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LA-ICP-MS analysis of platinum-group elements and other elements of interest in ancient gold

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ABSTRACT One of the most promising methods for ancient gold analysis is laser ablation–inductively coupled plasma mass spectrometry (LA-ICP-MS). It is a quasi-non-destructive multi-elemental analytical method with detection limits in the range of ppm or below, depending on the element. Internal and external standardizations are used. Different types of standards are necessary to measure major (required for the internal standardization), minor and trace elements. High-purity gold standards doped with trace elements as well as ancient gold coins were found suitable for that purpose. The reproducibility and the accuracy of the results obtained are good enough to consider LA-ICP-MS as reliable to determine trace-element concentrations in ancient gold.

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1 Introduction

Determining the chemical composition of gold in archaeological and historical studies has several purposes: the concentrations of the major elements primarily provide information regarding manufacturing technology while trace elements may be used to undertake provenance studies. Especially, platinum-group elements should be helpful for that purpose since they have a high melting point and are less likely than other elements to separate from gold during the melting and refining processes. Several analytical methods allow the determination of major elements in gold samples (particle induced X-ray emission (PIXE), X-ray fluorescence, proton activation analysis (PAA)) but few of them are suitable to analyze trace elements. Neutron activation analysis, used to determine trace elements in a wide range of materials, would be difficult to use because of strong background activity produced by gold. One of the most promising analytical methods for this purpose is laser ablation–inductively coupled plasma mass spectrometry (LA-ICP-MS). It is a multi-elemental analytical method with low detection limits, which requires such small samples to be taken that the damage is almost invisible to the naked eye. First attempts

to determine trace elements in gold using LA-ICP-MS date back to 1994. Two different approaches were investigated. Semi-quantitative analyses were performed to fingerprint gold sources without standardization [1] and quantitative analyses allowed the determination of the concentrations of trace elements in gold and silver industrial standards [2]. LA-ICP-MS has been involved since then in ancient gold studies. Trace-element patterns have been determined by semi-quantitative analyses of gold artifacts for comparison studies [3]. The main inconvenience with such analyses lies in the impossibility to compare them directly with data from other laboratories or obtained with different analytical methods, but they were the better way to proceed due to the lack of standards. Subsequently, a procedure was proposed to perform quantitative analyses using ancient gold coins as standards [4]. However, the accuracy of the results for some trace elements was considered as not good enough due to problems in the transportation process between the laser and the plasma, and LA-ICP-MS as not suitable to determine trace-element concentrations in ancient gold. In spite of these not encouraging results, a new procedure has been developed to determine trace-element concentrations in ancient gold. Internal and various external standards have been used to be able to determine as accurately as possible major, minor and a maximum number of trace elements. Comparisons with data obtained by other analytical techniques have been undertaken.

2 The method

The instrumentation is a Perkin Elmer Elan 6000 inductively coupled plasma mass spectrometer (ICP-MS). A Cetac LSX-200 *Plus* UV laser is used for direct introduction of solid samples.

The parameters of the ICP-MS are optimized to ensure a stable signal with a maximum intensity over the full range of masses of the elements and to minimize oxides and double-ionized species formation (XO^+/X^+ and $X^{++}/X^+ < 0.03\%$). For that purpose, nebulizer gas flow, lens voltage, detector analog stage voltage and detector pulse stage voltage are adjusted. A dual-detector calibration, which matches the analog and pulse detector stages, is required to be able to measure major, minor and trace elements at the same time.

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The choice of the parameters of the laser ablation not only will have an effect on the sensitivity of the method and the reproducibility of the measurements but also on the damage to the sample. To be able to determine elements with concentrations in the range of ppm while leaving a trace on the surface of the sample almost invisible to the naked eye, we use the single point analysis mode with a laser-beam diameter of 100 μm , operating in Q -switch mode at 100% of the laser energy (4.8 mJ) and at a pulse frequency of 20 Hz. A pre-ablation time of 40 s was set in order, first, to eliminate the transient part of the signal and, second, to be sure that a possible surface contamination does not affect the results of the analysis.

To improve reproducibility of measurements, the use of an internal standard is required to correct possible instrumental drifts or changes in the ablation efficiency. The element chosen as internal standard has to be present in relatively high concentration so its measurement is as accurate as possible. In order to obtain absolute concentrations for the analyzed elements, the concentration of the internal standard has to be known. Gold is the more logical choice but this element has only one isotope that produces a much too intense signal at

the parameters used for the trace elements. To overcome that problem the AuAr⁺ (gold argide) species is measured [2]. We checked that the production of this ion in the plasma is stable, i.e. the Au/AuAr⁺ ratio is constant in time. The relative standard deviation (RSD) calculated with eight measurements on one afternoon is 3%. Figure 1 shows signals after normalization.

Fully quantitative analyses are possible by using external standards. To prevent matrix effects, the composition of the standards has to be as close as possible to that of the samples. Three different series of standards are used to measure major, minor and trace elements.

The first series of external standards are gold–silver–copper alloys manufactured by the Royal Canadian Mint with certified concentrations for gold and silver (NIST SRM 8068, 8077 and 8074). Assuming that the sum of the weight percentages of the three elements (gold, silver and copper) is 100%, we are able to determine their concentrations in any gold samples.

The second series of external standards, also manufactured by the Royal Canadian Mint, are made of high-purity gold doped with sixteen trace elements with concentrations

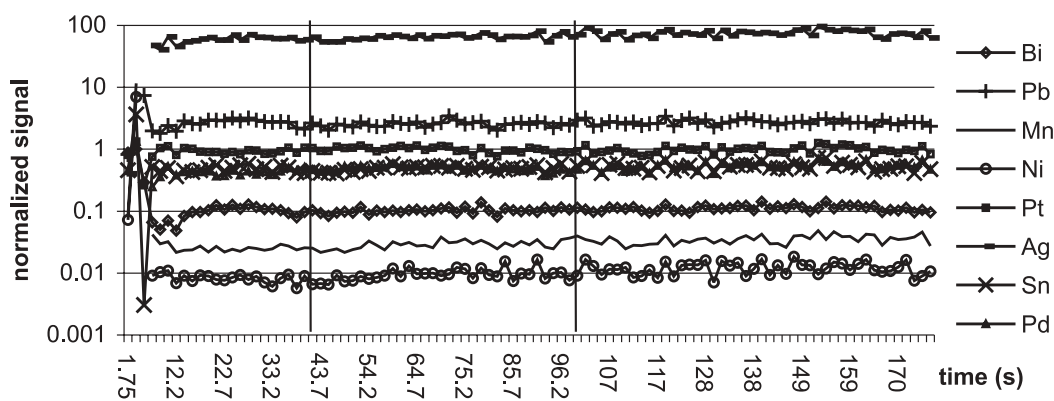


FIGURE 1 Signals of some elements normalized on the gold argide signal. Acquisition of the signal lasts about 1 min and begins 40 s after the beginning of the ablation

Date Origin	Coin 1 (ppm) 8th C. AD Islamic	Coin 2 (ppm) 10th C.–11th C. AD Islamic	Coin 3 (ppm) 12th C.–13th C. AD Islamic	Coin 4 (ppm) 18th C.–19th C. AD Islamic	Coin 5 (ppm) End of the 19th C. AD Russian
Sb	nm	nm	27	7	30
Co	1	<u>1</u>	2	0.2	1
Ir	4	<u>5</u>	1	4	7
Fe	893	508	54	451	124
Ni	7	13	11	3	57
Os	3	218	9	3	50
Pd	14	<u>15</u>	25	231	20
Pt	181	<u>59</u>	143	383	320
Rh	0.5	<u>0.3</u>	1.2	2	3
Ru	0.5	6	0.2	0.1	0.4
As	8	<u>22</u>	41	<u>2</u>	50
Bi	<u>0.2</u>	<u>16</u>	12	3	7
Cu	<u>598</u>	M	M	1674	M
Pb	18	<u>144</u>	420	<u>110</u>	112
Ag	M	M	M	nm	nm
Sn	7	59	85	<u>293</u>	14
Zn	65	61	1675	50	15

TABLE 1 Trace- and minor-element contents of the five coins tested to be used as standards, determined by ICP-MS. The homogeneity of the coins has been evaluated using LA-ICP-MS. Four measurements on different parts of the coins have been made: values in *bold letters* mean that the relative standard deviation (RSD) of these four measurements is less than 10%. *Underlined values* are for a RSD ranging from 10% to 15%. The other values are for a RSD > 15%. M is for major elements (concentration > 1%) and nm is for not measured

ranging from 1 to about 100 ppm (NIST SRM 8053, 8059, 8062 and 8065). To be able to determine more elements and to have a wider range of concentrations, we use ancient gold coins as a third series of standards.

Indeed, ancient gold coins are supposed to be made with less refined gold and are supposed to be rich in a wide range of trace elements. We investigated several kinds of gold coins: Islamic and Russian gold coins struck between the 8th and the 19th C. AD.

For each of the five coins selected, homogeneity was checked. The more recent coins (coins 3, 4 and 5 in Table 1) are the more homogeneous and will be more suitable for standardization purposes. For all the coins, a wide dispersion of the results for Ir, Ru and Os, probably due to heterogeneous distribution of these elements in the gold samples, jeopardizes an accurate measurement of their concentrations. The trace-element concentrations of the coins were determined by ICP-MS after acid digestion of a few hundred micrograms (Table 1).

3 Interferences, detection limits, reproducibility and accuracy

Interferences occur even if the absence of solvent makes them less common with laser ablation than when samples are in solution. Multi-charged species, polyatomic species (including oxides) and isobaric species may cause interferences. The choice of the nebulizer gas flow and the choice of some non-interfered isotopes contribute to minimize or to avoid interferences but some of them remain and should be corrected.

To determine the limits of detection of the method, the background induced by the gold matrix of the samples is taken into account, using a high-purity gold standard (NIST SRM 685). The limits of detection are calculated as the concentrations equivalent to three times the standard deviation of

signal intensities obtained with 10 analyses of the high-purity gold standard. The limits of detection of iron and copper may have been overestimated due to the presence of impurities in SRM 685 as indicated in the certificate of analysis ($0.1 \text{ ppm} < \text{Cu} < 0.26 \text{ ppm}$; $0.16 \text{ ppm} < \text{Fe} < 0.50 \text{ ppm}$). Traces of Cr, Mg, Mn, Ni, Sn and Zn are mentioned too but at lower levels. The limits of detection of most of the elements range from 0.01 to 0.1 ppm. All limits of detection are below 1 ppm (Fig. 2).

Reproducibility is calculated as the relative standard deviation obtained for 10 analyses over several months of the SRM 8053. Except for Ag, the reproducibility is below 10% and ranges between 4% and 7% for the other elements (Table 2). The low reproducibility for Ag could be explained by instrumental contamination due to the high silver contents of some coins (especially coin 3 with silver content higher than 30%), which causes big variations in the background noise at the mass of silver.

Accuracy is calculated as the relative deviation between the average values obtained for 10 analyses of the SRM 8053 over several months and the certified values given for that gold standard. Accuracy is better than 6% for all the elements (Table 2).

4 Comparison between LA-ICP-MS and other analytical methods

Major and minor elements (Au, Ag and Cu) of three samples have been measured by X-ray fluorescence (R. Cunningham, SCMRE) or PAA (Centre E. Babelon, CNRS, Orléans, France).

The results obtained for the three samples by LA-ICP-MS concur quite well with data obtained elsewhere (Table 3).

Trace elements have been measured by ICP-MS. The samples were dissolved in aqua regia made with ultra-pure hydrochloric acid (3 vol) and ultra-pure nitric acid (1 vol). A mi-

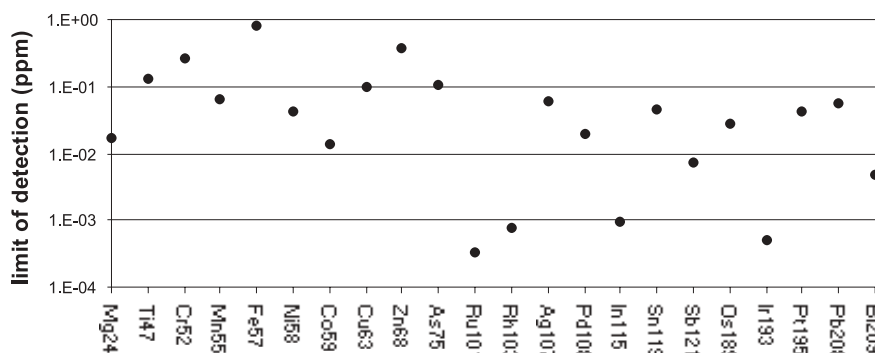


FIGURE 2 Limits of detection

Element and isotope	As 75	Bi 209	Cr 52	Cu 63	Fe 57	Pb 208	Mg 24	Mn 55	Ni 58	Pd 108	Pt 195	Ag 107	Sn 119	Ti 47	Zn 68
Certified concentration (ppm)	10	24	32.6	98.1	11.6	21.9	34	58.9	32.5	43.1	87.1	20.3	33.8	12.7	54.6
Average of 10 measurements (ppm)	9.7	22.6	31.7	97.3	10.9	22.0	32.7	61.8	32.1	43.1	88.7	21.2	32.0	12.3	56.7
RSD	6%	4%	6%	5%	5%	5%	7%	7%	4%	6%	6%	12%	5%	7%	7%
Accuracy	3%	6%	3%	1%	6%	1%	4%	5%	1%	0%	2%	5%	5%	3%	4%

TABLE 2 Evaluation of the reproducibility and of the accuracy of the results obtained by LA-ICP-MS

Sample Analytical method	1 – American gold – 19th C.		2 – American gold – 19th C.		French coin – 18th C.	
	LA-ICP-MS	X-ray fluorescence	LA-ICP-MS	X-ray fluorescence	LA-ICP-MS	PAA
Au	91.2%	91.1%	93.4%	93.7%	90.2%	90.9%
Ag	8.9%	8.3%	6.3%	6.7%	7.1%	6.3%
Cu	0.021%	nd	0.051%	nd	2.71%	2.71%

TABLE 3 Comparison of the results obtained by LA-ICP-MS with data obtained using other analytical techniques (nd is for not detected)

Element	Number of coins taken into account	Range of concentrations (ppm)	Slope	R-square value
Pt	6	60–2560	1.0534	0.9983
Pd	6	14–152	1.0591	0.9952
Ni	4	7–57	1.1688	0.9954
Fe	6	54–2150	1.0715	0.976
Cu	4	598–95 355	1.0066	0.9996
Zn	5	15–119	0.991	0.9966
Sn	5	7–418	0.934	0.9969
Pb	5	18–210	1.0192	0.9553

TABLE 4 Slopes and R-square values of correlation curves for results obtained by ICP-MS against results obtained by LA-ICP-MS. The results concern the French coins quoted above and the five coins tested as standards

crowave digestion was performed at a temperature of 260 °C and at a pressure of 30 Pa. Silver chloride precipitate was removed by filtering the solutions. Matched matrix standard solutions were made by adding aliquots of multi-element standard solutions to a gold solution obtained by digesting pure gold.

To compare results obtained by ICP-MS of dissolved samples and results obtained by LA-ICP-MS we calculated the correlation parameters, for some elements, between results obtained by either technique on a series of samples. The two series of values are all the more consistent as the slope and the R-square value of the correlation curve are close to 1. The agreement is quite good for many of the elements of interest (Table 4).

In some cases not all samples have been taken into account because results obtained by ICP-MS and LA-ICP-MS do not agree. These differences between the results by LA-ICP-MS and ICP-MS could be explained by the heterogeneous distribution of some elements in some coins.

5 Conclusion

The use of sets of different standards makes LA-ICP-MS a suitable method to determine some major, minor and trace elements of interest in ancient gold with a good accuracy and reproducibility, with damage hardly visible to the naked eye. Problems met in determining some platinum-group elements (Ir, Os and Ru) may be due to the heterogeneous distribution of these elements in gold samples. Only bulk analysis could overcome those problems.

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