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6 April 2016

Reference: TSW278

Investigation into the Development of a Quantitative LA-ICP-MS Analytical Protocol for the Analysis of Gold

Background

The Geological Survey of Western Australia approached TSW Analytical to investigate the potential to use LA-ICP-MS to facilitate the quantitative analysis of gold with the intention of ultimately using these protocols to quantitatively profile alluvial gold. Three gold standards were provided for analysis - AURM 1, AURM 2 (Produced by the London Bullion Market Association, United Kingdom) and RJW (Produced by the Perth Mint, Western Australia). The experiment detailed in this report was designed to try and establish a quantitative gold analysis protocol based around these three standards which could ultimately form the basis of a protocol that could be used to determine the concentration of a range of analytes in naturally occurring gold.

Analysis

Gold standards (AURM 1, AURM 2 and RJW) and samples were analysed using a New Wave UP213 laser ablation unit coupled to an Agilent Technologies 7500c Inductively Coupled Plasma Mass Spectrometer. The ICP-MS instrument was tuned at the beginning of each analytical run in order to achieve optimum operating conditions. A number of experimental combinations of laser ablation conditions were investigated until two were established as appropriate in terms of ablation frequency (10 Hz), spot and traverse section width (100 µm) and ablation pattern (both spot and traverse). Under these conditions, the optimum signal

intensity was obtained with spot and traverse sizes that were not too large as to visibly damage the samples. These operating conditions are detailed in Table 1.

Table 1: Generic operating conditions for LA-ICP-MS.

Conditions	Spot Ablation	Traverse Ablation
Laser Frequency (Hz)	10	10
Laser Power (mJ)	0.33-0.38	0.33-0.38
Ablation Diameter (μm)	100	100
Laser Warm-Up (seconds)	5	5
Laser Ablation Duration (seconds)	60	60
Laser Traversing Speed (μms^{-1})	0	22

Gold standards were ablated in triplicate at four points around their perimeter and in the centre to establish if there were differences between the compositions of the gold at various points on the sample and to obtain an indication as to the homogeneity of the bulk material.

Results

The three gold standards used had been analysed independently to determine concentrations of a range of analytes (Table 2). Unfortunately, all analytes did not occur in all standards and consequently, since the data had all been corrected for background signal on each analyte mass, a 0:0 intercept was used to construct analytical calibration curves for analytes where three values were not available. This approach will obviously have to be changed if the developed protocol is to be used for quantitative analytical purposes, however, for the purpose of the initial investigation it is perfectly adequate for use to interpret the possibility of quantitative analysis of gold using LA-ICP-MS.

Table 2: Average recommended values for AURM 1, AURM 2 and RJW.

Analytes present (ppm) average value				Analytes required				Analytes required			
Analyses required	AURM1	AURM2	RJW	Analyses required	AURM1	AURM2	RJW	Analyses required	AURM1	AURM2	RJW
Li7				As75	14.50	47.10	0.30	Nd146			
Be9				Se77				Sm152			
B10				Se82				Eu153			
B11				Rb85				Gd158			
Na23				Sr88				Tb159			
Mg24	30.10	9.90	0.10	Y89				Dy162			
Mg25	30.10	9.90	0.10	Zr90				Ho165			
Al27	9.60	28.30		Nb93				Er166			
Si29	9.40	28.00		Mo95				Tm169			
K39				98.00				Yb174			
Ca43	9.60	28.00		Ru101				Lu175			
Ca44	9.60	28.00		Rh103	7.30	39.60		Hf178			
Sc45				Pd104	9.70	29.20	1.20	Ta181			
Ti49	10.50	31.60	0.20	Pd106	9.70	29.20	1.20	W182			
V51				Pd108	9.70	29.20	1.20	Re185			
Cr52	9.40	27.70		Ag109	20.00	99.60	11.60	Os190			
Cr53	9.40	27.70		Cd111				Ir193			
Fe54	10.60	30.10		In115				Pt195	10.30	30.20	0.40
Mn55	9.70	28.20	0.60	Sn120	9.70	29.40	14.60	Au197			
Fe57	10.60	30.10	5.40	Sb121	35.70	11.30		Hg202			
Co59				Sb123	35.70	11.30		203.00			
Ni60	9.80	29.20	0.20	Te125	40.70	12.00		204.00			
Cu63	13.50	31.60	2.50	Te126				Ti205			
Zn64	10.30	31.40	0.40	Cs133				Pb206	9.80	28.90	0.40
Cu65	13.50	31.60	2.50	Ba137				207.00	9.80	28.90	0.40
Zn66	10.30	31.40	0.40	138.00				Pb208	9.80	28.90	0.40
Ga69				La139				Bi209	30.40	9.70	0.50
Ga71				Ce140				Th232			
Ge73				Pr141				U238			

From the inspection of all counts vs time graphs for all standards it was obvious that there were inclusions on the micron size level of some of the analytes (Fig. 1). Consequently, it was necessary to view each counts vs time graph for all analytes as a csv file and make a subjective decision as to where the most appropriate areas of this graph should be sampled to give quantitative data and not to include spikes due to the ablation of inclusions and polymetallic species. In addition, these graphs indicate that there is a significant difference between the nature of the inclusions which makes it impossible to use a data reduction software system such as Glitter™ to undertake an automatic data compilation.

To undertake this procedure, each series of scans for each sample were plotted as a table of analyte counts verses scan number and the areas (values) where inclusions and polymetallic species had been ablated were removed. The remaining data were integrated to give a counts per second (CPS) value for each analyte isotope. The process was repeated for each standard. In addition to this the scans for background were also evaluated for photon incidents and a background calculated for each analyte isotope. The background values were subtracted from each analyte signal and a background corrected figure (CPS) for each analyte isotope calculated. Using this data, a series of calibration graphs can be drawn for each of the analyte isotopes studied. A cross section of these graphs is included in this report as Figure 2.

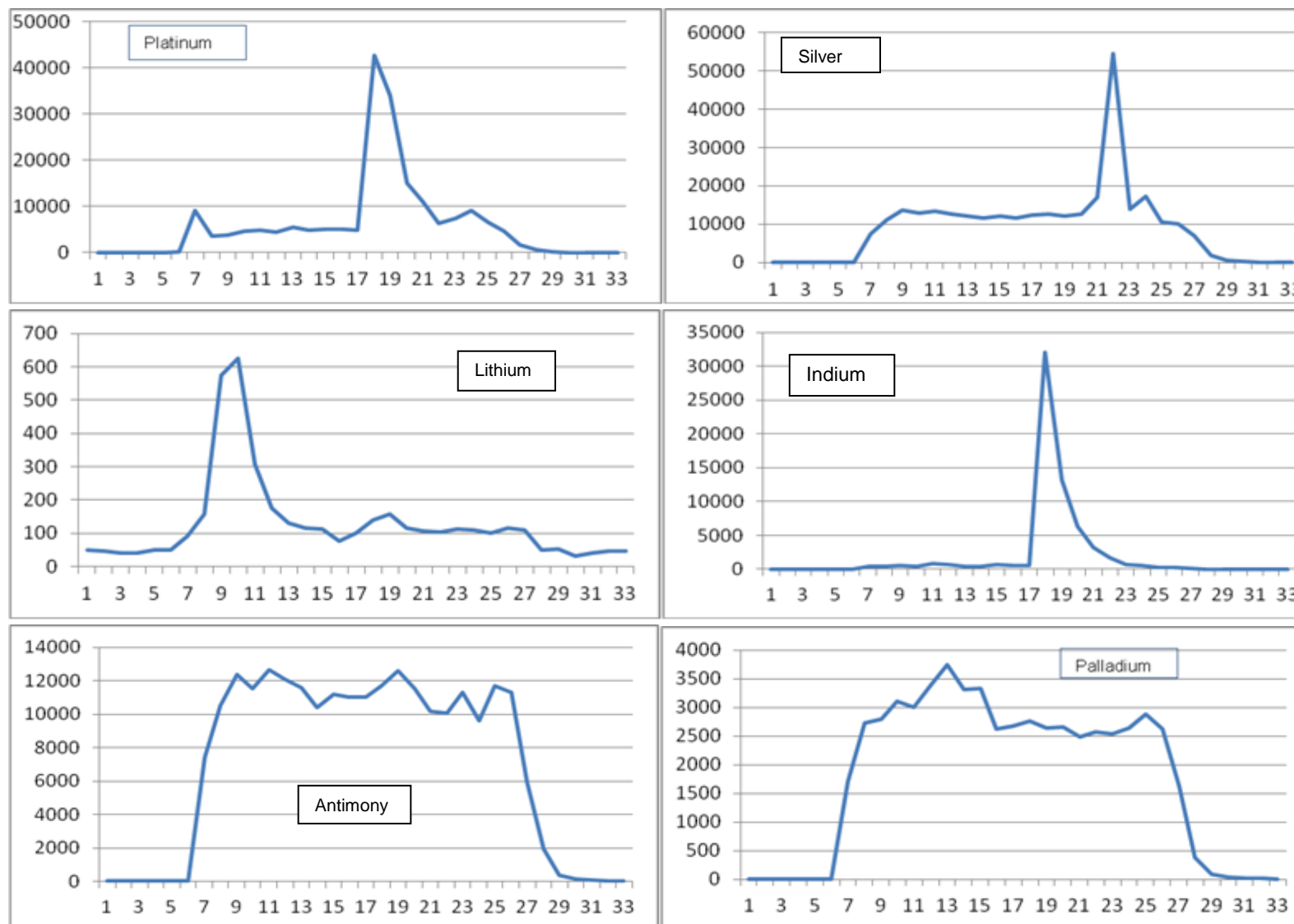


Figure 1: Intensity vs Time graphs showing inhomogeneities in the gold standards (counts data shown on the ordinate and scan numbers on the abscissa).

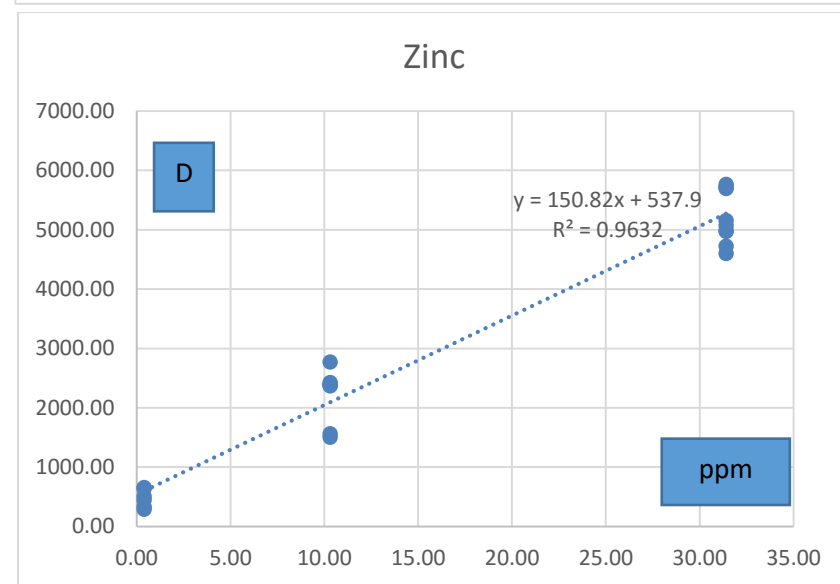
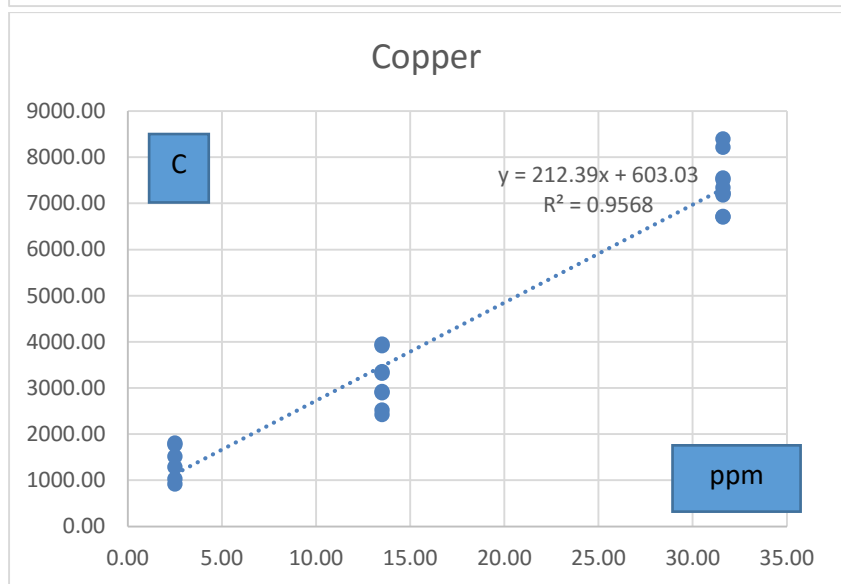
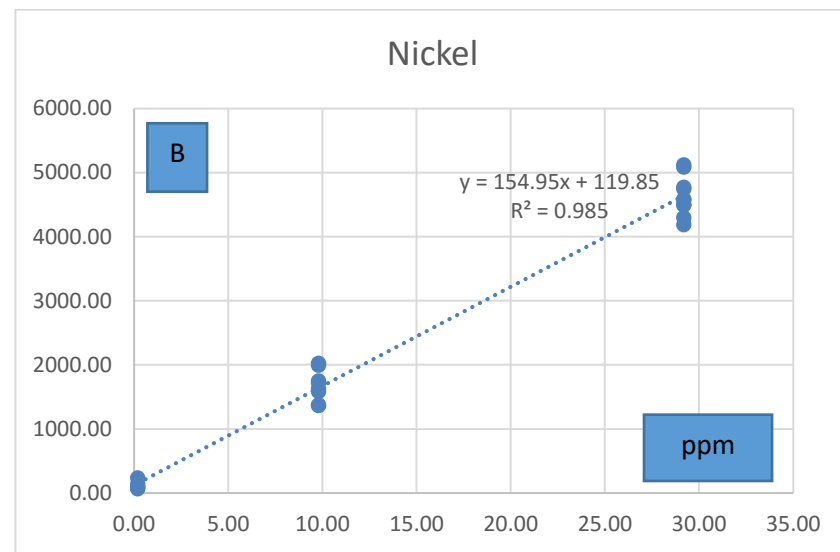
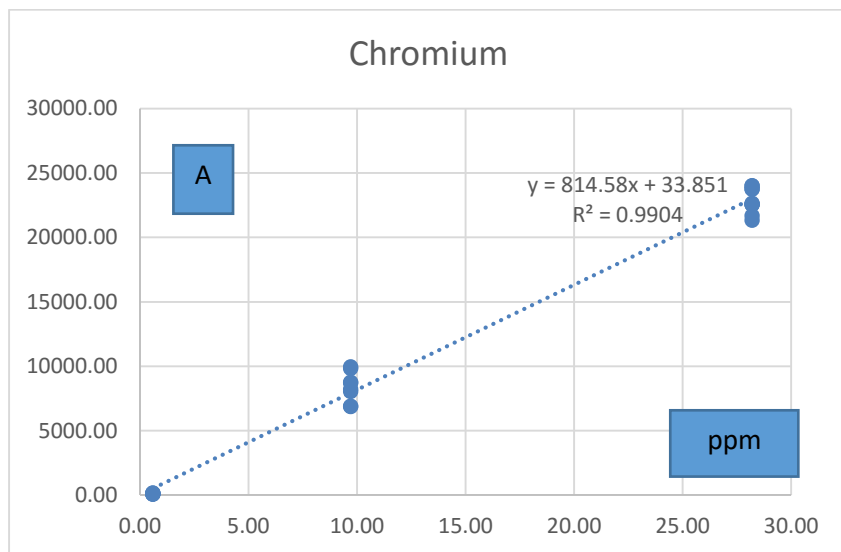


Figure 2 A-D: Calibration graphs for selected analytes in all three standards using both spot and traverse data combined.

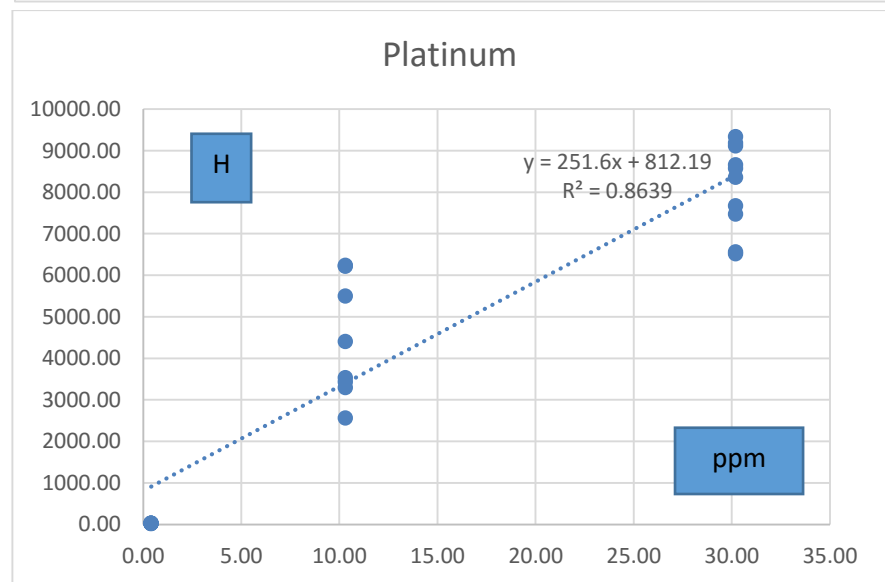
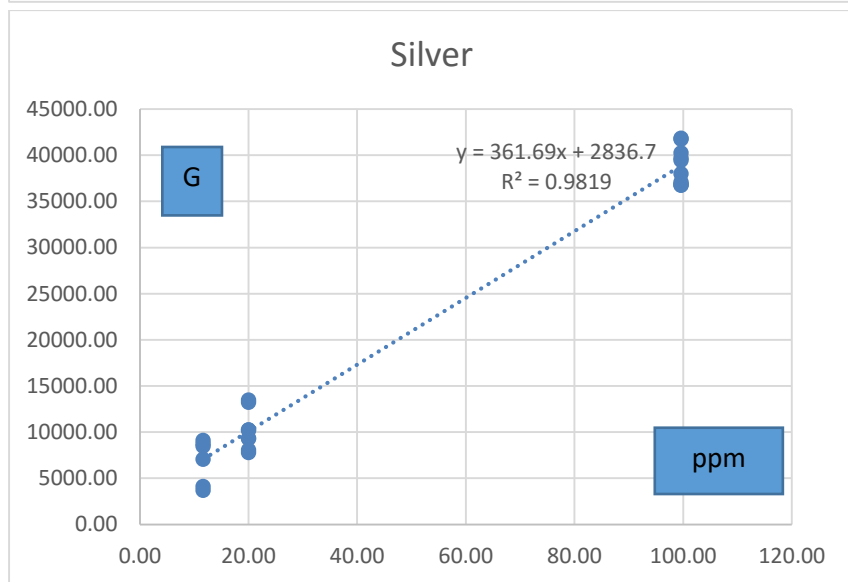
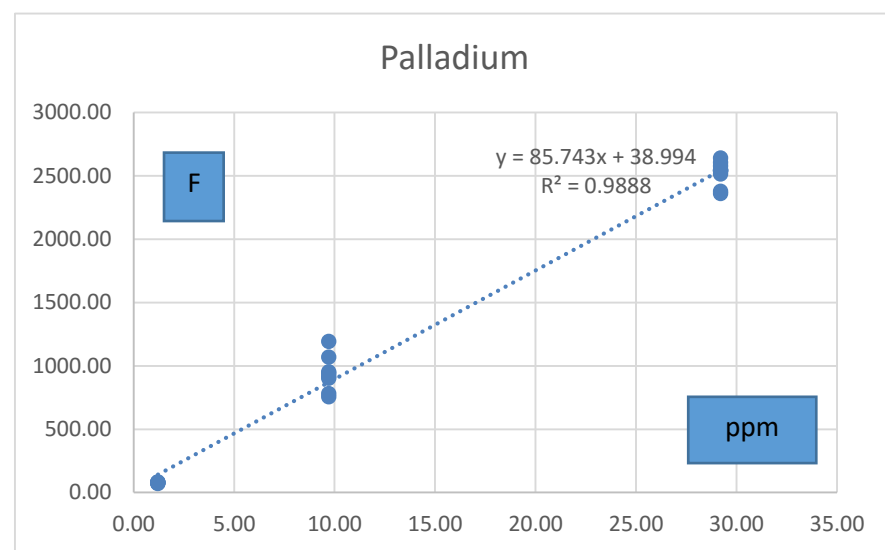
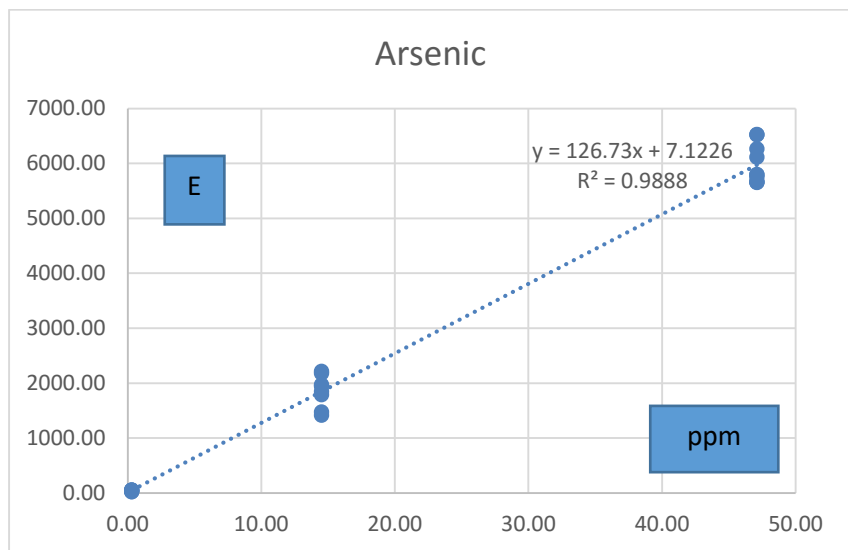


Figure 2 E-H: Calibration graphs for selected analytes in all three standards using both spot and traverse data combined.



From these graphs it is obvious that a significant number of analytes have the possibility of being quantitatively determined in gold samples while others have to be examined in more detail and experiments undertaken with additional gold standards to confirm the possibility of their being determined quantitatively.

In these graphs, both spot and traverse data have been incorporated. The reason for plotting the graphs this way is that under certain circumstances it may be necessary to undertake one or other of the protocols described here in a single analytical run and consequently the closer the data are together, the better for the validity and applicability of the method. Some analytes, especially platinum, appear to be more inhomogeneously distributed throughout the standards than others, nonetheless there is the potential, with more refining of the methodology, for even these to produce excellent calibration graphs.

At this stage of the development project it is only necessary to indicate that the protocols that have been developed as a preliminary investigation into the feasibility of LA-ICP-MS quantitative analysis of gold have the potential to provide robust and accurate data. The calibration graphs detailed in this report have been produced using extremely expensive and very homogenous standards, a situation that will not occur in nature where the entrained analytes will have a very inhomogeneous distribution. Consequently, while having considerable promise, the protocol must be validated against naturally occurring gold samples and the protocol modified to facilitate the analysis of this type of material.

Conclusions

1. From the data obtained during this preliminary investigation it would appear to be entirely possible to develop a quantitative analytical protocol for the LA-ICP-MS analysis of impurities in gold:
2. Inhomogeneity of analytes in the available standards needs to be investigated further to establish a robust method to quantitatively determine the concentrations of inhomogeneously distributed analytes in natural samples.
3. Nonetheless, it is the opinion of the authors that it should be possible to achieve this



outcome.

4. Calibration graphs for many analytes are linear and have excellent r^2 values. This implies that even if standards are not available for specific analytes it will be possible to develop analytical curves for quantitation of these analytes using alternative, pre-analysed (solution ICP-AES and ICP-MS) samples and in-house standards such as those used routinely by TSW Analytical as standards for gold fingerprinting exercises.



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The contents of this report and interpretation of data apply only to the samples as received.