

# New Platinum Analytical Standard

## SYNTHETIC ROUTE TO A KNOWN IMPURITY COMPOSITION

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Relatively low levels of metallic and non-metallic impurities can cause severe degradation of platinum components used at high temperatures, for example in equipment for manufacturing specialised glass. Thus strict control of the impurity contents is required in order to ensure that the properties of the platinum are not impaired at these high temperatures.

To help to provide this control the Johnson Matthey Technology Centre has prepared a platinum standard containing fifteen impurity elements at concentrations of 100 ppm. The preparative route selected consisted of adding the elements as solutions to a high purity platinum sponge which, after drying, milling, blending and subsequent reduction under a hydrogen atmosphere, was spin-riffle sampled into 0.5 gram portions for analysis. Part of the sponge was compacted and forged down into wire, for use in spectrographic analysis of fabricated material.

Initially the doped sponge was analysed in two Johnson Matthey laboratories using Inductively Coupled Plasma Emission Spectrometry (ICPES) and also at the Institute of Geological Sciences, London, using Inductively Coupled Plasma/Mass Spectrometry (ICPMS) to establish that the material had been homogenised correctly and to confirm that no major, unexpected losses had occurred.

As the contents of the impurities in the platinum standard had been established by means other than analysis, it was considered that a unique opportunity existed to involve other analysts outside the Johnson Matthey Group in a co-operative exercise designed to evaluate current analytical procedures. The authors are very grateful to the eight organisations that took part.

Results were received from sixteen laboratories. Six different techniques were employed, although the majority of laboratories used only one or two. Where sufficient results were available from the use of a particular technique, the means and standard deviations for that technique could be calculated separately. Four groups of results could be treated in this way. These were Atomic Absorption spectrophotometry (AA), Direct Reading Emission Spectrometry (DRES), Photographic Emission Spectrometry (PHES), and Plasma Emission Spectrometry which included results from both ICPES and Direct Current Plasma Emission Spectrometry (DCPES). Statistical analysis of the combined results was carried out using robust methods able to take account both of outliers and of the fact that some of the groups of results were non-normally distributed.

The mean values and standard deviations for each technique are presented in Table I, together with the overall mean values and 95 per cent confidence limits. The full results for two typical impurity elements, one a platinum group metal and the other a base metal, are shown in Figures 1(a) and 1(b), respectively. The data form typical "S" curves, from which it can be seen that the majority of the results cluster around the true content, although some outliers are obvious.

The elements which were deliberately added to the platinum standard were: antimony, arsenic, cobalt, copper, gold, iridium, iron, lead, magnesium, nickel, palladium, rhodium, ruthenium, silver, and zinc. Aluminium and calcium, which were also reported, may be expected as minor impurities in the starting sponge. The single outlier result of 138 ppm for calcium obtained by AA strongly influenced the overall mean for that element. Without it the

Table 1 Mean Values and Standard Deviations for the Various Major Analysis Method Groups Compared with the Overall Mean Value										
Analysis method	AA (1)		ICPES (2)		DRES (3)		PHES (4)		All results	
	Mean value	Standard deviation	Mean value	Standard deviation	Mean value	Standard deviation	Mean value	Standard deviation		
Element	parts per million									
Ag	114.6	12.6	106.7	13.8	94.8	22.6	83.0	22.1	101.6	8.7
Al	—	—	21.2 <sup>(a)</sup>	0.0	4.6	6.4	7.7	10.7	8.3	12.7
As	90.7	48.6	90.3	42.9	63.0	24.6	77.0	20.7	74.8	21.7
Au	103.4	8.7	107.1	11.5 <sup>(b)</sup>	93.2	37.1	84.9	11.3	100.5	9.1
Ca	138.0 <sup>(a)</sup>	0.0	—	—	3.2	2.2	2.6 <sup>(a)</sup>	0.0	18.3	84.7
Co	105.0	13.0	101.5	9.8 <sup>(b)</sup>	100.3	3.1	93.7	16.8	101.4	6.9
Cu	97.8	4.6 <sup>(b)</sup>	100.3	4.9 <sup>(b)</sup>	118.9	19.8 <sup>(b)</sup>	94.9	15.9 <sup>(b)</sup>	100.8	9.2
Fe	97.3	2.0 <sup>(b)</sup>	107.7	13.5 <sup>(b)</sup>	87.1	2.8 <sup>(b)</sup>	97.2	14.4	101.7	11.7
Ir	99.2	1.2	118.6	29.6	116.8	38.2	89.2	12.9 <sup>(b)</sup>	109.1	15.9
Mg	110.1	14.8	93.6	19.5	100.4	12.6	96.2	7.2 <sup>(b)</sup>	98.4	8.7
Ni	100.9	0.8 <sup>(c)</sup>	115.1	23.6	94.5	45.5	109.2	31.8	109.9	12.4
Pb	95.2	2.0 <sup>(b)</sup>	93.4	22.2	100.5	42.8	82.2	20.7 <sup>(d)</sup>	93.1	12.5
Pd	132.2	5.9 <sup>(b)</sup>	132.9	14.0	112.0	36.8	123.2	39.6	125.4	10.8
Rh	103.8	9.4	100.6	10.1	108.1	1.5 <sup>(b)</sup>	107.9	6.2 <sup>(b)</sup>	103.4	4.7
Ru	97.0 <sup>(a)</sup>	0.0	108.7	8.0	101.2	26.0	103.1	6.3 <sup>(b)</sup>	107.3	7.9
Sb	75.0	9.9	86.6	9.4 <sup>(c)</sup>	101.7	33.5	104.9	19.0	99.2	15.4
Si	—	—	39.9	13.3	52.2	33.5	54.8	13.5 <sup>(b)</sup>	53.5	26.3
Zn	92.7	6.0	97.1	9.3 <sup>(c)</sup>	117.4	31.7	91.4	20.7	97.1	8.3

<sup>(a)</sup>—only one result reported for this technique

<sup>(b)</sup>—one outlier excluded in calculation of the mean and standard deviation

<sup>(c)</sup>—two outliers excluded in calculation of the mean and standard deviation

<sup>(d)</sup>—data not normally distributed

Fig. 1 Means and standard deviations of the analysis results for 100 ppm additions of (a) rhodium and (b) copper to the platinum standard are shown. The results have been plotted in ascending order of mean value, and produce the usual "S" shaped curve typical of the normal distribution. The captions to the results consist of a number referring to the method used:

- 1—AA
- 2—ICPES
- 3—DRES
- 4—PHES

together with a letter indicating the laboratory. The overall mean value, ZH, calculated by a robust statistical method is included in the main distribution. A secondary group at the base of the figure presents the means of the different techniques used together with the arithmetic mean value:

- ZD—DRES mean and standard deviation
- ZS—PHES mean and standard deviation
- ZA—AA mean and standard deviation
- ZZ—Arithmetic mean and standard deviation
- ZI—ICPES mean and standard deviation

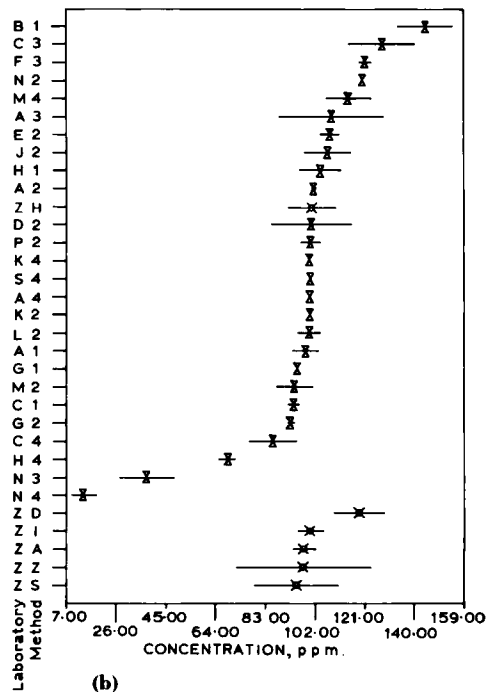
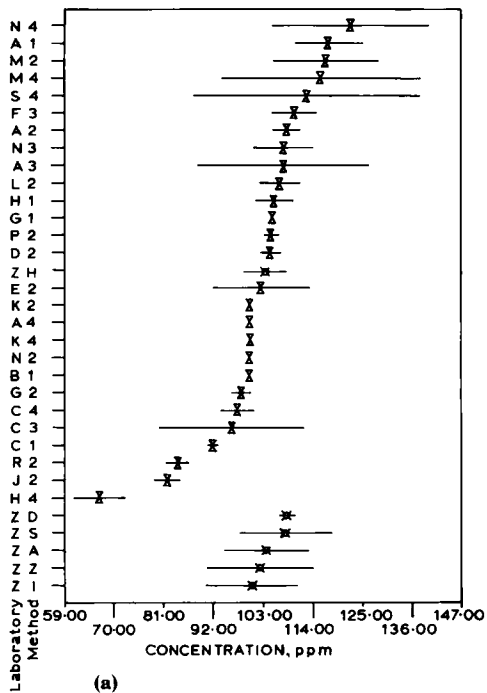


Table II Mean Absolute Variations in Assay Values for Thirteen of the Added Elements	
Technique	Average differences, ppm
AA (1)	7.5
ICPES (2)	13.7
DRES (3)	21.7
PHES (4)	16.6

overall mean was 3 ppm which is much more reasonable. As expected, silicon was picked up from the trays used for the sponge reduction stage.

The high palladium result is unlikely to be due to palladium in the starting sponge. A possible explanation may be that an error occurred during the preparation, resulting in a true content of 125 ppm. For most of the remaining elements the results are in close agreement with the true content of 100 ppm. The exceptions are antimony and arsenic, where some volatilisation during the reduction stage was expected even though the temperature was kept as low as practicable.

### Summary of the Results and Conclusions

On the evidence of the results, and providing that sufficient care is taken, AA should be preferred for standardisation assays on non-synthetic standard materials, since the values found agree well with the true contents and the variability is the lowest for the four methods. This may be visualised independently by summing the absolute differences from the standard value for all the elements. For thirteen of the added elements, and with the value for palladium taken as 125 ppm, the average differences for the four techniques are given in Table II. The advantages of ICPES are speed and, for some of the elements, sensitivity, but these may have been offset by the complex effects of the high platinum loadings which can

directly affect sensitivity and necessitate careful background correction.

The variability of the results both between laboratories and within laboratories when using different analysis methods has emphasised the need for standards of the type produced. The spread of results also means that analytical differences of less than 10 ppm (10 per cent relative) between samples may have no significance, unless large numbers of samples are analysed.

The successful method of preparation used for platinum is generally applicable, and is currently being used for some of the other platinum group metals.

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### Palladium in a Modified Steel

The degradation induced by the presence of hydrogen in some steels may be reduced or eliminated by the addition of palladium, but the mechanism for this effect is not fully understood. Little is known about the distribution of the palladium in such modified steels so a recently published study by M. K. Miller, of the Oak Ridge National Laboratory, and S. S. Brenner and M. G. Burke, of the University of Pittsburg, used high resolution atom probe field-ion microscopy and conventional transmission electron microscopy to examine the microstructure and microchemistry of laboratory melted low carbon alloy steels containing 0.31 and 0.65 atomic per cent palladium (*Metall. Trans.A*, 1987, **18A**, (4), 519-523).

The authors concluded that the solubility of palladium in the tempered steel was between 0.25 and 0.5 atomic per cent, considerably less than indicated by the iron-palladium phase diagram. Although most of the palladium remained in solution in the ferrite, some had segregated to the ferrite-ferrite lath boundaries where it formed a mono-atomically thick adsorbate layer. Palladium-manganese precipitates were detected both at lath boundaries and in the ferrite matrix.