

## Gold traces to trace gold

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### Abstract

Tracing gold back to its source by means of the elemental composition of objects contributes to the knowledge of the trade routes used in the past. The analysis of a large number of ancient gold objects showed that in most cases only a few elements are useful to characterize the metal. Quantitative analysis of these elements was performed on a set of gold samples with different techniques: inductively coupled plasma mass spectrometry in liquid mode and with laser ablation, 12 MeV proton activation analysis, fast neutron activation analysis, particle induced X-ray emission (PIXE) and PIXE induced X-ray fluorescence. The aim of this paper is to present a discussion on the possibilities and limitations of these techniques to characterize gold.

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### 1. Gold ores

Gold is found in Nature in its native form as dust and nuggets in alluvial deposits. As it can be obtained by simple panning and washing it was very early worked by Man. Most of the known sources are of placer type (secondary deposits), however, this metal can also be found in primary deposits, in quartz veins, as tellurides, and also with pyrites and arsenopyrites [25,32].

Gold was found as a gold/silver alloy (that may reach 98% of gold in nuggets) with silver up to 40%, copper below 1% and quite frequently iron up to 5% [1,7,34]. In placers heavy minerals are concentrated and relative proportions of certain minerals are in general related, as for example the log/log coefficients of correlation between gold and uranium which seem to be characteristic for each placer (Ref. [31], p. 298). Depending on the soil geology, very different heavy elements (like platinum) set down with gold. The presence of platinum has been observed in objects but not in minerals from the same region [24]. Therefore, the difference between a mined (primary) and an alluvial (secondary) gold ore

from the same region might only be the concentration of the elements recovered by panning—we must also mention tin, common in alluvial gold as cassiterite.

To refine native gold Man accomplished cupellation, to get rid of the base metals by oxidation, and cementation, which is the separation of gold and silver by reacting the latter with salt or sulphur leaving behind refined gold [6,12]. During the separation and purification processes, at high temperatures, many elements are susceptible to oxidation and loss by evaporation from gold or absorbed by the cupel. Among the elements that are affected by those processes but can still be considered as characteristic of the gold ores we must mention platinum and palladium which have very high melting points. However, we must be aware of several platinum group element (PGE) associations like those of ruthenium, osmium and iridium that form inclusions of different densities [29] as well as their loss during cupellation [40]. The PGE oxidation and removal as well as their association are extensively discussed by P. Craddock (Ref. [6], Appendix 4).

When we deal with ancient gold objects, chemical analysis is aimed at getting information on the manufacture technology of the objects and the provenance of the ores. On one hand we must be able to determine major and minor elements and on the other hand some trace

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elements or ratios of elements that characterize the ores. In fact, the measurement of lead isotope ratios, very useful in identifying the origin of copper and silver ores, fails for most gold objects as the lead content is too low to perform thermo ionization mass spectrometry (TIMS); if some tellurides may contain enough lead, objects made with alluvial gold are characterized by little (inferior to 100 ppm) or the absence of lead.

The identification of a gold source is a difficult task since most of the exploited mines are exhausted. Sometimes the situation of the mines and the geology of the soil are unknown. We have also to consider the re-cycling and re-use of gold and the subsequent loss of information on trace elements. The debasement of gold by addition of silver and/or copper ores complicates the fingerprinting [20].

The cases of gold ores from very particular geological contexts like South American mines are the easiest to study from the analytical point of view, as one single trace element might be sufficient to characterize and 'follow' gold. This is the case of platinum in the Colombian gold or palladium in the Brazilian gold. Usually the measurement of several elemental ratios is necessary to identify the ore. The analysis of very different gold objects from different regions and periods showed that in most cases a small group of elements is sufficient to describe a change in gold supply.

Most gold sources exploited in the past were responsible for historical events. The importance of gold is clearly shown by the coinages issued in certain regions. The first gold coin (as we define it nowadays), the croeseid, was issued in Lydia by Croesus (6th century BC) who owned the Pactolus river and Mount Tmolus gold sources. The conquest of that territory by Alexander the Great introduces the Greek stater also struck in Macedonia using ores coming for example from Mount Pangaeus. The coins struck from the 6th to the 2nd century BC showed changes in the gold supplies identified by the platinum, tin and palladium contents [14].

The dinar struck by the Arabs after the 7th century AD in all the Mediterranean basin shows changes of gold supplies identified by the platinum, gallium and antimony content for the Eastern regions and the platinum, tin and gallium content for the Western ones [14,37]. In addition, the Byzantine gold is identified by its platinum content [33] and Wisigothic gold by the platinum, palladium and tin content [19].

South American gold ores that strongly influenced the European economy after the 16th century, like Colombian and Brazilian gold ores, are characterized respectively by their platinum and palladium contents (Peruvian gold showing lower contents of these elements [22]) whereas platinum is the element that also characterizes the contemporary Eastern European gold [18]. The other Latin American gold ores can be traced back

with the platinum, palladium, tin and antimony contents. Only the gold struck in India after the 16th century showed very different trace elements typical of the use of a telluride [21].

## 2. The analytical techniques

The aim of this work is to compare the possibilities and limitations of very different techniques to analyze gold objects (Table 1) in order to search for the provenance of the metal. We used here activation analysis with protons (PAA) or with fast neutrons (FNAA), inductively coupled plasma mass spectrometry in liquid (ICP-MS) or in solid (LA-ICP-MS) mode and particle induced X-ray emission (PIXE) together with particle induced  $\gamma$ -ray emission (PIGE) and PIXE induced X-ray fluorescence (PIXE-XRF). We present here the main characteristics of the first group of techniques and the new developments for gold of the association of the last three techniques.

### 2.1. Activation analysis

Activation analysis is based on the bombardment of the object with an incident beam and the measurement of the delayed gamma radiation emitted by the radionuclide [17]. The development of these techniques using fast neutron and proton beams from a cyclotron to analyze ancient coins was done in the 1960s by P. Meyers [30]. The set-up used in this work for PAA with 12 MeV protons was first published by Barrandon et al. in 1976 [2] for the analysis of gold and improved by J. Poirier in the 1980s [33]. At 12 MeV only (p,n) nuclear reactions are produced by protons in gold samples, minimizing interference and improving the detection limits. The interposition of a 3 mm thick lead sheet between the detector and the sample absorbs the  $\gamma$ -ray emission from the two Hg197 isomers produced in gold and allows gamma-ray spectrometry to be performed immediately after irradiation. Quantitative calculations are made by using flux monitoring and the Ricci and Hann [35,36] mean  $\sigma$  method. The proton path in gold is of about 240  $\mu$ m and so the measurement is not affected by the gold surface enrichment due to oxidation and removal of copper. We can measure routinely major, minor and some trace elements with limits of detection down to 1 ppm [17].

The use of fast neutron fluxes of about 8 MeV average energy produced by a 17.5 MeV deuteron beam of 30  $\mu$ A impinging on a thick Be target (FNAA) allows the analysis of the entire sample but only major elements can be evaluated for gold alloys. The procedure used for FNAA was published by Beauchesne and Barrandon in 1986 [3] for the global analysis of copper alloys. Gondonneau et al. [15] showed that very small gold

Table 1  
Composition by PAA of the samples used as reference material

Reference	%			ppm													
	Au	Ag	Cu	As	Cr	Fe	Ga	Hg	Pb	Pd	Pt	Ru	Sb	Sn	Te	Ti	Zn
A1	92.9	3.0	3.9	9	13	664	ND	ND	169	195	478	ND	63	56	4	0.3	63
F1	90.2	6.3	2.9	82	10	1998	ND	ND	203	147	2924	ND	109	272	15	1	129
R1	90.3	0.3	9.4	70	ND	128	ND	ND	ND	16	286	ND	31	ND	ND	0.2	6
M1	79.1	19.5	1.3	8	ND	385	1	ND	165	8	ND	ND	7	63	ND	1	53
M2	98.2	1.7	0.0	1	3	807	2	ND	24	5	90	ND	ND	4	ND	1	13
M3	89.7	7.4	2.8	26	ND	637	3	ND	ND	25	72	ND	11	25	ND	9	24
M4	87.8	9.8	2.3	74	ND	231	2	ND	154	5	112	ND	36	9	ND	25	27
M6	90.3	6.9	2.6	22	ND	678	4	ND	126	4	78	ND	4	22	ND	1	71
M7	98.9	0.8	0.2	5	ND	401	5	10	693	11	164	ND	2	7	ND	7	30
M8	99.0	0.9	0.014	2	3	621	ND	9	36	11	65	ND	ND	ND	ND	7	69
M9	95.5	1.5	0.004	ND	ND	595	ND	1975	25000	1677	648	ND	6	227	ND	41	115
A66	93.5	6.1	0.3	ND	ND	240	ND	ND	ND	ND	217	ND	ND	188	ND	ND	ND
A72	47.8	48.0	4.1	ND	ND	ND	ND	ND	293	ND	254	ND	ND	ND	ND	ND	ND
A4	57.2	37.5	5.2	ND	ND	17	ND	ND	ND	ND	85	ND	ND	ND	ND	ND	ND
A37	68.3	28.5	3.1	ND	ND	142	ND	ND	111	ND	477	103	ND	52	ND	<1	ND
A57	64.6	33.5	1.9	ND	ND	159	ND	ND	101	8	219	ND	ND	100	ND	1	ND
A59	74.6	23.6	1.7	ND	ND	932	ND	ND	ND	ND	274	ND	ND	237	ND	ND	ND

Samples are mostly pieces of ancient gold coins and PAA results are used as 'certified' compositions. ND, not determined under the detection limits.

samples (less than 2 mg) can be analyzed using gamma-ray spectrometry immediately after a 2 h 30 min irradiation time. The results obtained on a set of samples taken from reference material show a good agreement with the PAA values in Table 2.

## 2.2. ICP-MS

ICP-MS is used to determine a very wide range of trace elements in gold at very low levels. The sample can be introduced in liquid or in solid mode, the latter by laser ablation. The LA-ICP-MS technique was first used by Watling et al. in 1994 [38] for the qualitative analysis of ancient gold with an IR laser and was developed in 1999 by Gondonneau and Guerra [13] for the quantitative analysis of gold with a UV laser.

We used a Fisons PlasmaQuad PQXS instrument combined with a 2 mJ pulsed VG Nd:YAG laser working on Q-switched mode and in the UV wavelength with a shot frequency of 6 Hz. Acquisition was

performed using pick jumping mode, 10.24 ms dwell time, 60 s acquisition time after 10 s of pre-ablation and 3 by 3 raster scan pattern. Craters are of about 40  $\mu\text{m}$  in diameter and 130  $\mu\text{m}$  in depth, and sampling is of about 1  $\mu\text{g}$  per crater. The limits of detection range from 10 ppb to 1 ppm on a high purity NBS SRM685 gold standard using  $\text{AuAr}^+$  ion as internal standard [28]. We must be aware of interference connected to molecular ions formed in the plasma with major and minor elements, such as ion  $\text{CuAr}^+$  with the same mass as rhodium. Moreover, some elements may be lost during the laser/sample interaction and the transportation to the plasma, as evidenced by the loss of linearity already noticed for lead by Williams and Jarvis [39].

The recent development of ICP-MS using liquid mode with a Fisons PlasmaQuad PQXS instrument was published by Gondonneau et al. in 2000 [15]. Acquisition was performed using the pick jumping mode, 10.24 ms dwell time, 30 s acquisition time and

Table 2  
Composition of major elements by FNAA of a group of drilled samples from the objects considered as reference material (see Table 1 for 'certified' compositions)

Reference	mg	Au%		Ag%		Cu%	
		PAA	FNAA	PAA	FNAA	PAA	FNAA
		R1	1.9	90.3	90.1	0.3	—
A1	2.5	92.9	92.3	3.0	3.1	3.9	4.5
F1	2	90.2	91.7	6.3	5.7	2.9	2.6
M2	1.9	98.4	97.3	1.5	1.9	0.04	0.8
a37	3.5	68.3	73.8	28.5	23.7	3.1	2.5
a66	6.9	93.5	94.3	6.1	5.6	0.3	0.1
a57	7.4	64.6	68.7	33.5	29.5	1.9	1.8
a59	6.1	74.6	78.6	23.6	19.7	1.7	1.7
a72	12.1	47.8	49.3	44.0	41.9	8.1	8.8

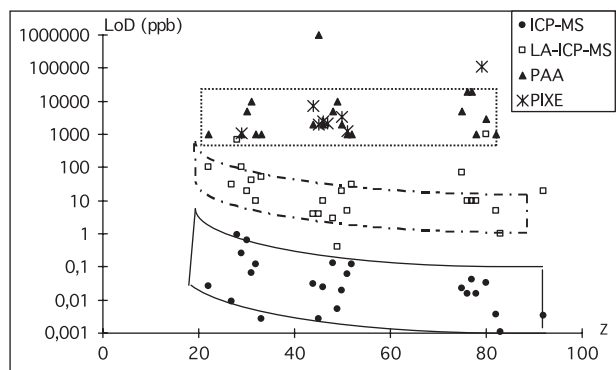


Fig. 1. Comparison of the detection limits obtained under optimized conditions for PAA and under the normal analytical conditions for LA-ICP-MS, ICP-MS and PIXE.

Table 3

Composition of three 'reference' samples and detection limits (indicated by LoD) of the measured elements by Zn filtered PIXE

Reference	Technique	%		ppm					
		Au	Ag	Cu	Ru	Rh	Pd	Sn	Sb
A1	PAA	92.9	3.0	3.9	—	—	195	56	63
	PIXE	93.9	4.1	1.7	139	11	335	119	86
	LoD	1346	25	14	90	20	24	41	15
F1	PAA	90.2	6.3	2.9	—	—	147	272	109
	PIXE	91.4	7.0	1.3	140	27	147	494	120
	LoD	1237	21	11	78	21	25	33	13
a37	PAA	68.3	28.5	3.1	103	—	—	52	—
	PIXE	78.7	19.9	1.2	96	—	—	126	8
	LoD	1134	46	13	70	57	71	51	21

three repeated runs for gold samples of about 2 mg. Limits of detection vary from 0.01 to 10 ppb. The comparison of the limits of detection obtained by LA-ICP-MS, ICP-MS and PAA can be found in Fig. 1.

### 2.3. PIXE, PIGE and PIXE-XRF

PIXE has been used for the analysis of ancient gold since the 1970s (for example see Ref. [11]). This method based on the use of a few MeV proton beams to excite the atoms detects the characteristic X-ray emitted by the sample and allows the measurement of major, minor and a few trace elements [10,16]. Being a near-surface technique (less than 30  $\mu\text{m}$  for gold), the measurement is influenced by the heterogeneity of the surface (copper is eliminated from the surface of gold alloys by oxidation). However, PIXE has the advantage of using external

Table 4

Comparison of the major element composition of a group of reference materials from Table 1 by PIXE, PIGE and PAA as well as that of three gold standards (CV for certified values)

Reference	Au%			Ag%			Cu%		
	PAA	PIGE	PIXE	PAA	PIGE	PIXE	PAA	PIGE	PIXE
A1	92.9	93.1	93.9	3.0	3.7	4.1	3.9	3.2	1.7
F1	90.2	90.3	91.4	6.3	7.4	7.0	2.9	2.3	1.3
R1	90.3	91.0	91.5	0.3	—	0.3	9.4	9.0	8.0
M1	79.1	77.9	81.7	19.5	20.8	17.4	1.3	1.2	0.9
M2	98.2	97.5	97.5	1.7	2.4	2.1	0.05	0.1	0.1
M9	99.5	100.0	93.8	0.2	—	0.1	0.004	—	0.1
66	93.5	92.7	92.7	6.1	7.0	6.8	0.3	0.3	0.3
A37	68.3	75.1	78.7	28.5	22.8	19.9	3.1	2.1	1.2
A59	74.6	79.5	81.9	23.6	19.2	17.1	1.7	1.3	0.9
zere4	96.5	99.3	97.6	2.4	0.7	0.7	0.005	—	0.1
zere9	91.8	91.7	73.7	7.4	8.3	5.1	0.019	—	0.1
	CV			CV			CV		
std6917	76	74.8	75.9	17	18.2	17.2	6	6.9	6.7
std6905	75	74.7	75.2	6	6.6	6.4	19	18.7	18.3
std6906	75	75.0	75.4	12.5	12.5	12.3	12.5	12.5	12.0

$\mu$ -beams and providing elemental maps [5] as well as, together with RBS, elemental depth concentration profiles [9].

We used a 3 MeV external proton beam with 30  $\mu\text{m}$  diameter and two Si(Li) detectors to collect the emitted X-rays (see Ref. [4] for the set-up). The first is dedicated to the measurement of major elements while the other one, covered with a 75  $\mu\text{m}$ -Zn selective filter to absorb the Au L-lines, is used to determine the trace element contents. Elemental maps are obtained by mechanically moving the sample under the fixed beam. With an

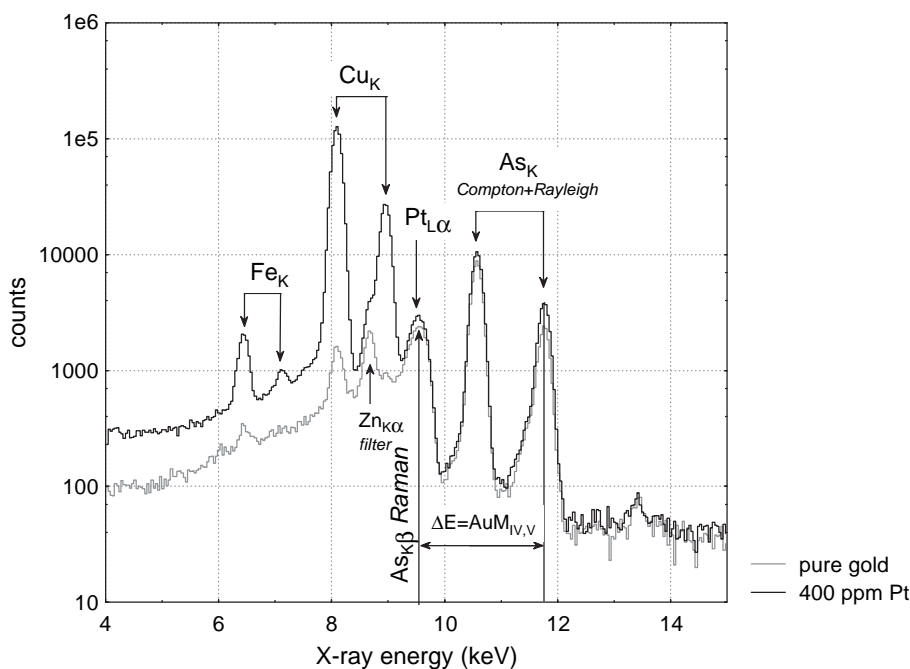


Fig. 2. PIXE-XRF spectra for a 1000  $\mu\text{C}$  integrated dose of sample A1 compared with a pure gold standard. The quantity of platinum is evaluated by subtraction of the Raman and Rayleigh contributions.

Table 5

Results obtained for gold and copper (silver is lost during dissolution) for a group of drilled samples from reference material of Table 1 analyzed by ICP-MS in liquid mode using either the element mass in analogue detection mode (ANL mode) or the ions AuAr<sup>+</sup> and CuAr<sup>+</sup> formed in the plasma in pulse counting mode (PC mode)

Element	Reference	PAA		ANL mode		PC mode	
		%	ppm in solution	%	ppm in solution	%	ppm in solution
Au	c12	53.2	45	73.3	62	74.5	63
	c9	60.9	57	53.4	50	64.1	60
	A1	92.9	59	50.4	32	55.1	35
	M8	98.8	80	88.9	72	88.9	72
	M4	87.8	120	137.6	188	107.6	147
	M1	76.7	147	47.0	90	51.1	98
	M3	89.7	244	90.4	246	92.3	251
	R1	90.3	318	101.4	357	104.5	368
Cu	c12	8.2	7.0	10.2	8.7	10.5	8.9
	c9	7.8	7.3	8.3	7.8	8.5	8.0
	M2	0.04	0.07	0.1	0.12	0.1	0.12
	M8	0.02	0.02	0.03	0.03	0.03	0.03
	M4	2.4	3.2	2.5	3.3	2.8	3.7
	M1	1.6	2.5	1.9	3.0	1.9	2.9
	M3	2.8	7.6	2.8	7.7	2.6	7.1
	R1	9.4	33.1	7.3	25.7	7.3	25.7

integrated dose of 8 μC and 15 min acquisition time, the limits of detection (see Table 3) reach 13–90 ppm for the measured elements. The background produced by nuclear reactions in the sample constrains the limits of detection.

Simultaneous PIXE and PIGE measurements were carried out. Since gamma-rays are not attenuated in the sample, major elements are less sensitive to the possible heterogeneity of the surface. We used a 30% efficiency HPGe detector placed at 45° from the beam and the

Table 6

Major element composition of a set of samples from Table 1 analyzed three times (three runs per analysis) by LA-ICP-MS

Element	Reference	PAA	LA1	LA2	LA3	Average	σ
Au%	M1	79.1	79.2	75.6	76.1	77.0	2.0
	F1	90.2	92.7	90.7	89.5	91.0	1.6
	R1	90.3	92.7	89.2	83.8	88.6	4.5
	A1	92.9	94.6	92.9	91.5	93.0	1.6
	M2	98.2	98.5	98.2	98.3	98.3	0.2
Ag%	R1	0.3	0.4	0.4	—	0.4	0.0
	M2	1.7	1.8	1.5	1.4	1.6	0.2
	A1	3.0	4.0	3.4	2.6	3.3	0.7
	M6	6.9	7.9	6.8	6.1	6.9	0.9
	M1	19.5	22.4	—	18.3	20.4	2.9
	F1	6.3	—	5.4	4.9	5.2	0.4
Cu%	R1	9.4	10.4	6.9	—	8.7	2.5
	M2	0.05	0.03	0.02	0.04	0.0	0.0
	A1	3.9	3	2	2.8	2.6	0.5
	M6	2.6	3.5	2.3	4.6	3.5	1.2
	M1	1.3	2	—	2.7	2.4	0.5
	F1	2.9	—	1.9	3.9	2.9	1.4

279, 309 and 152 keV gamma-ray lines for the measurement of gold, silver and copper, respectively. Table 4 shows the results obtained by PIXE, PIGE and PAA for a group of gold samples.

The importance of platinum content for gold sourcing led us to develop a PIXE-XRF set-up. We used the quasi-monochromatic X-ray radiation emitted by a primary target under proton bombardment in order to excite platinum without exciting gold. This technique can only be used for the determination of the element (or two elements) with an atomic number immediately inferior to the matrix number [8]. In the present case we used an arsenic target. However, the limit of detection is ruled by various physical processes (Raman and Rayleigh scattering, see Ref. [27]) leading to a sensitivity of about 100 ppm for platinum. Fig. 2 shows the spectra of sample A1 containing 470 ppm of platinum and a pure gold sample.

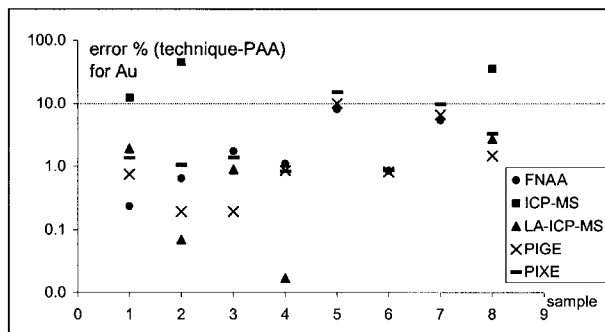
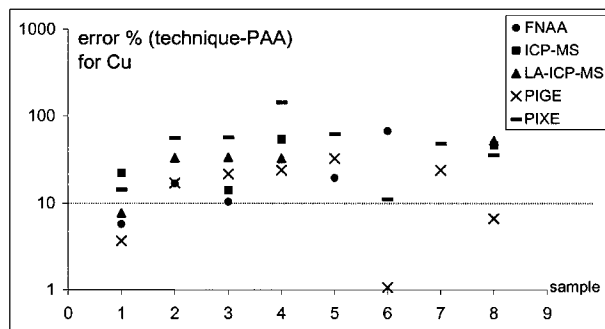
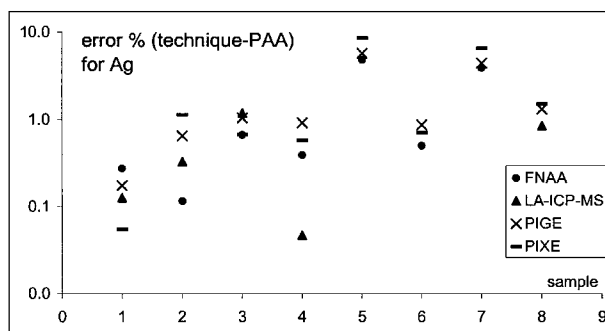


Fig. 3. Comparison of the results obtained by all the techniques for the concentrations of the major elements of a group of samples from Table 1.



### 3. The analytical results

#### 3.1. Major elements

Gold alloys with high contents of copper tend to present surface heterogeneities. As we can see in Table 4 where we compare PIXE and PIGE to PAA results, PIXE gives good agreement with PAA but PIGE concentrations are closer to the stated reference concentrations. We must notice that samples named zero 4 and zero 9 are gold nuggets and thus the measured concentrations depend on the analyzed region. However, PIGE having bad detection limits, about 1000 ppm, may be considered as a complementary technique to PIXE.

ICP-MS in solid mode (LA) provides the contents in all the three major elements, but in liquid mode silver is eliminated during sample dissolution. Table 5 shows the results obtained by ICP-MS using the two possible acquisition modes: major elements in analogue mode and trace elements in pulse counting mode. In the latter mode  $\text{CuAr}^+$  and  $\text{AuAr}^+$  ions formed in the plasma were used for copper and gold determination. Those results agree for both acquisition modes but they are quite far from the expected values, as shown by sample

A1 which has measured gold concentrations of 50% and 55% but an expected concentration of 93%.

Table 6 contains the data obtained for three different sets of laser ablations on a group of reference samples. It is clear that LA-ICP-MS gives very dispersed results, as shown by sample R1 which has measured gold concentration varying from 84% to 93%.

When performing solid or liquid ICP-MS, major elements must be measured by another non-surface technique. Fig. 3 reports the results obtained with all the techniques used in this work for a small set of reference samples. We can observe that in general the closest values to the 'reference' concentrations are obtained by PIGE and FNAA.

#### 3.2. Trace elements

Trace elements were obtained by ICP-MS in liquid and laser modes as well as by PIXE and PAA. We know that ICP-MS allows the measurement of a wide range of elements with good detection limits, but considering that only a few elements are important for the characterization of gold, only a subset was considered in this work.

The data obtained with eight different LA-ICP-MS analyses performed on nine samples as well as the

Table 7

Range of concentrations and average values of nine analyses (three runs per analysis) by LA-ICP-MS of the trace elements present in a group of samples from Table 1

Reference	Content by	ppm									
		As	Ga	Pb	Pd	Pt	Sb	Sn	Te	Ti	Zn
A1	PAA	9	ND	169	195	478	63	56	4	0.3	63
	ICP-MS	50–151	1–4	129–185	216–335	712–784	69–150	78–131	5	0.4	77–154
	Average	90	3	159	307	740	99	96	5	0.4	102
M1	PAA	8	1	165	8	ND	7	63	ND	ND	53
	ICP-MS	1–14	3	129–185	5–8	4–6	3–4	45–105	0.4–0.5	ND	41–101
	Average	6	3	161	7	5	3	71	0.4	–	64
F1	PAA	82	ND	203	147	2924	109	272	15	ND	129
	ICP-MS	10–180	1–3	141–185	91–156	1783–2701	88–208	197–459	12	ND	83–203
	Average	90	2	169	128	2380	131	311	12	–	123
M3	PAA	26	3	ND	25	72	11	25	ND	9	24
	ICP-MS	3–46	4–15	29–42	14–24	38–63	7–17	23–53	0.2	1–2	22–53
	Average	23	10	37	20	54	10	35	0.2	2	33
M6	PAA	22	4	126	4	78	4	22	ND	1	71
	ICP-MS	4–64	2–8	124–178	5–8	62–102	6–14	15–36	0.5–1	0.2	38–94
	Average	31	5	156	7	88	9	24	1	0.2	57
M7	PAA	5	5	693	11	164	2	7	ND	7	30
	ICP-MS	0.2–3	6–23	22–31	7–12	81–133	1–3	2–5	0.1	2	22–54
	Average	1	15	27	10	115	2	3	0.1	2	33
M8	PAA	2	ND	36	11	65	ND	ND	ND	7	69
	ICP-MS	0.2–3	0.2–1	3–4	13–23	55–91	0.3–1	1–2	0.05–1	ND	1–3
	Average	1	0.2	4	20	76	0	1	0.1	–	2
R3	PAA	70	ND	ND	16	286	31	ND	ND	0.2	6
	ICP-MS	12–211	0.3–1	59–85	9–15	192–314	29–63	5–11	1	0.2	5–12
	Average	109	1	75	12	265	42	7	1	0.2	8
M2	PAA	1	2	24	5	90	ND	4	ND	1	13
	ICP-MS	0.1–1	0.5	31–34	4–6	59–97	0.3–1	2–3	0.5–1	1	5–8
	Average	1	0	32	6	82	0	2	1	1	7

ND, not determined under the detection limits.

Table 8  
Concentration of trace elements obtained by ICP-MS in liquid mode on drilled samples from a set of objects from Table 1

Reference	ppb in solution													
	Added	Cr	Fe	Ir	Pb	Pd	Pt1	Pt2	Rh	Ru	Sb	Sn	Te	Zn
A1		8	617	6	136	232	395	410	7	0.49	17	138	4	49
A2	315	8	508	292	148	567	718	690	316	312	374	450	312	45
F1		16	1749	7	172	111	1320	1222	10	1	44	232	14	88
F4	585	12	2061	705	179	700	2573	2813	595	605	693	804	576	
M1			171		165	5	3	3	0.1	1	1	1	1	36
M1.2	56	2	251	53	166	59	58	55	52	55	63	53	59	36
M2		1	181	0.1	34	5	66	61	0.3	1	0.1		0.3	
M2.2	67	3	149	45	37	74	123	114	64	69	77	66	66	
R1		2	22	4	43	9	235	224	0.4	0.4	10		1	3
R2	56	1	119	74	51	64	306	316	53	54	74	52	61	
M3			291	0.4	34	18	52	52	1	0.4	1		0.2	
M4		0.5	18	0.1	182	5	94	87	0.5	0.4	30		1	
M8		0.1	250		2	11	54	53	1	1	1		0.3	
M9		31	318	0.2	222	4	49	47	0.3	1	36	709	1	24

Several solutions were produced by addition of liquid trace element standards (added identifies the number of ppb) to initial solution (identified by number 1).

average values are reported in Table 7. If we consider the PAA values as the reference values, we can see that, if we except lead in sample M7 or arsenic in sample A1, concentrations are contained in the LA-ICP-MS results. However, the range of ICP-MS is very large, sometimes the maximum value being double or triple the minimum value, which means that it is hard to quantify the results.

In Table 8 we can see the concentrations obtained for a set of samples by ICP-MS in liquid mode. In order to have a larger spectrum of composition, solutions were also fabricated by addition of liquid standards to five base-solutions. The base-solutions were obtained by dissolution of samples taken from the reference material. The small fluctuation for iron is explained by the use of nickel extraction cones; zinc and lead show good agreement with the reference values if we except samples M3 and M8. For all the other elements, except sometimes antimony, the data correspond to the expected values. However, we must also consider the uncertainty of the PAA results (about 10%). No reference concentration was obtained by PAA for iridium and rhodium due to the bad detection limits.

In Table 9 we present the results obtained by PIXE for the measured elements under routine analytical conditions. If we except iron that presents some fluctuations (for alluvial gold maybe due to the black iron and iron-titanium oxides) and the heterogeneous nuggets named zere 4 and zere 9, we have a general good agreement with the PAA concentrations. However, we must remark that the PIXE limits of detection under routine conditions shown in Table 3 are in the same order of magnitude as those of PAA under optimized conditions (Fig. 1).

Fig. 4 shows a PIXE mapping for iron and platinum for sample F1. We can notice the heterogeneous distribution of these elements which explains the lack of agreement of the data obtained on this sample by the

various techniques. This sample is a European 18th century gold coin fabricated either with South American gold or with an Eastern European gold. We must remark that some South American gold ores have Pt-Fe and Pt-Pd-Fe compounds [26] and gold ores in the Urals have Pt-Fe compounds [40].

#### 4. Conclusion

All the major elements of the gold alloys—gold, silver and copper—can be determined by all the techniques used in this work except ICP-MS in liquid mode since silver is lost during sample dissolution. However, the concentrations obtained are sometimes quite far from the expected values, mainly for the ICP-MS techniques. On the other hand, PIXE might be influenced by the

Table 9  
Concentration of trace elements obtained by PIXE for a group of samples, nuggets (entitled zere) and standards (entitled std, certified values in Table 4)

Reference	%				ppm					
	Au	Ag	Cu	Pb	Fe	Ru	Rh	Pd	Sn	Sb
a37	78.7	19.9	1.2		953	69	31	20	107	0
R1	91.5	0.3	8.0		1056	5	17	21	94	63
A1	93.9	4.1	1.7		848	194	33	342	225	89
M2	97.5	2.1	0.1		1288	95	0	7	0	0
M1	81.7	17.4	0.9		1140	48	0	0	171	0
a66	92.7	6.8	0.3		580	37	0	86	348	9
F1	91.4	7.0	1.3		2047	119	46	216	496	61
a59	81.9	17.1	0.9		959	62	0	0	316	78
M9	93.8	0.1	0.1	5.9	874	248	27	15	194	4
zere4	97.6	0.7	0.1		20312	105	6	0	82	50
zere9	73.7	5.1	0.1		210067	355	0	5	126	45
std6917	75.9	17.2	6.7		416	53	37	40	0	39
std6905	75.2	6.4	18.3		1152	104	0	6	101	0
std6906	75.4	12.3	12.0		755	120	0	0	0	5

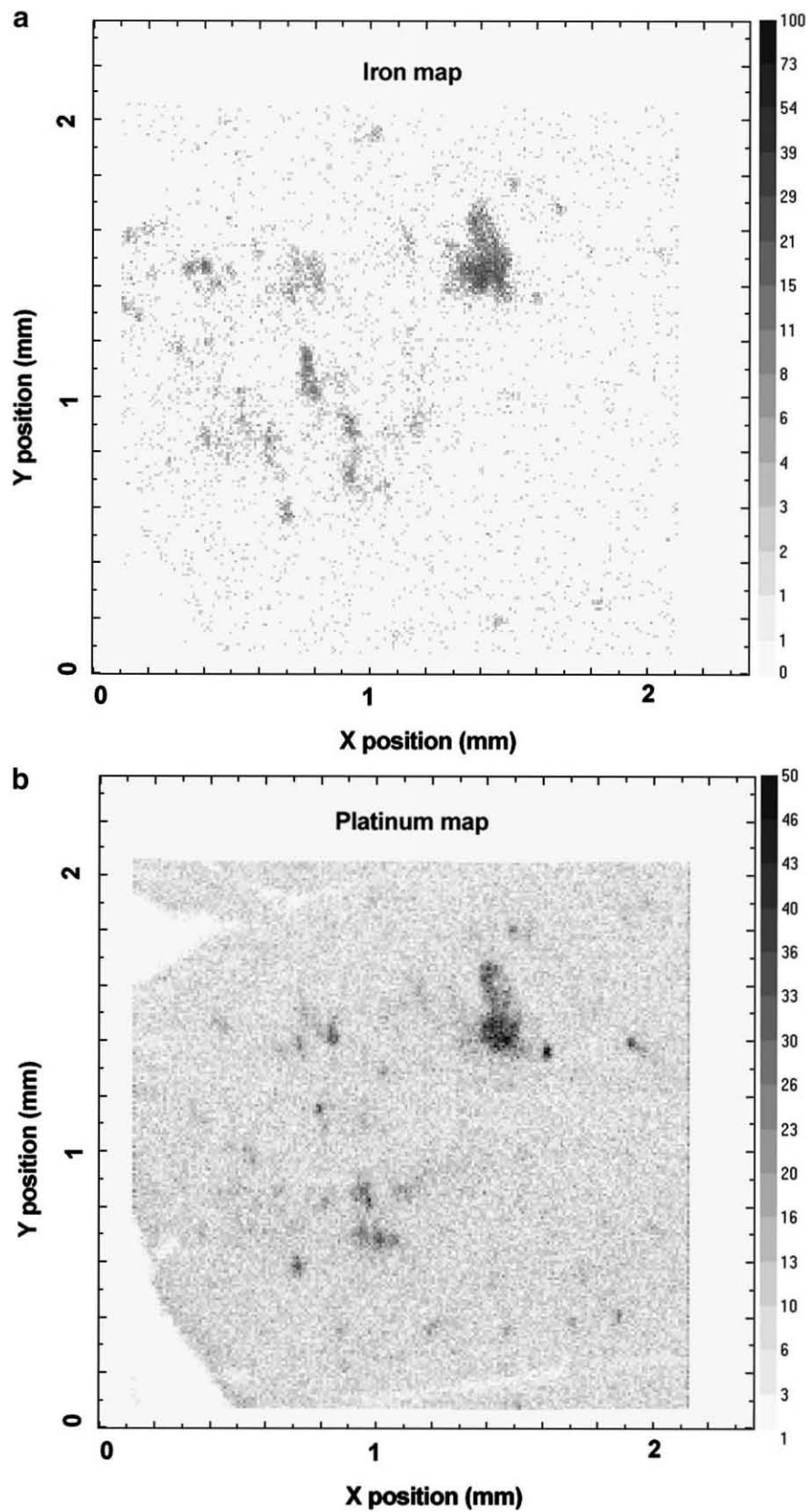


Fig. 4. PIXE mapping showing the heterogeneous distribution in sample F1 of (a) Fe and (b) Pt (scale indicates the number of counts).



heterogeneous composition of the surface, mostly for major elements (loss of copper). PAA, PIGE and FNAA yield coherent results but PAA cannot be performed on very small samples and FNAA measurement is quite time-consuming, expensive and cannot be performed on large samples. PIGE with a  $\mu$ -beam associated with PIXE is a good compromise as both techniques have complementary detection limits for silver and copper.

For the determination of trace elements, ICP-MS is the best technique when dealing with a large number of elements but only in liquid mode as laser ablation does not give quantitative results. However, ICP-MS needs a 2 mg sample to perform the analysis with a previous determination of the major elemental composition by another technique. PAA allows the determination of major and some trace elements, but this technique is time-consuming, expensive and very hard to adapt to the analysis of very large, very small or still composite objects. PIXE together with PIXE-XRF allows the determination of some trace elements with good detection limits for any type of object with an external beam, but elements like lead, giving information on debasement technology [23], cannot be measured with good detection limits. Wavelength dispersion spectrometry (WDS) associated with PIXE may overcome this problem as the lines resolution is better than in energy dispersive (EDS) mode.

PIXE, PIGE and PIXE-XRF can be used to obtain the first non-destructive information on a set of gold objects that can be improved by the later analysis of a subset of objects by ICP-MS in liquid mode selected according to their chemical composition.

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