}Pt: 16%, ^{194}Pt: 13%, ^{195}Pt: 14%, ^{196}Pt: 12% and ^{198}Pt: 12%.

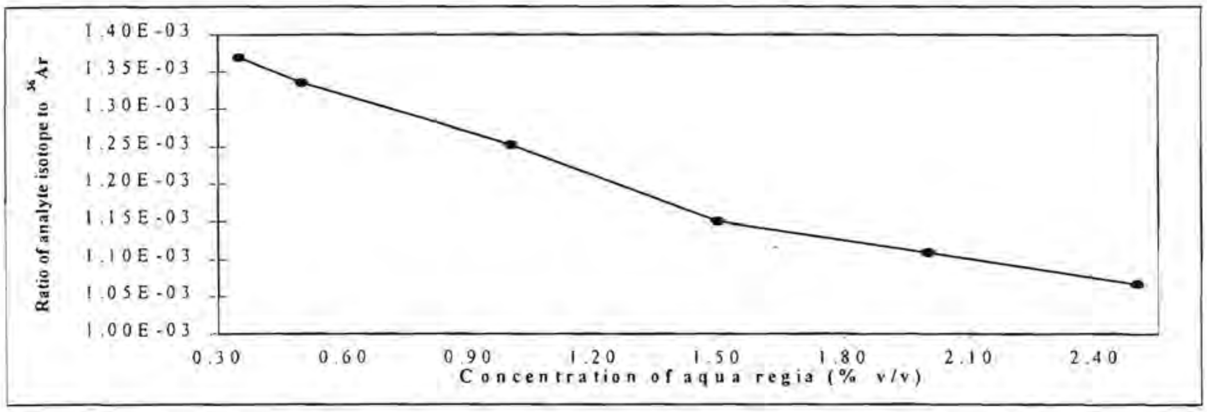

Figure 3.7: Effect of aqua regia concentration on the ratio of the rhodium isotope to the ^{36}Ar isotope. RSD for ^{103}Rh to ^{36}Ar ratio is 10%.

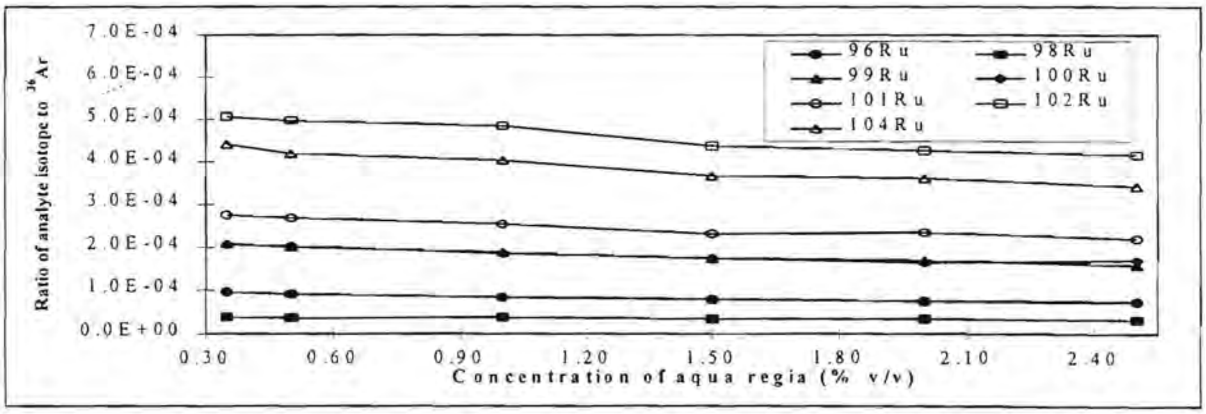

Figure 3.8: Effect of aqua regia concentration on the ratios of the ruthenium isotopes to the ^{36}Ar isotope. RSD for analytes to ^{36}Ar ratios is ^{96}Ru: 11%, ^{98}Ru: 7%, ^{99}Ru: 11%, ^{100}Ru: 10%, ^{101}Ru: 9%, ^{102}Ru: 9% and ^{104}Ru: 10%.

Effect of aqua regia concentration on the ratios of the isotopes of the platinum group elements and gold to ^{45}Sc

Figures 3.9 to 3.14 show a reasonably good correlation in the behaviour of the analyte isotopes relative to that of Sc. In general, a decrease in the ratio with an increase in aqua regia concentration is also observed. The decreases in the ratios over the concentration range studied was below 10% for Ru, Pd and Rh, i.e. the elements of lower mass. Relative standard deviations of less than 4% are observed for Ru, Pd and Rh and 5 - 7% for Au, Ir and Pt, with the exception of the low abundant ^{192}Pt isotope. From these curves it is seen that Sc could serve as a possible internal standard for the quantitative determination of the platinum group elements and gold, especially those of lower mass.

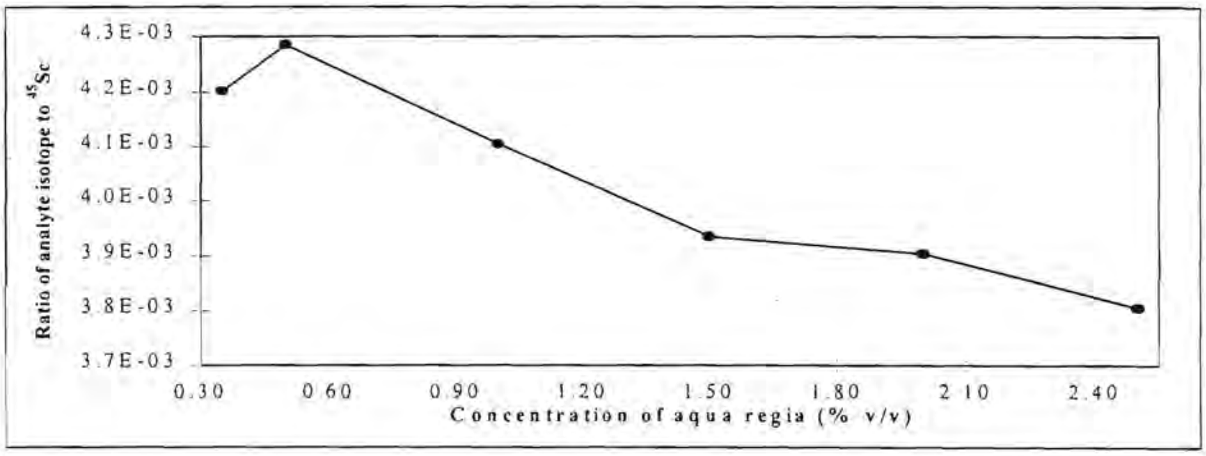

Figure 3.9: Effect of aqua regia concentration on the ratio of the gold isotope to the ^{45}Sc isotope. RSD for ^{197}Au to ^{45}Sc ratio is 5%.

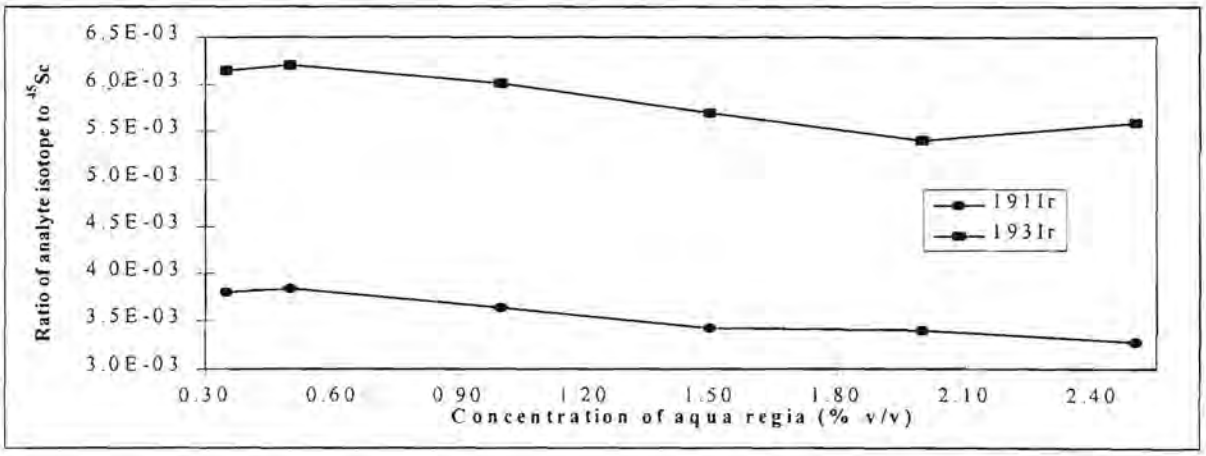

Figure 3.10: Effect of aqua regia concentration on the ratios of the iridium isotopes to the ^{45}Sc isotope. RSD for analytes to ^{45}Sc ratios is ^{191}Ir: 6% and ^{193}Ir: 6%.

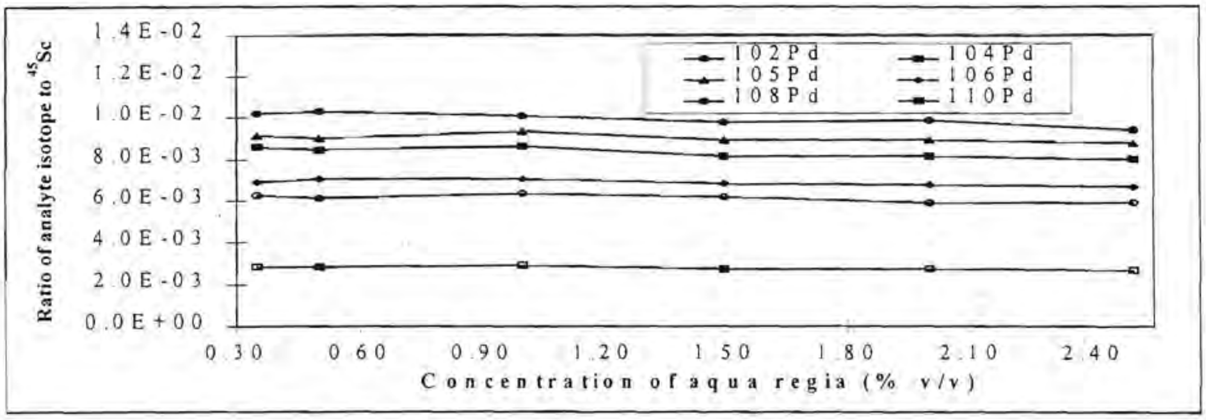

Figure 3.11: Effect of aqua regia concentration on the ratios of the palladium isotopes to the ^{45}Sc isotope. RSD for analytes to ^{45}Sc ratios is ^{102}Pd: 3%, ^{104}Pd: 3%, ^{105}Pd: 2%, ^{106}Pd: 2%, ^{108}Pd: 3% and ^{110}Pd: 3%.

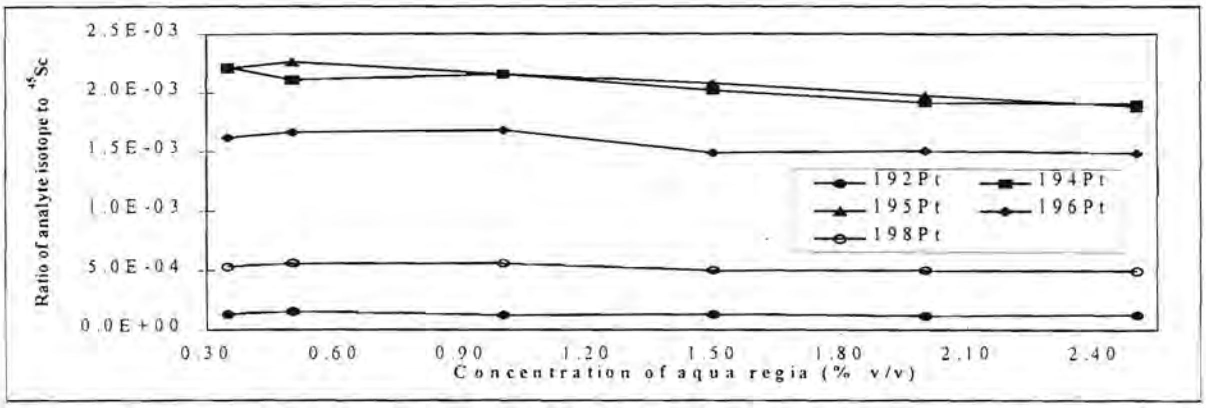

Figure 3.12: Effect of aqua regia concentration on the ratios of the platinum isotopes to the ^{45}Sc isotope. RSD for analytes to ^{45}Sc ratios is ^{192}Pt: 10%, ^{194}Pt: 6%, ^{195}Pt: 7%, ^{196}Pt: 6% and ^{198}Pt: 6%.

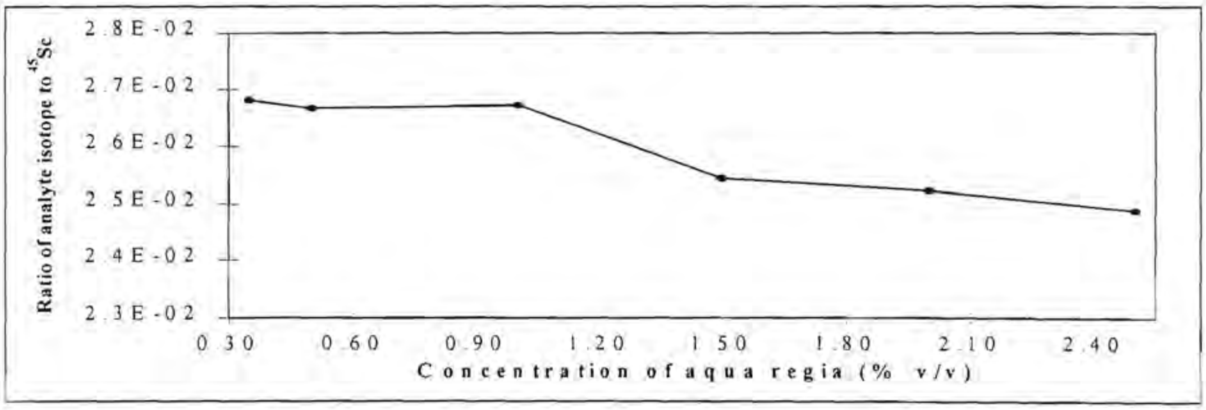

Figure 3.13: Effect of aqua regia concentration on the ratio of the rhodium isotope to the ^{45}Sc isotope. RSD for ^{103}Rh to ^{45}Sc ratio is 3%.

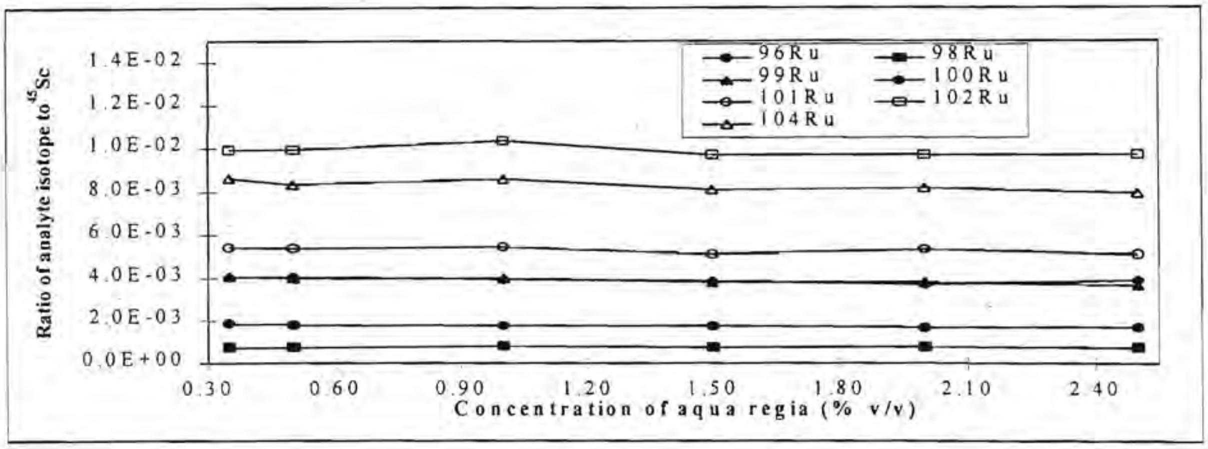

Figure 3.14: Effect of aqua regia concentration on the ratio of the ruthenium isotopes to the ^{45}Sc isotope. RSD for analytes to ^{45}Sc ratios is ^{96}Ru: 4%, ^{98}Ru: 3%, ^{99}Ru: 4%, ^{100}Ru: 3%, ^{101}Ru: 3%, ^{102}Ru: 3% and ^{104}Ru: 3%.

Effect of aqua regia concentration on the ratios of the isotopes of the platinum group elements and gold to ^{89}Y

Figures 3.15 to 3.20 show an excellent correlation between the behaviour of the platinum group elements and gold isotopes and the Y isotope. A maximum relative standard deviation of 3% for the ratios of the analytes to Y was observed for the platinum group elements of lighter mass. For Au, Ir and Pt (with the exception of ^{192}Pt) the corresponding value is 5%. Y shows great potential as an internal standard for the platinum group elements and gold, and more so for those of lighter mass.

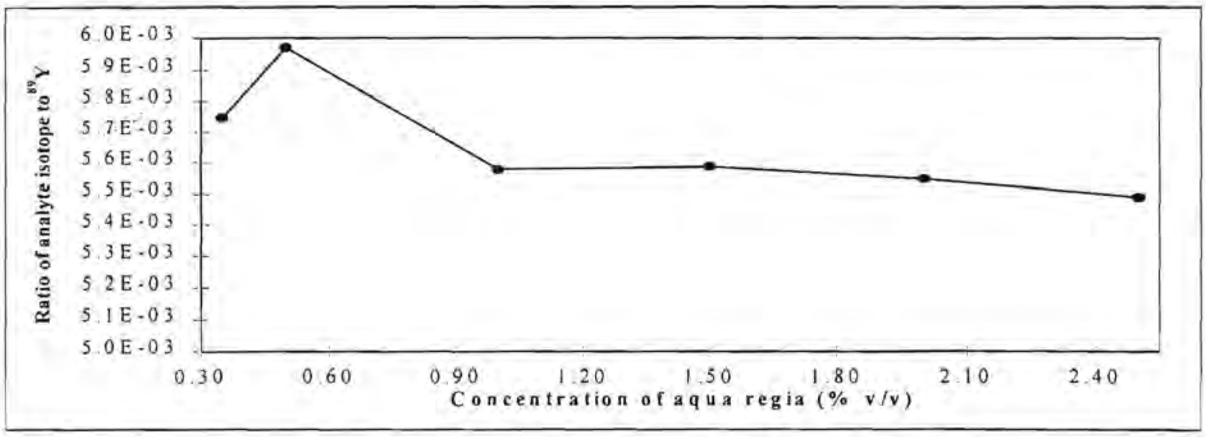

Figure 3.15: Effect of aqua regia concentration on the ratio of the gold isotope to the ^{89}Y isotope. RSD for ^{197}Au to ^{89}Y ratio is 3%.

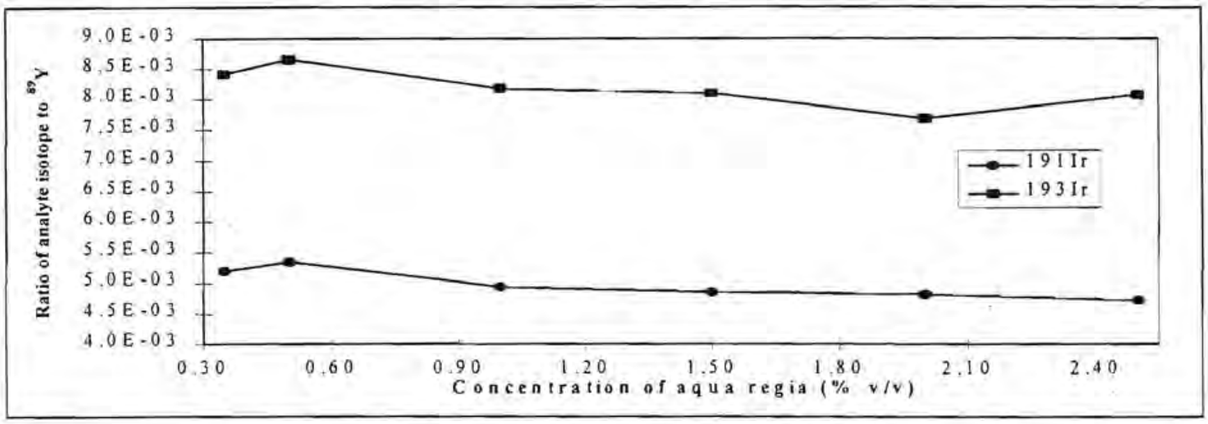

Figure 3.16: Effect of aqua regia concentration on the ratios of the iridium isotopes to the ^{89}Y isotope. RSD for analytes to ^{89}Y ratios is ^{191}Ir: 5% and ^{193}Ir: 4%.

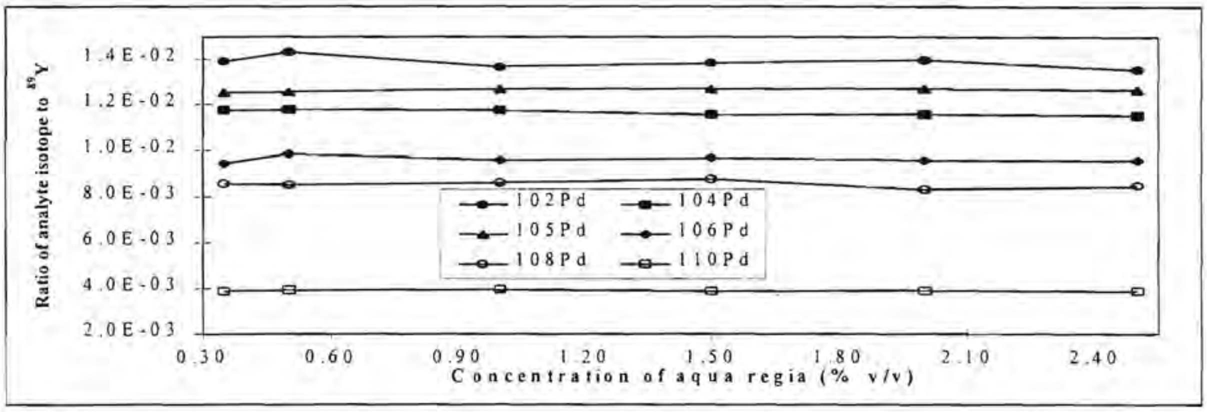

Figure 3.17: Effect of aqua regia concentration on the ratios of the palladium isotopes to the ^{89}Y isotope. RSD for analytes to ^{89}Y ratios is ^{102}Pd: 2%, ^{104}Pd: 1%, ^{105}Pd: 1%, ^{106}Pd: 1%, ^{108}Pd: 2% and ^{110}Pd: 1%.

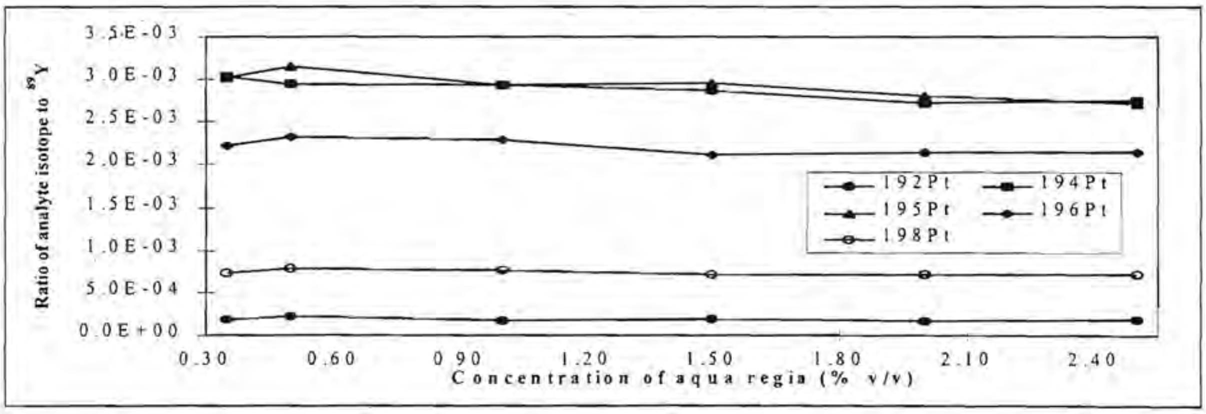

Figure 3.18: Effect of aqua regia concentration on the ratios of the platinum isotopes to the ^{89}Y isotope. RSD for analytes to ^{89}Y ratios is ^{192}Pt: 10%, ^{194}Pt: 4%, ^{195}Pt: 5%, ^{196}Pt: 4% and ^{198}Pt: 4%.

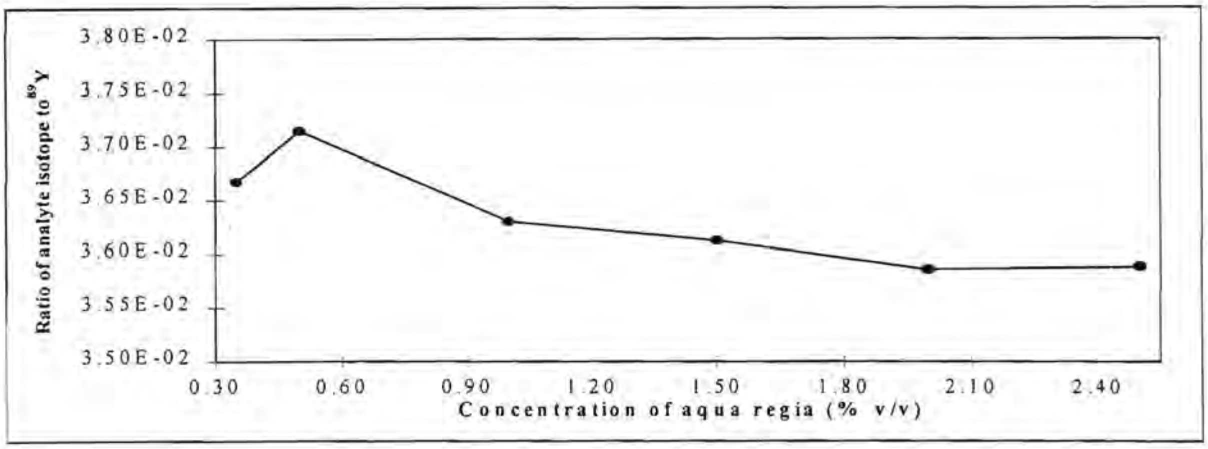

Figure 3.19: Effect of aqua regia concentration on the ratio of the rhodium isotope to the ^{89}Y isotope. RSD for ^{103}Rh to ^{89}Y ratio is 1%.

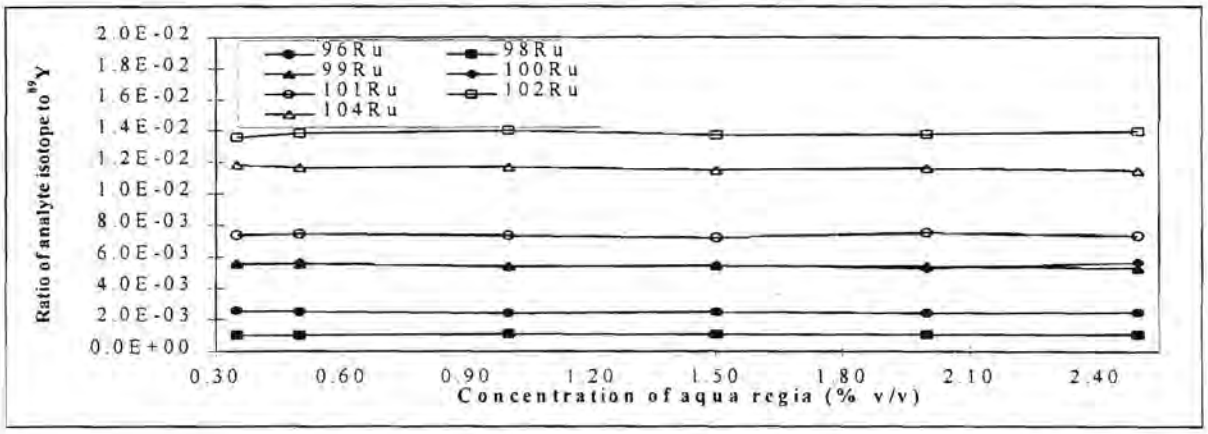

Figure 3.20: Effect of aqua regia concentration on the ratios of the ruthenium isotopes to the ^{89}Y isotope. RSD for analytes to ^{89}Y ratios is ^{96}Ru: 3%, ^{98}Ru: 3%, ^{99}Ru: 2%, ^{100}Ru: 3%, ^{101}Ru: 1%, ^{102}Ru: 1% and ^{104}Ru: 1%.

Effect of aqua regia concentration on the ratios of the isotopes of the platinum group elements and gold to ^{138}La

The ratios of the analytes to ^{138}La over the concentration range studied can be seen in figures 3.21 to 3.26. The less abundant isotope of La shows great potential as an internal standard for the analytes investigated since the variation in the ratios in aqua regia appears to be less than 6% (except for ^{192}Pt).

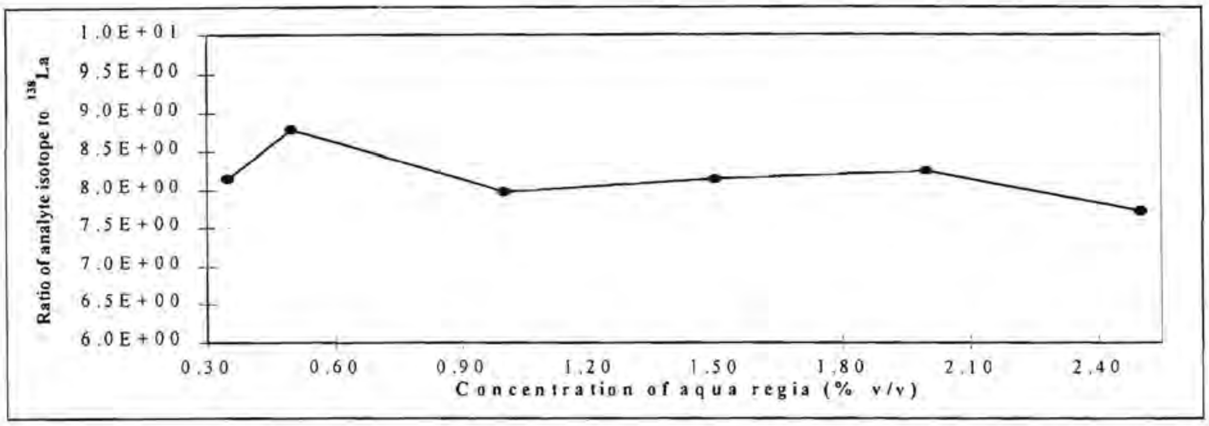

Figure 3.21: Effect of aqua regia concentration on the ratio of the gold isotope to the ^{138}La isotope. RSD for ^{197}Au to ^{138}La ratio is 4%.

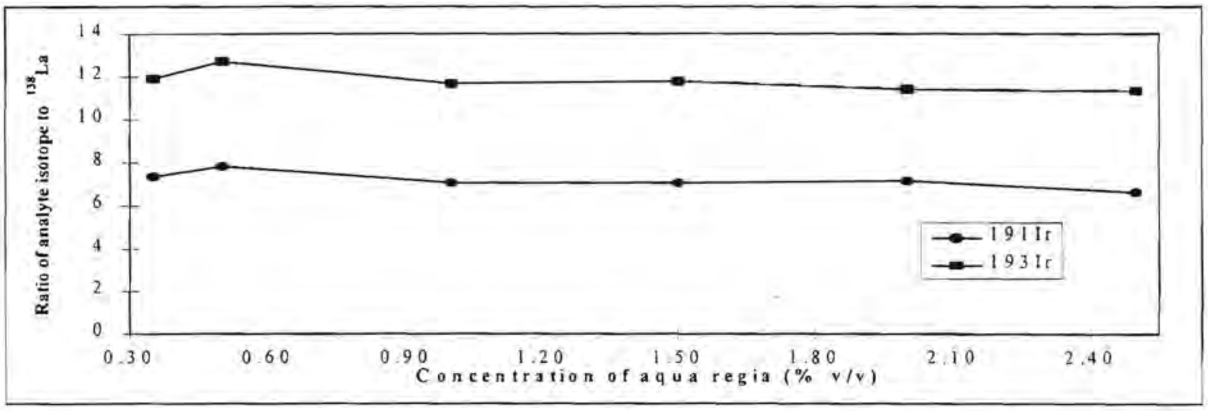

Figure 3.22: Effect of aqua regia concentration on the ratios of the iridium isotopes to the ^{138}La isotope. RSD for analytes to ^{138}La ratios is ^{191}Ir: 6% and ^{193}Ir: 4%.

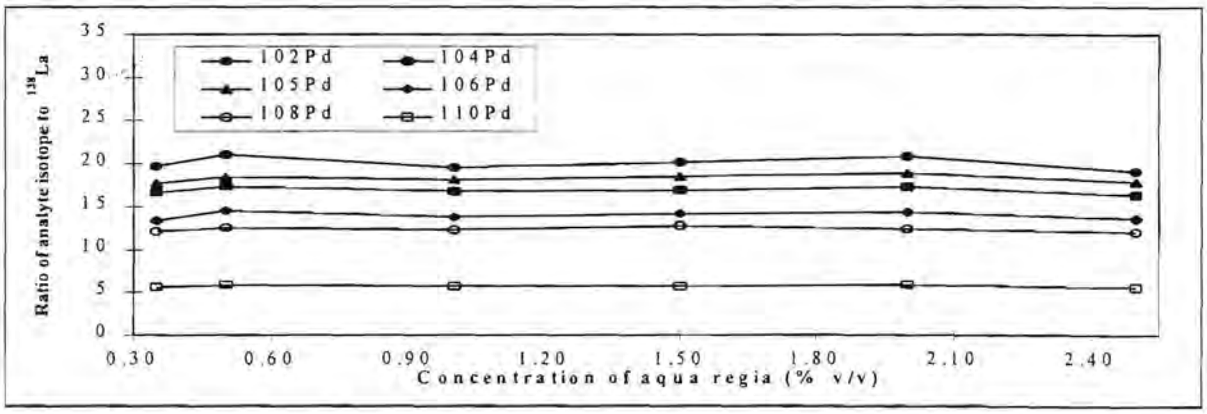

Figure 3.23: Effect of aqua regia concentration on the ratios of the palladium isotopes to the ^{138}La isotope. RSD for analytes to ^{138}La ratios is ^{102}Pd: 2%, ^{104}Pd: 2%, ^{105}Pd: 3%, ^{106}Pd: 3%, ^{108}Pd: 3% and ^{110}Pd: 3%.

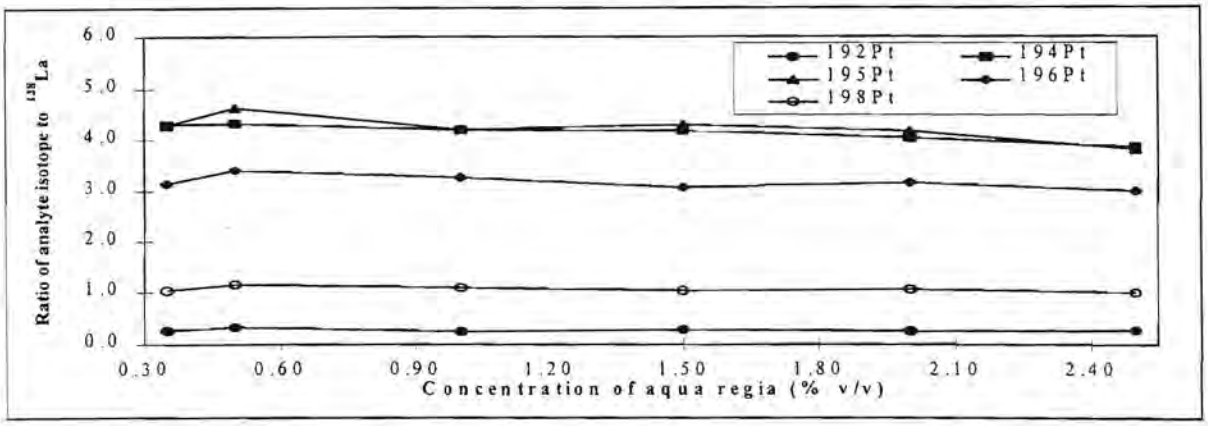

Figure 3.24: Effect of aqua regia concentration on the ratios of the platinum isotopes to the ^{138}La isotope. RSD for analytes to ^{138}La ratios is ^{192}Pt: 11%, ^{194}Pt: 4%, ^{195}Pt: 6%, ^{196}Pt: 5% and ^{198}Pt: 5%.

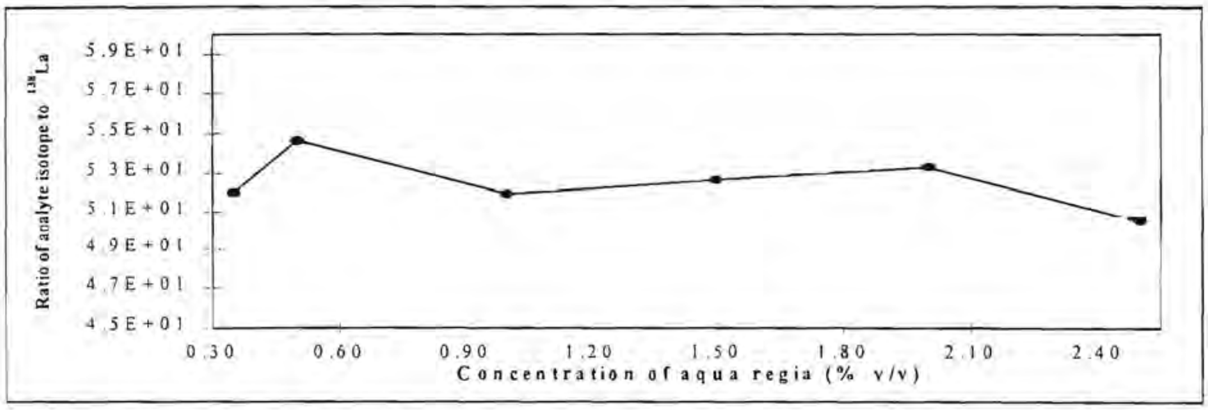

Figure 3.25: Effect of aqua regia concentration on the ratio of the rhodium isotope to the ^{138}La isotope. RSD for ^{103}Rh to ^{138}La ratio is 3%.

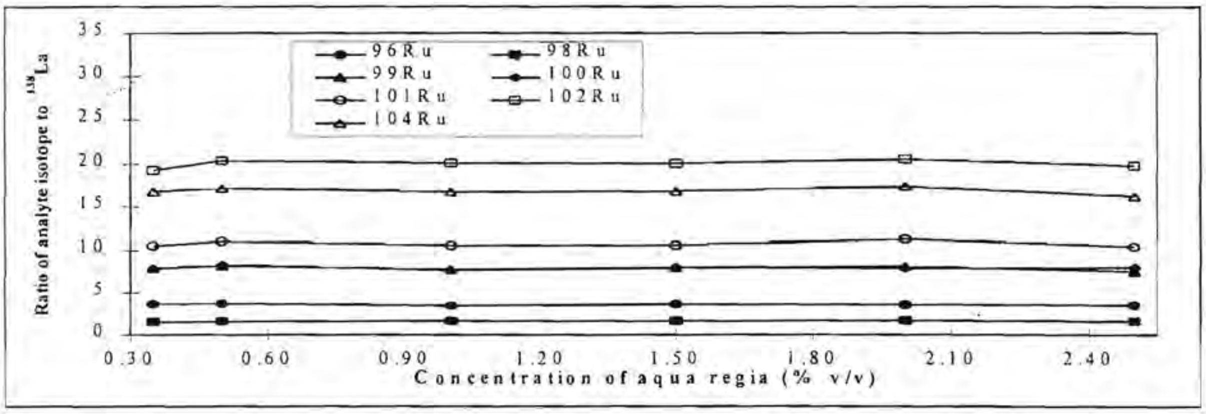

Figure 3.26: Effect of aqua regia concentration on the ratios of the ruthenium isotopes to the ^{138}La isotope. RSD for analytes to ^{138}La ratios is ^{96}Ru: 3%, ^{98}Ru: 4%, ^{99}Ru: 3%, ^{100}Ru: 3%, ^{101}Ru: 3%, ^{102}Ru: 2% and ^{104}Ru: 2%.

Effect of aqua regia concentration on the ratios of the isotopes of the platinum group elements and gold to ^{139}La

Figures 3.27 to 3.32 show the behaviour of the ^{139}La isotope relative to those of the analytes investigated in solutions containing 0.35 to 2.50% aqua regia. Excellent agreement in the various behaviour patterns is observed. This is also reflected in the relative standard deviations which are generally ≤ 3%.

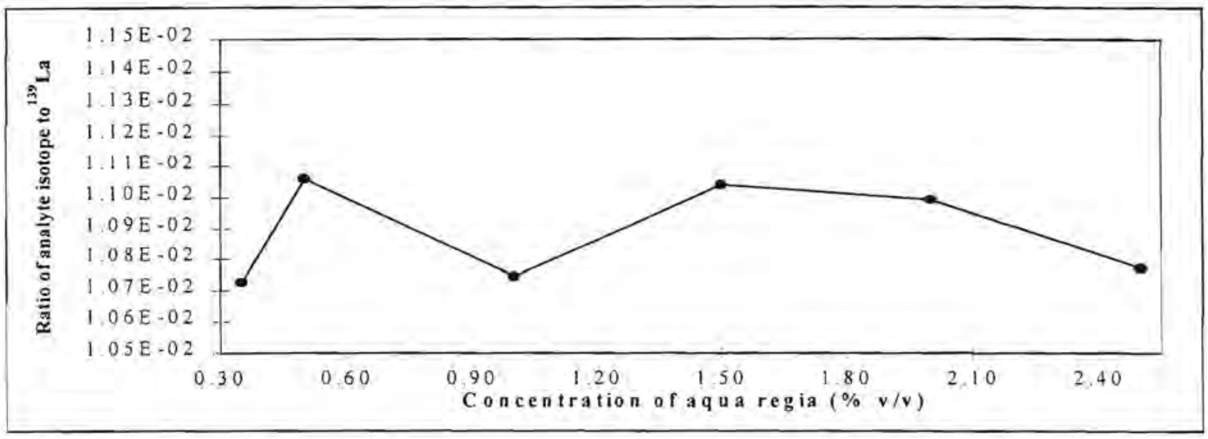

Figure 3.27: Effect of aqua regia concentration on the ratio of the gold isotope to the ^{139}La isotope. RSD for ^{197}Au to ^{139}La ratio is 1%.

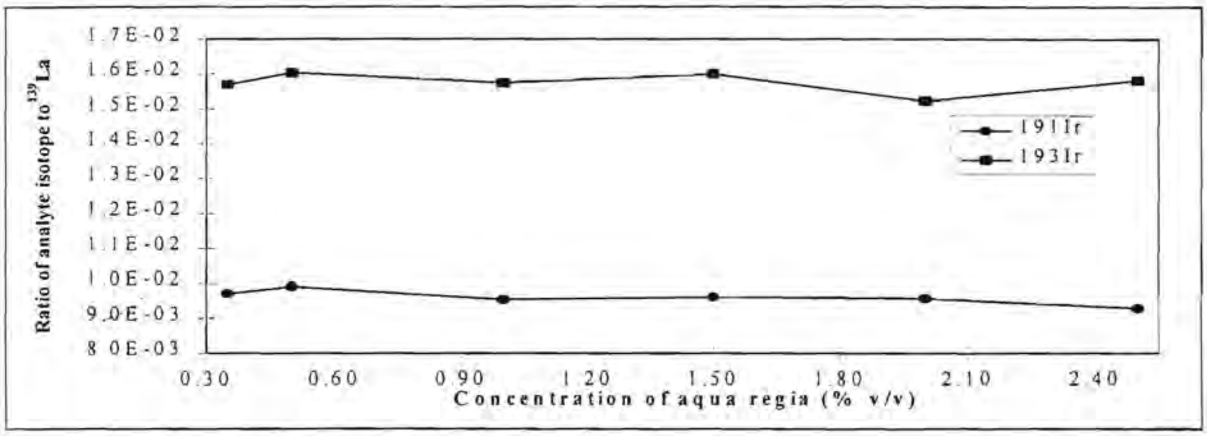

Figure 3.28: Effect of aqua regia concentration on the ratios of the iridium isotopes to the ^{139}La isotope. RSD for analytes to ^{139}La ratios is ^{191}Ir: 2% and ^{193}Ir: 2%.

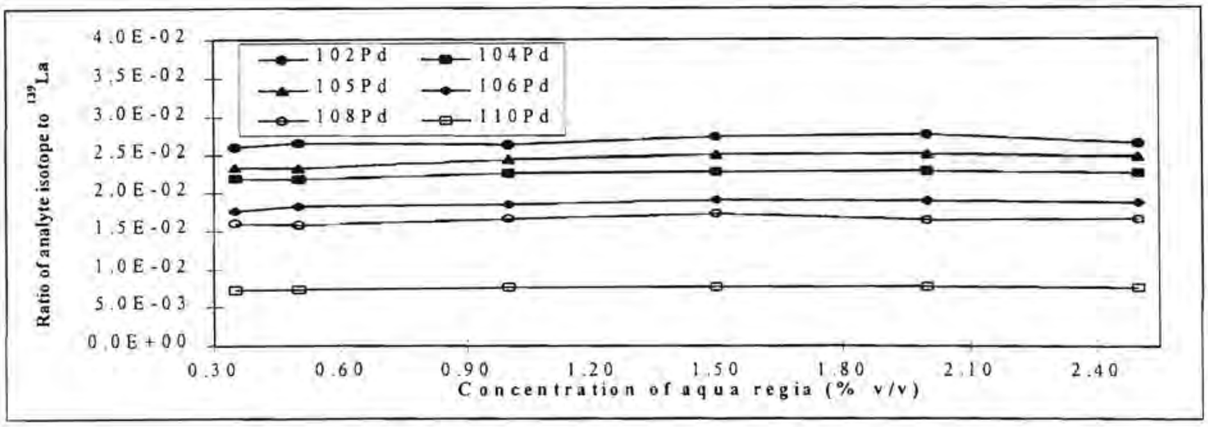

Figure 3.29: Effect of aqua regia concentration on the ratios of the palladium isotopes to the ^{139}La isotope. RSD for analytes to ^{139}La ratios is ^{102}Pd: 2%, ^{104}Pd: 2%, ^{105}Pd: 3%, ^{106}Pd: 3%, ^{108}Pd: 3% and ^{110}Pd: 3%.

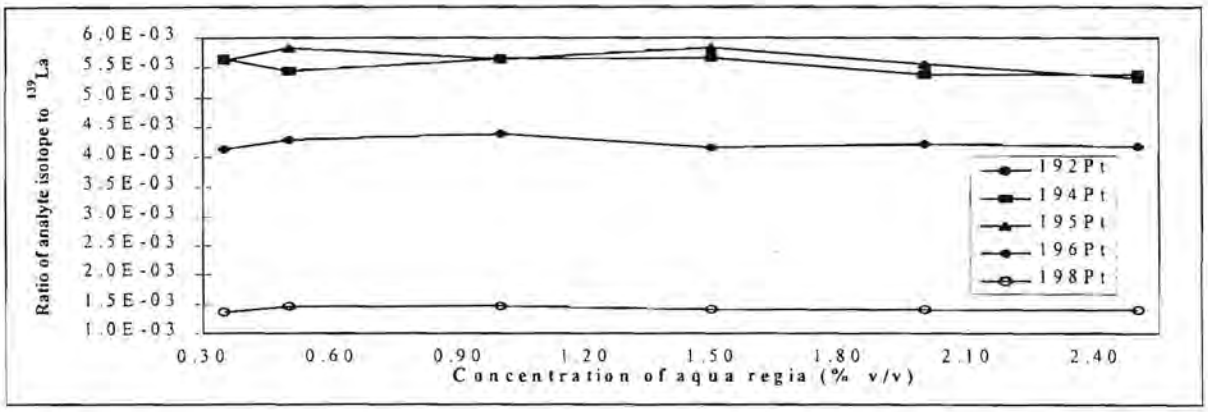

Figure 3.30: Effect of aqua regia concentration on the ratios of the platinum isotopes to the ^{139}La isotope. RSD for analytes to ^{139}La ratios is ^{192}Pt: 9%, ^{194}Pt: 2%, ^{195}Pt: 3%, ^{196}Pt: 2% and ^{198}Pt: 3%.

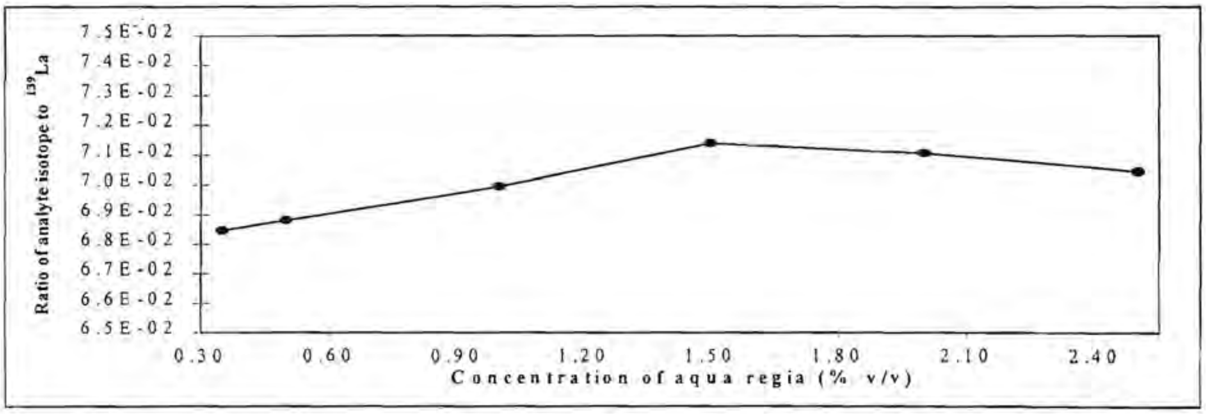

Figure 3.31: Effect of aqua regia concentration on the ratio of the rhodium isotope to the ^{139}La isotope. RSD for ^{103}Rh to ^{139}La ratio is 2%.

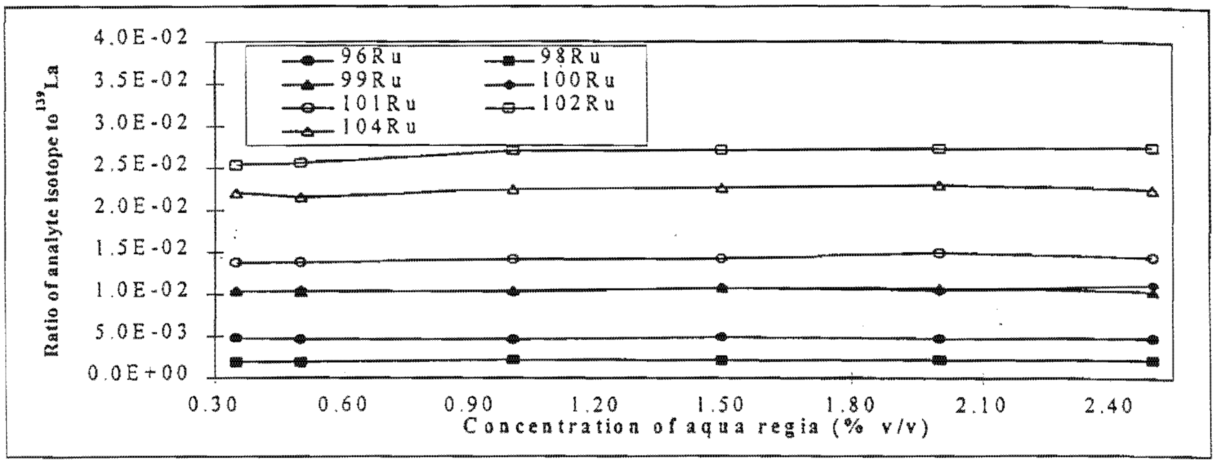

Figure 3.32: Effect of aqua regia concentration on the ratios of the ruthenium isotopes to the ^{139}La isotope. RSD for analytes to ^{139}La ratios is ^{96}Ru: 2%, ^{98}Ru: 6%, ^{99}Ru: 2%, ^{100}Ru: 3%, ^{101}Ru: 3%, ^{102}Ru: 3% and ^{104}Ru: 2%.

3.3.4 *Calibration curves*

For each of the isotopes of the platinum group elements and gold the following calibration data were compiled: 1) correlation coefficient of the curve, 2) slope of the calibration curve, 3) intercept of the calibration curve, 4) detection limit of the calibration curve and 5) the standard error of the predicted y-value. In the cases of 2) and 3) the x-range was taken as the concentration in μg dm^{-3} and the y-range was taken as the measured intensity. In 4) the detection limit (in μg dm^{-3}) was calculated as [(3 x s) / slope of the calibration curve] where s is the standard deviation of the blank standard. 5) refers to the standard error of the predicted y-value for each x in the regression. The standard error is a measure of the amount of error in the prediction of y for an individual x. For these calculations the y-range is taken as the concentration in μg dm^{-3} and the x-range is taken as the measured intensities. Also, the concentration was calculated using the measured intensity and the regression statistics; this value was compared to the "certified" concentration value of the standard and the % difference calculated. The above-mentioned data were compiled for the following cases: 1) no internal standard (tables 3.8 to 3.15, Addendum B), 2) ^{36}Ar as internal standard (tables 3.16 to 3.23, Addendum B), 3) ^{45}Sc as internal standard (tables 3.24 to 3.31, Addendum B), 4) ^{89}Y as internal standard (tables 3.32 to 3.39, Addendum B), 5) ^{138}La as internal standard (tables 3.40 to 3.47, Addendum B) and 6) ^{139}La as internal standard (tables 3.48 to 3.55, Addendum B).

Regression data with no internal standard

Correlation coefficients were 0.999 or better, except for ^{105}Pd, ^{192}Pt, ^{198}Pt and ^{98}Ru. Detection limits ranged from ≤ 1 μg dm^{-3} for most of the isotopes to 13 μg dm^{-3} for ^{105}Pd, 26 μg dm^{-3} for ^{192}Pt, 5 μg dm^{-3} for ^{198}Pt and 7 μg dm^{-3} for ^{98}Ru. The standard error of the predicted y-value generally proved to be ≤ 4%. Calibration curves in the concentration range 0 to 150 μg dm^{-3} in 1% v/v HCl produced good regression statistics when no internal standard was employed.

Regression data with ^{36}Ar as internal standard

When ^{36}Ar is employed as internal standard the correlation coefficients of the calibration curves were 0.99 or better, except for ^{192}Pt. Detection limits similar to the case where no internal standard was used, were observed. In this case the standard errors of the predicted y-values were generally ≤ 4%, but for individual isotopes higher standard errors were observed than for the above-mentioned case where no internal standard was employed. Worse regression data were observed in the case of ^{36}Ar as internal standard than for the case when no internal standard was used.

Regression data with ^{45}Sc as internal standard

Correlation coefficients were 0.999 or better, except for ^{192}Pt and ^{198}Pt. Although similar detection limits were observed as in the cases where no internal standard was used and when ^{36}Ar was used as internal standard, the standard errors of the predicted y-values were lower in the case of ^{45}Sc as internal standard. Calibration curve data for the platinum group elements and gold suggest that ^{45}Sc could be used as an internal standard in quantitative analysis.

Regression data with ^{89}Y as internal standard

Except for a few cases correlation coefficients were 0.9999 or better. The standard errors of the predicted y-values were generally ≤ 2%. In the low concentration range studied for the platinum group elements and gold, i.e. 0 to 150 μg dm^{-3}, ^{89}Y shows great potential as an internal standard for quantitative determinations of these analytes.

Regression data with ^{138}La as internal standard

Correlation coefficients calculated for calibration curves when ^{138}La is used as internal standard were in most cases between 0.990 and 0.999. Standard errors of predicted y-values were generally quite high and values between 5 and 10% are observed. The calculated regression data does not prove ^{138}La a good reference element for the analytes investigated.

Regression data with ^{139}La as internal standard

Generally, correlation coefficients of 0.9999 or better were calculated. The standard errors of the predicted y-values proved to be more or less the same as in the case when ^{89}Y was used as internal standard. The very good regression statistics obtained suggests that ^{139}La could also be used as an internal standard for the quantitative determination of the platinum group elements and gold.

3.3.5 Concentrations as calculated from the calibration curves

The accuracy of quantitative determinations using the calibration curves of the various internal standards are illustrated in figures 3.33 to 3.54.

Quantitative values obtained for Au

With no internal standard the 50 μg dm^{-3} calibration standard showed values slightly higher than 50 μg dm^{-3} which could be due to a slight drift in the calibration curve. From figure 3.33 it can be seen that with an aqua regia concentration of $\leq$ 1% v/v values slightly lower than 50 μg dm^{-3} were obtained.

With ^{36}Ar as internal standard the calibration standard quantitated at about 50 μg dm^{-3} but at aqua regia concentrations of $\leq$ 1% v/v too high values were observed while too low values were observed at higher aqua regia concentrations. Similar trends were observed for ^{45}Sc as internal standard although the deviations from the 50 μg dm^{-3} value were not as severe as in the case of ^{36}Ar.

With ^{89}Y as internal standard the solutions with aqua regia concentrations of $\geq$ 1.50% v/v were quantitated at values lower than 50 μg dm^{-3}. With ^{138}La as internal standard deviations from the accepted value of 50 μg dm^{-3} were observed for the calibration standard as well as for the solutions containing 50 μg dm^{-3} Au in other matrices. ^{139}La showed to be the best internal standard for Au analyses as the 50 μg dm^{-3} calibration standard and the sample solutions all returned values of about 50 μg dm^{-3}.

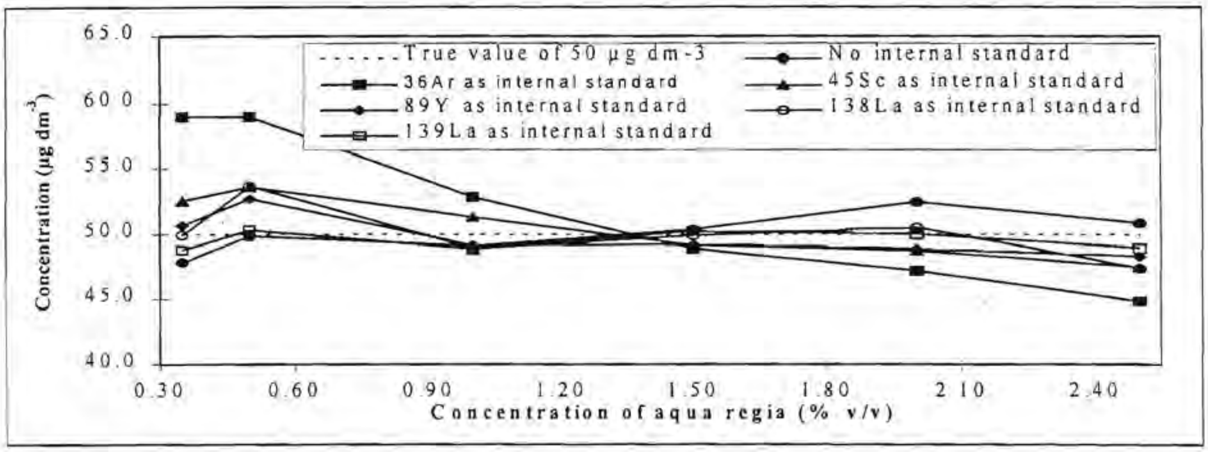

Figure 3.33: Effect of the concentration of aqua regia on the quantitative determination of Au (as ^{197}Au) using different internal standards.

Quantitative values obtained for Ir

Both the isotopes of Ir returned values of 50 μg dm^{-3} for solutions containing aqua regia when no internal standard was employed (see figures 3.34 and 3.35). The calibration standard in 1% v/v HCl however showed values higher than 50 μg dm^{-3} also possibly due to calibration curve drift.

^{36}Ar did not prove a good internal standard for Ir as both isotopes returned too high values at aqua regia concentrations of less than 1% v/v and too low values at concentrations of more than 1.5% v/v . ^{45}Sc showed similar trends as ^{36}Ar for Ir determinations but the deviations from 50 μg dm^{-3} were not as severe.

With ^{89}Y as internal standard too low values were observed for both the Ir isotopes at higher aqua regia concentrations. With ^{138}La as reference isotope, generally too low values were observed for the Ir containing solution. ^{139}La proved to be the best internal standard for the quantitative determination of Ir as both isotopes returned values close to 50 μg dm^{-3}.

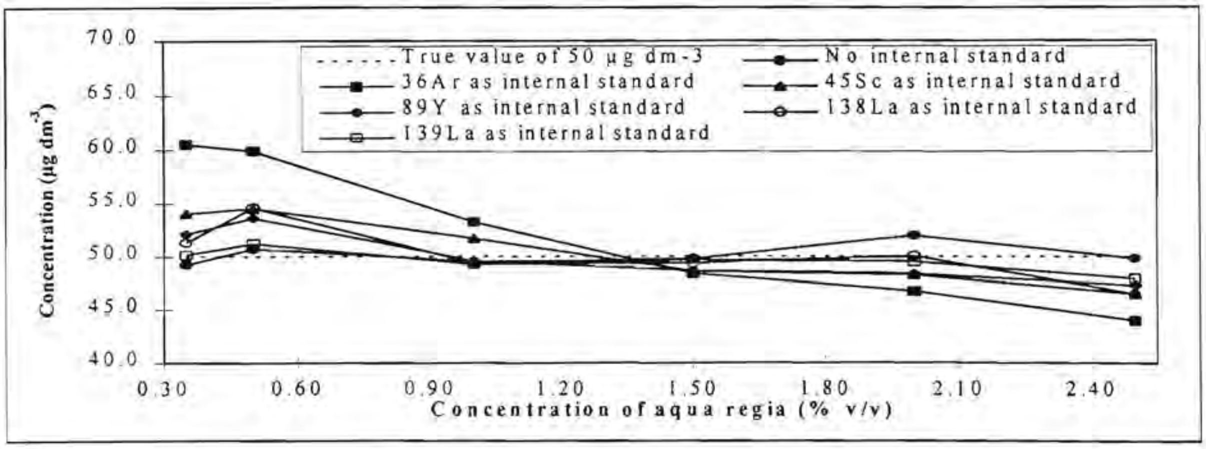

Figure 3.34: Effect of the concentration of aqua regia on the quantitative determination of Ir (as ^{191}Ir) using different internal standards.

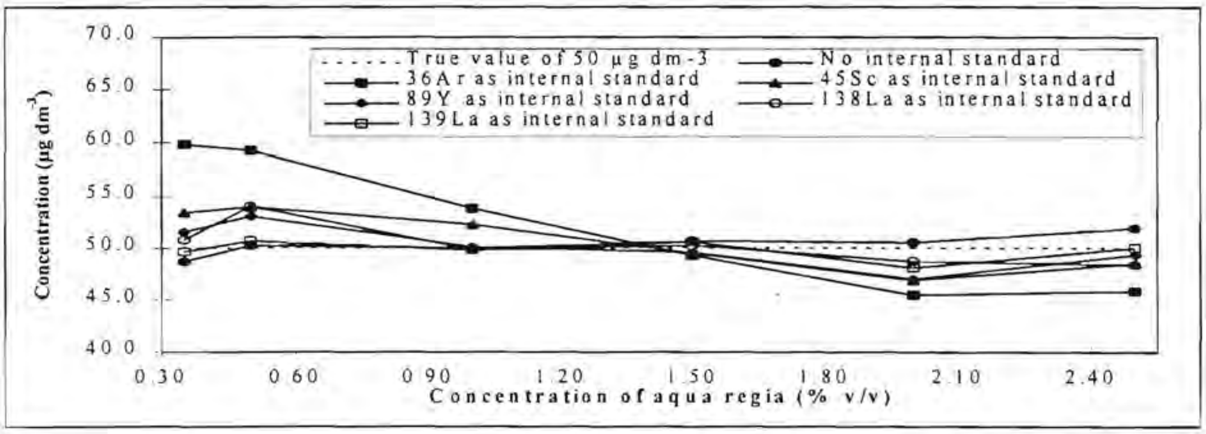

Figure 3.35: Effect of the concentration of aqua regia on the quantitative determination of Ir (as ^{193}Ir) using different internal standards.

Quantitative values obtained for Pd

Figures 3.36 to 3.41 show the effect of aqua regia on the quantitative determination of the various isotopes of Pd. In general too low values are observed for the Pd isotopes when no internal standard is used at aqua regia concentrations of less than 1% v/v .

With ^{36}Ar as internal standard too high values are observed at aqua regia concentrations of less than 1% v/v and too low values at higher aqua regia concentrations. Again ^{45}Sc showed similar trends as ^{36}Ar but the effect is less severe and reasonably good quantitative values were observed.

^{89}Y as reference element for Pd showed values very close to 50 μg dm^{-3} especially for the ^{104}Pd and ^{105}Pd isotopes. ^{138}La performed worse than ^{139}La as a possible internal standard for the isotopes of Pd and the values close to 50 μg dm^{-3} were observed for ^{104}Pd with ^{139}La as internal standard.

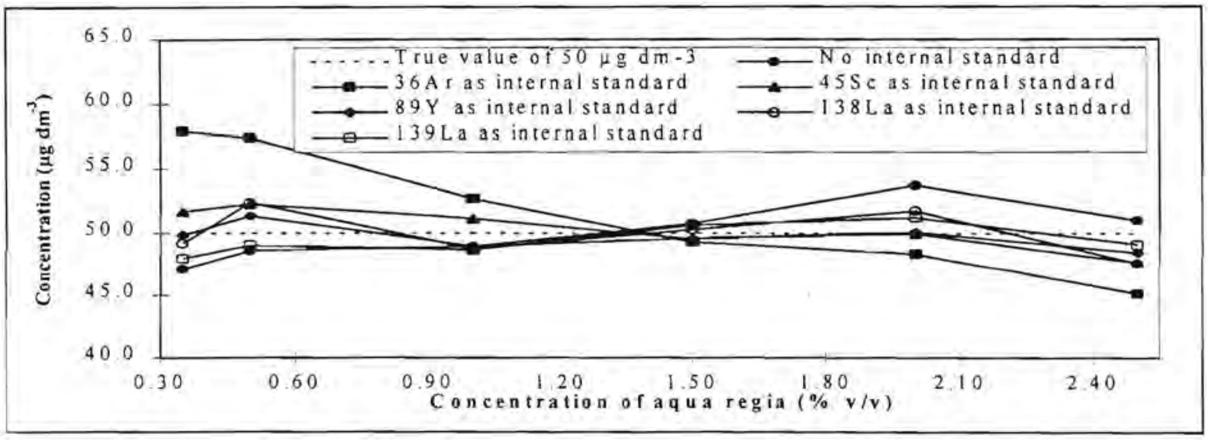

Figure 3.36: Effect of the concentration of aqua regia on the quantitative determination of Pd (as ^{102}Pd) using different internal standards.

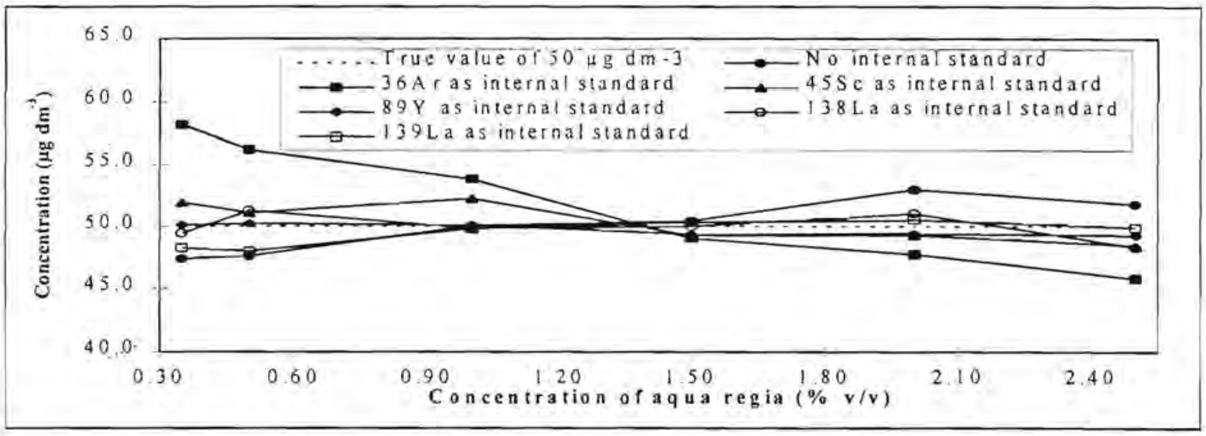

Figure 3.37: Effect of the concentration of aqua regia on the quantitative determination of Pd (as ^{104}Pd) using different internal standards.

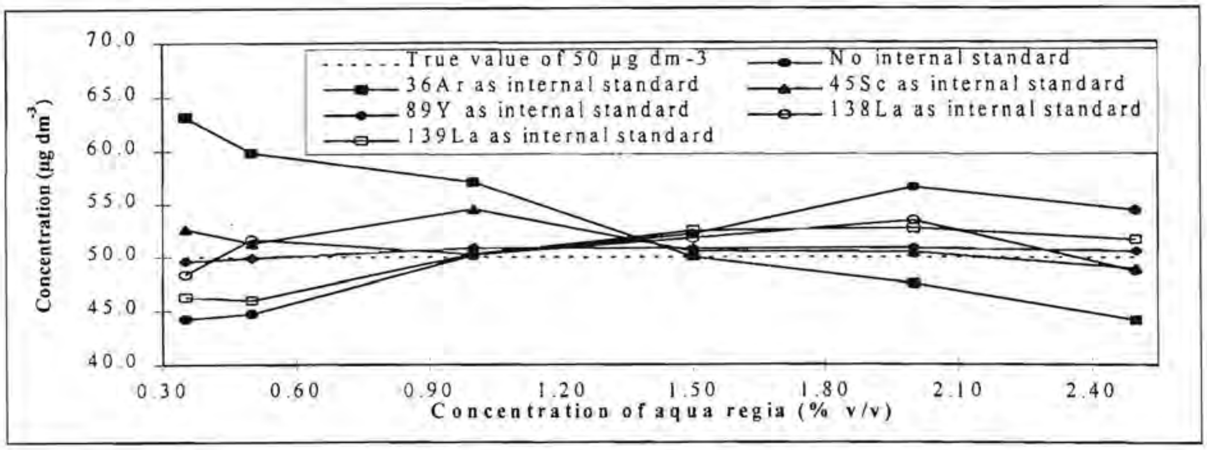

Figure 3.38: Effect of the concentration of aqua regia on the quantitative determination of Pd (as ^{105}Pd) using different internal standards.

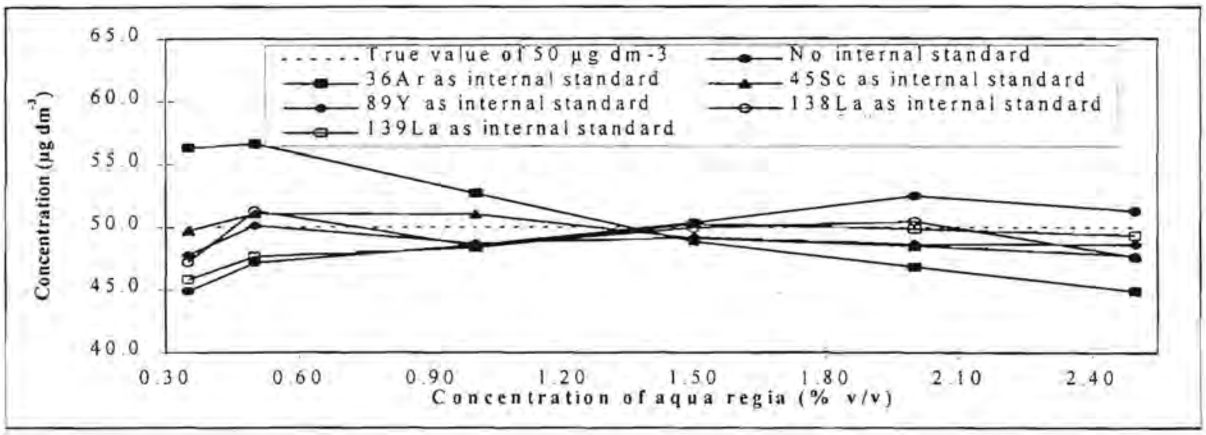

Figure 3.39: Effect of the concentration of aqua regia on the quantitative determination of Pd (as ^{106}Pd) using different internal standards.

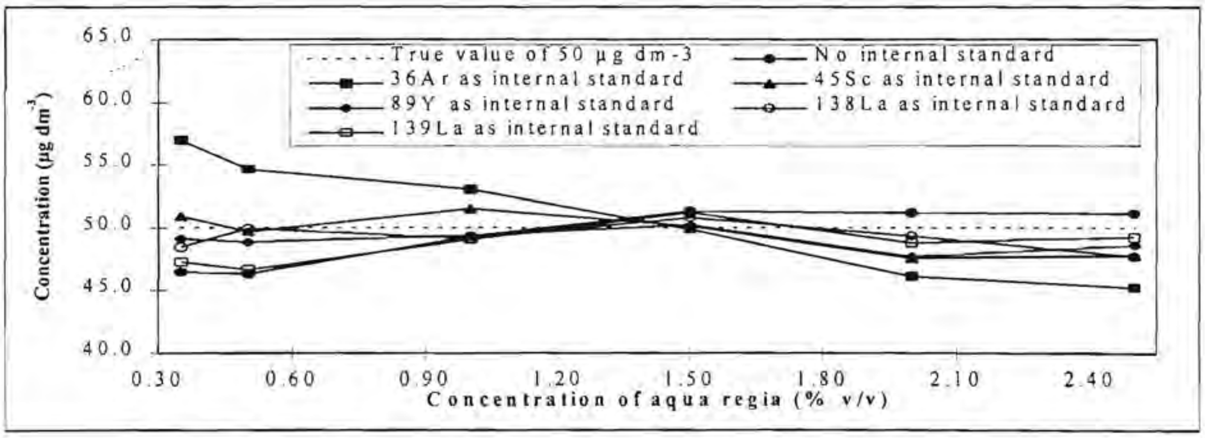

Figure 3.40: Effect of the concentration of aqua regia on the quantitative determination of Pd (as ^{108}Pd) using different internal standards.

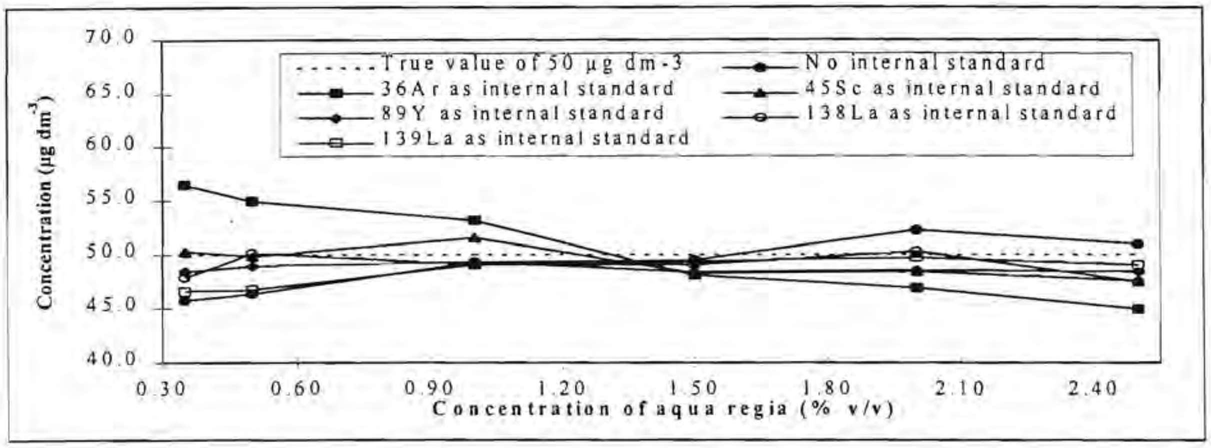

Figure 3.41: Effect of the concentration of aqua regia on the quantitative determination of Pd (as ^{110}Pd) using different internal standards.

Quantitative values obtained for Pt

The values observed for ^{192}Pt deviated very much from 50 μg dm^{-3} and this isotope of Pt was not considered any further.

With no internal standard employed too low values were observed at low aqua regia concentrations and the 50 μg dm^{-3} calibration standard also showed a drift (see figures 3.42 to 3.46).

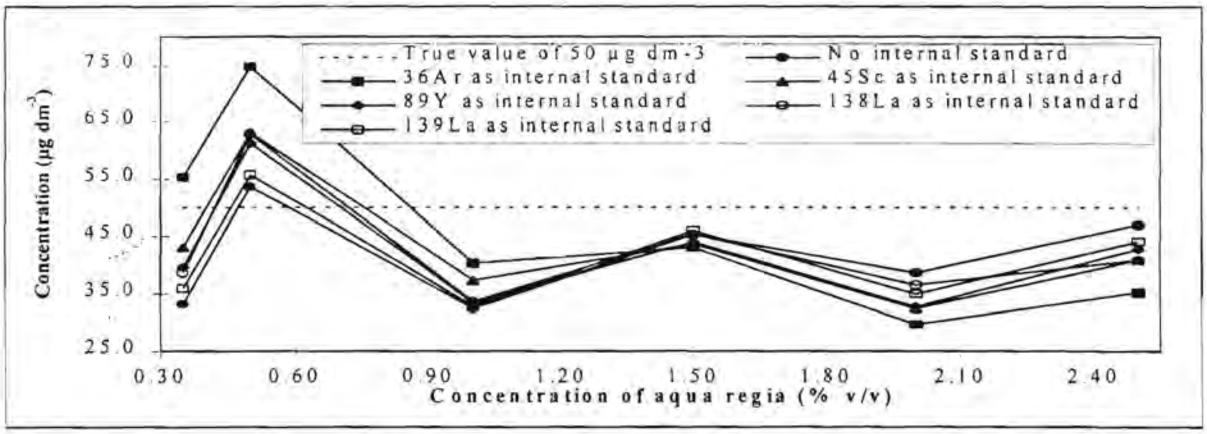

Figure 3.42: Effect of the concentration of aqua regia on the quantitative determination of Pt (as ^{192}Pt) using different internal standards.

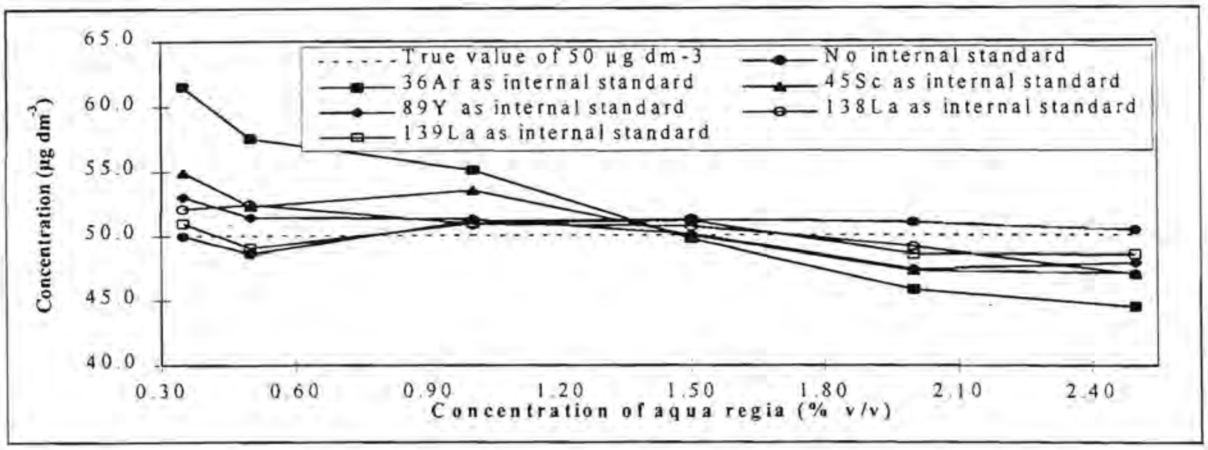

Figure 3.43: Effect of the concentration of aqua regia on the quantitative determination of Pt (as ^{194}Pt) using different internal standards.

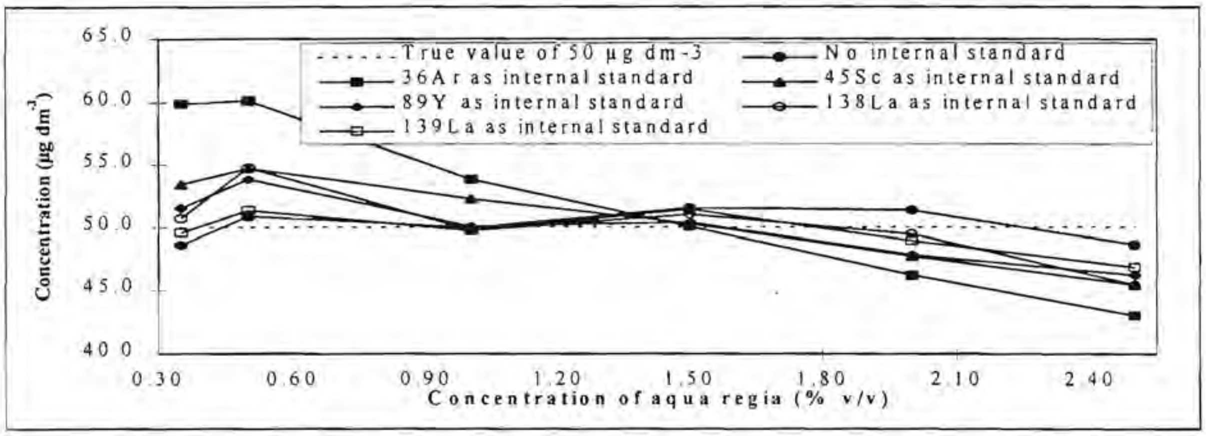

Figure 3.44: Effect of the concentration of aqua regia on the quantitative determination of Pt (as ^{195}Pt) using different internal standards.

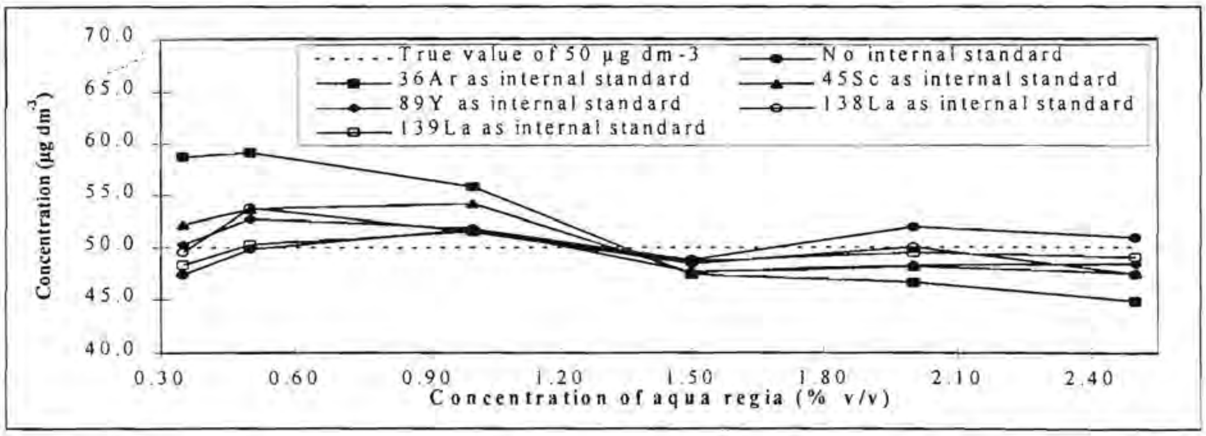

Figure 3.45: Effect of the concentration of aqua regia on the quantitative determination of Pt (as ^{196}Pt) using different internal standards.

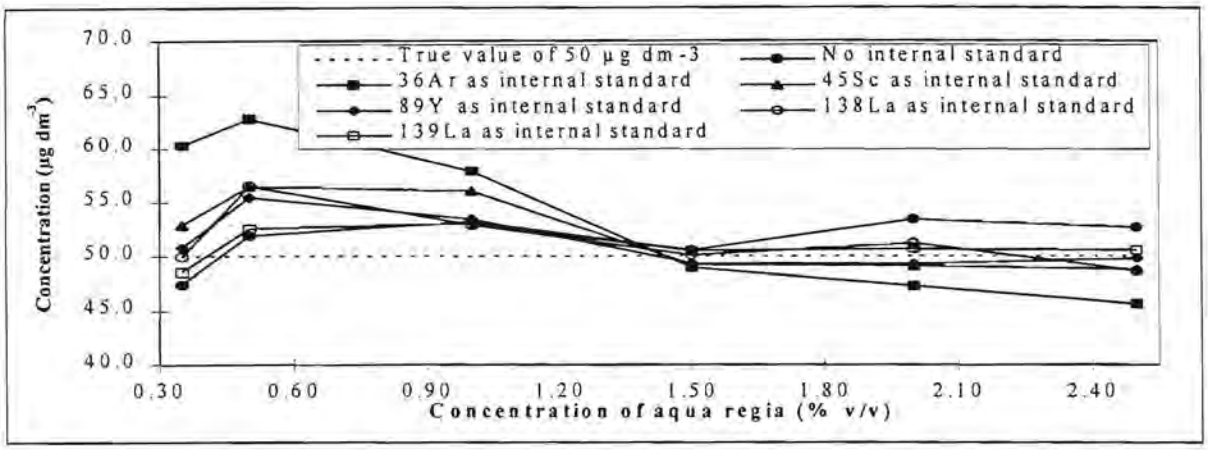

Figure 3.46: Effect of the concentration of aqua regia on the quantitative determination of Pt (as ^{198}Pt) using different internal standards.

^{36}Ar as reference element returned too high values at low aqua regia concentrations and too low values at higher aqua regia concentrations. Although ^{45}Sc and ^{89}Y returned similar trends as ^{36}Ar when employed as internal standards, the deviations were not so great as with ^{36}Ar. Of the two isotopes of La, ^{139}La showed the most potential as an internal standard for the quantitative determination of Pt, especially with ^{194}Pt, ^{195}Pt and ^{196}Pt.

Quantitative values obtained for Rh

See figure 3.47 for the effect of aqua regia on the quantitative determination of Rh when using different internal standards. When no internal standard is employed, slightly low values were recovered for Rh at low aqua regia concentrations and slightly high values at higher aqua regia concentrations.

^{36}Ar as internal standard returned too high values at low aqua regia concentrations and too low values when the matrices of the solutions consisted of higher aqua regia concentrations. ^{45}Sc and ^{89}Y showed good recovery values for Rh although the values for Y as reference element were closer to 50 μg dm^{-3} than for ^{45}Sc. Of ^{138}La and ^{139}La, ^{139}La returned values closer to 50 μg dm^{-3} when employed as internal standard for Rh analyses.

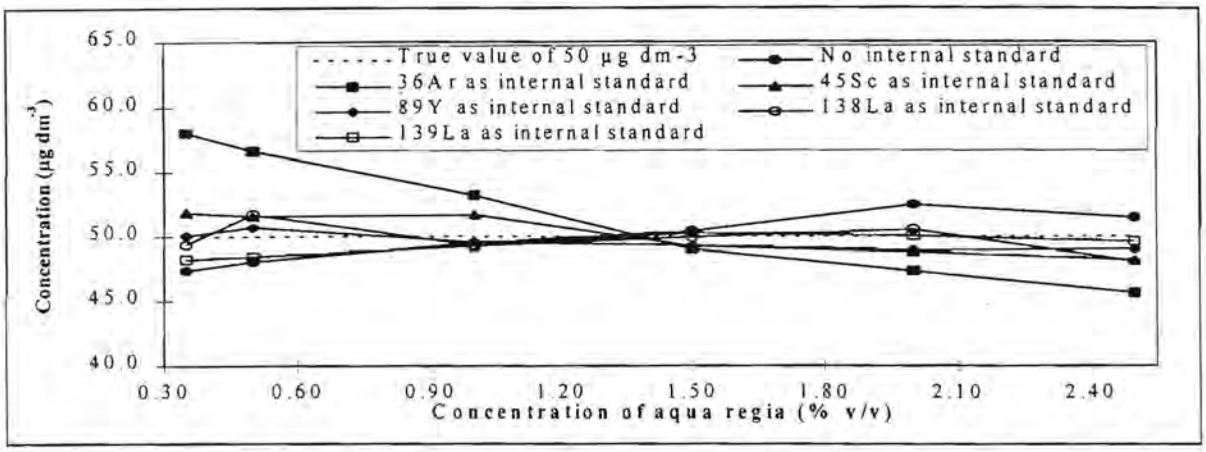

Figure 3.47: Effect of the concentration of aqua regia on the quantitative determination of Rh (as ^{103}Rh) using different internal standards.

Quantitative values obtained for Ru

Figures 3.48 to 3.54 show the effect of aqua regia on Ru analyses. Quantitative values for Ru isotopes are lower than 50 μg dm^{-3} at low aqua regia concentrations and higher than 50 μg dm^{-3} at higher concentrations of aqua regia, when no internal standard is used.

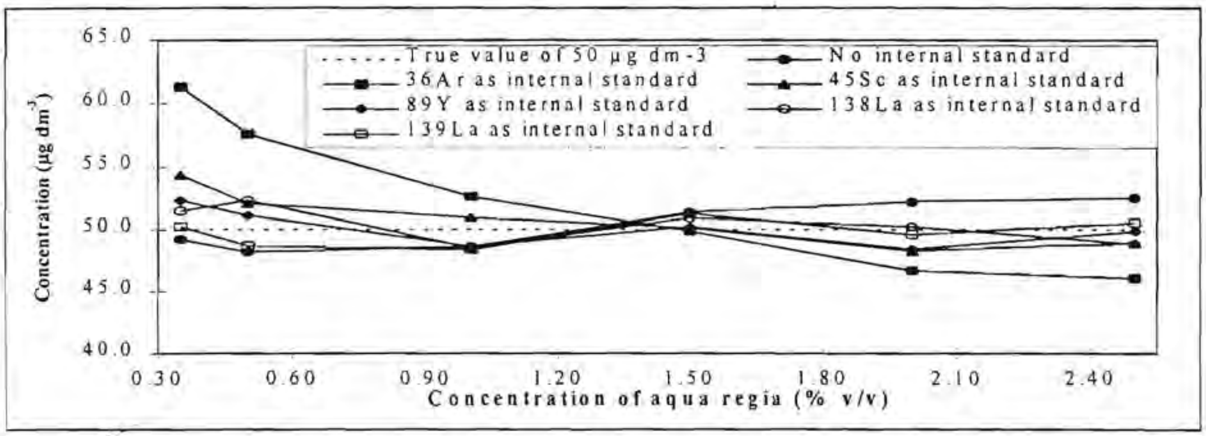

Figure 3.48: Effect of the concentration of aqua regia on the quantitative determination of Ru (as ^{96}Ru) using different internal standards.

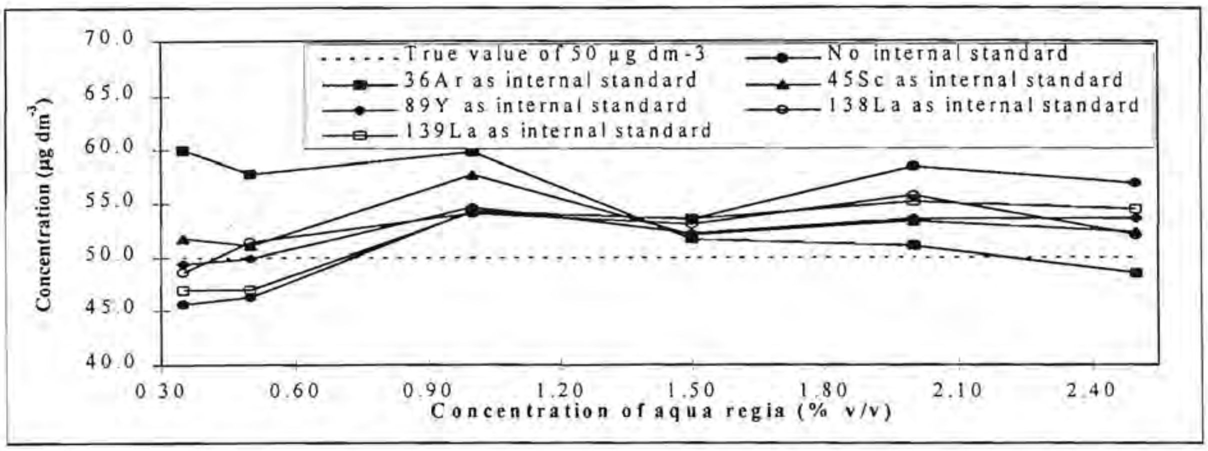

Figure 3.49: Effect of the concentration of aqua regia on the quantitative determination of Ru (as ^{98}Ru) using different internal standards.

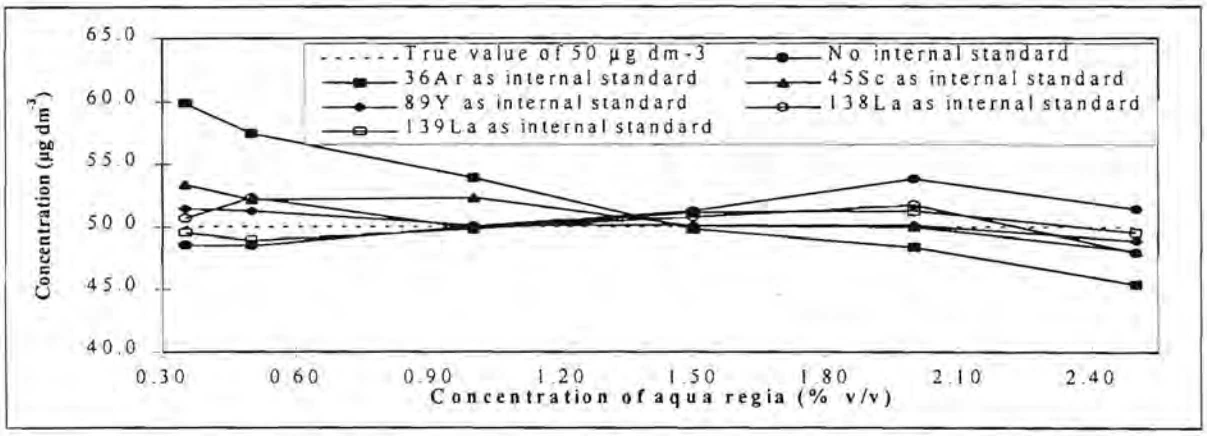

Figure 3.50: Effect of the concentration of aqua regia on the quantitative determination of Ru (as ^{99}Ru) using different internal standards.

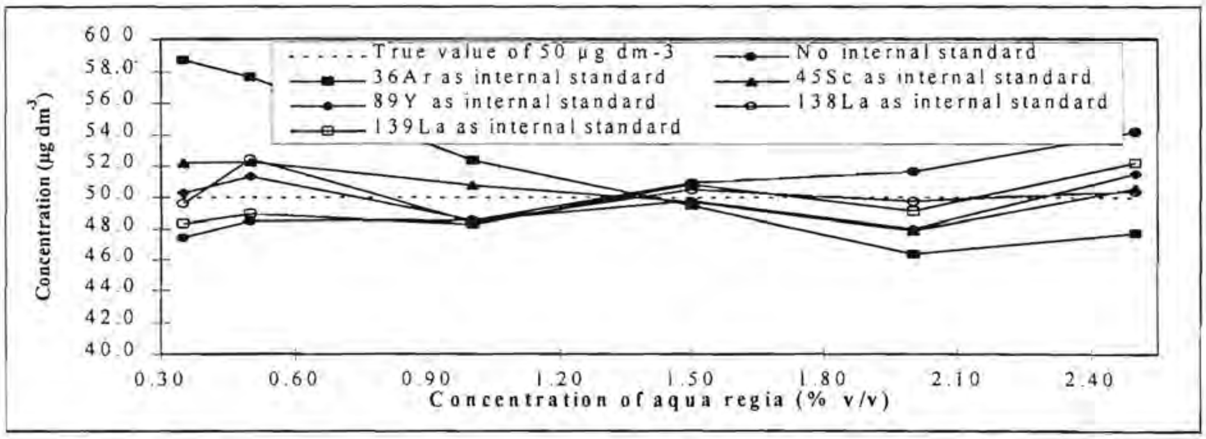

Figure 3.51: Effect of the concentration of aqua regia on the quantitative determination of Ru (as ^{100}Ru) using different internal standards.

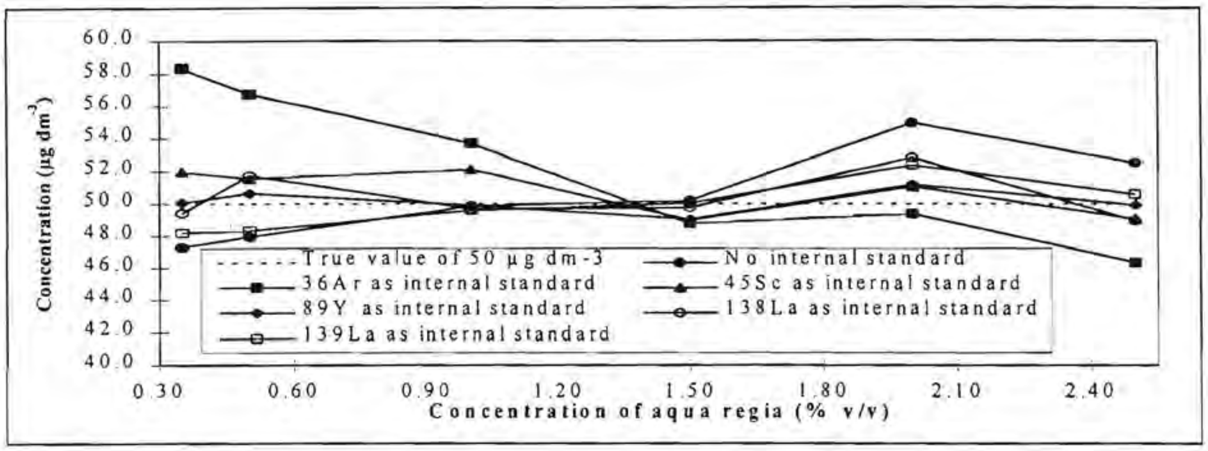

Figure 3.52: Effect of the concentration of aqua regia on the quantitative determination of Ru (as ^{101}Ru) using different internal standards.

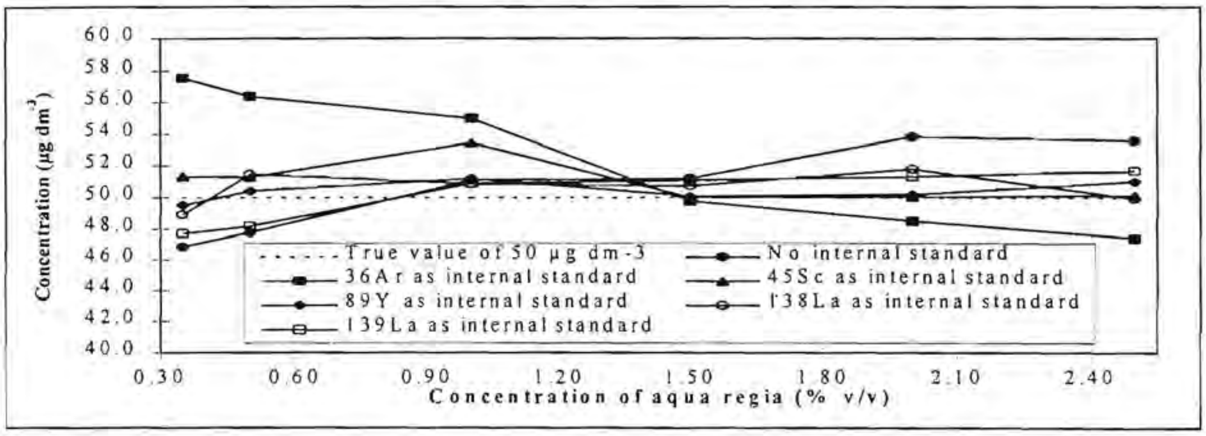

Figure 3.53: Effect of the concentration of aqua regia on the quantitative determination of Ru (as ^{102}Ru) using different internal standards.

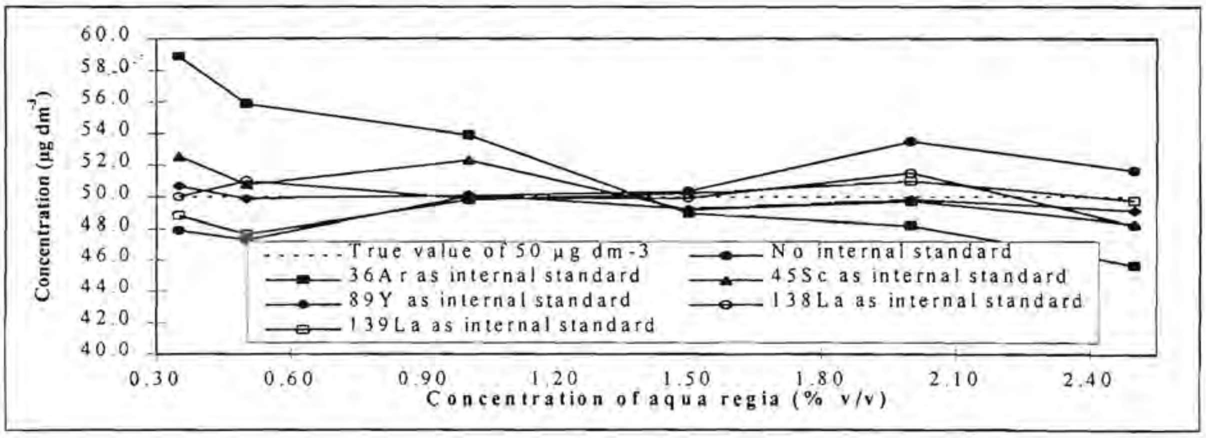

Figure 3.54: Effect of the concentration of aqua regia on the quantitative determination of Ru (as ^{104}Ru) using different internal standards.

^{36}Ar as internal standard returns too high and too low recovery values at lower and higher aqua regia concentrations, respectively. As internal standard ^{45}Sc returned values close to 50 μg dm^{-3} for ^{101}Ru and ^{102}Ru over the aqua regia concentration range studied. Except for ^{96}Ru and ^{98}Ru, ^{89}Y showed to be a good internal standard for the quantitative determination of Ru. For most isotopes of Ru, both the isotopes of La returned values fairly close to 50 μg dm^{-3} when used as internal standards.

3.4 Conclusion

As some drift was observed in the calibration curves of most of the isotopes of the platinum group elements and gold, it is necessary to employ one or more internal standards when performing quantitative analysis of these analytes.

Plots of the ratios of analyte isotopes to internal standard isotopes versus the aqua regia concentration present in solution showed: 1) ^{36}Ar not to be a possible internal standard, 2) ^{45}Sc to be a possible internal standard for Ru, Pd and Rh, 3) ^{89}Y to be possible internal standard for the lighter platinum group elements, 4) ^{138}La to be possible internal standard for the platinum group elements and gold and 5) ^{139}La to be a possible reference element for all the analytes investigated.

Calibration curves were constructed and very good regression data were obtained when ^{89}Y and ^{139}La were employed as reference elements for the platinum group elements and gold.

Quantitative values were calculated for the various calibration curves and from the results ^{139}La proved to be an excellent internal standard in the determination of Au, Ir, Pt and ^{89}Y proved to be a very good reference element for Ru, Pd, Rh. This confirms the need for the matching of the masses of the internal standards to the masses of the analytes analysed. The low abundant ^{192}Pt isotope returned values that deviated too much from the "true" value and should not be used in the quantitative determination of Pt.