Analysis of Archaeological Metals. The Place of XRF and PIXE in the Determination of Technology and Provenance

Maria Filomena Guerra*

CNRS, Centre de Recherche Ernest-Babelon, UPR 7548, 3D rue de la Férollerie, 45071 Orléans Cédex 2, France

Problems concerning the determination of technology and provenance of archaeological metals are presented using several historical examples and considering the heterogeneity of the alloys. PIXE and XRF are compared to other techniques (PIGE, nuclear activation, LA-ICP-MS); their limitations and complementary aspects in obtaining historical information are discussed. © 1998 John Wiley & Sons, Ltd.

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INTRODUCTION

Two questions are particularly important for archaeological metals, one concerning the evolution of the use of metals and the other the authenticity of the artefacts. As archaeometry is a relatively new field of research, we have at out disposal a large number of techniques. Chemical and metallographic techniques have been used to evidence the development of the gradual increase in the ability of Man in the manufacture of weapons, tools, vessels, ornaments and currency. However, in contrast to ceramics, there has been limited success in determining the provenance of ores and establishing trade routes.

The difficulties in the determination of the origin of metals are due to several problems such as the rarity of the ore deposits, the high temperature required for smelting, inducing changes in trace elements, the corrosion during burial periods and the fact that metals are easily re-melted and re-used to make other objects.

One of the first techniques used in the non-destructive analysis of archaeological objects was certainly X-ray fluorescence (XRF). The development of the milliprobe[1] and of small portable systems[2] in the 1960s, the replacement of the x-ray tube by an x-ray source and a Ge(Li) detector[3] and then the development of the isoprobe[4] at the beginning of the 1970s gave rise to an x-ray analysis boom and so to a large number of applications in art and archaeology.[5,6]

Although the suggestion of the use of protons as the incident beam for x-ray analysis was made in 1964,[7] only in 1970[8] was the first experiment performed with a van de Graaff accelerator. This showed the possibilities of the determination, in a thin sample, of elements with concentrations of about 10^{-12} g g^{-1}. Later, other beams were employed (heavy ions and α-particles[9]) and other accelerators were used to produce the beam (cyclotrons and more recently synchrotrons).

Although PIXE has had a huge application in several fields (biology, medicine, geology, etc.), only at the end of the 1970s did laboratories started to apply this technique to the study of archaeological and art objects.[10–13] During the 1970s the development of the external beams and of the first proton microprobe opened up new possibilities for the use of the technique in the anlaysis of bulky and irregularly shaped objects, inclusions, soldering, etc. Several PIXE laboratories are equipped with these two systems and apply them in archaeology and art.[14]

XRF AND PIXE TECHNIQUES

When we analyse archaeological metal objects, we want to cause a minimum of damage to the artefact: we must perform non-destructive analysis. However, in contrast to precious metals, the others tend to suffer corrosion during burial and so the surface layer may be thick compared with the penetration of the x-rays. For example, the analysed depths for tin by EDXRF in typical silver and gold matrices are about 200 and 30 µm, respectively.[15]

Both XRF and PIXE are non-destructive, fast, multi-element techniques which analyse the surface layer and determine major and minor as well as some trace elements in thin and thick samples of all sizes and forms. Surface profiles are determined mainly by PIXE, and also depth profiles which are hard to process owing to the first layer contribution corrections.

An enormous amount of work has been published on these two techniques. Whereas during the 1970s most work involved thin targets, several papers on thick targets appeared during the 1980s. A very interesting

paper summarizing the state of thick target PIXE (TTPIXE) was published by Campbell and Cookson,[16] where the problems of the analysis of archaeological artefacts were also mentioned. For EDXRF and TTPIXE, the secondary fluorescence correction for thick targets has been treated by several workers,[17–19] in addition to the correction for matrix effects.[20,21] One of the major problems posed by archaeological materials is the sample preparation. In fact, targets should be uniform and have a flat surface for accurate positioning and orientation relative to the beam and the detector. However, routine methods, which require cut and polished samples, cannot be used and so the flattest surface must be chosen for analysis.

For quantitative elemental evaluation on thick targets we can use either reference standards or algorithms describing the phenomena. The first solution is expensive for a wide range of matrices and compositions,[22] whereas the use of a semi-empirical equation describing the mechanism of the phenomena and introducing some measured parameters is an easy inexpensive solution.[23–25]

We have also used a semi-empirical equation for both EDXRF and PIXE. It describes the mechanism of the phenomena and introduces some measured parameters, with correction for matrix effects;[12,21] corrections for inter-element crossed effects are made empirically for some elements with reference standards. In fact, in the case of archaeological metals, we constrain the concentrations to 100%, which means that only relative x-ray intensities are required. The use of an internal standard eliminates further complicated measurements. The efficiency of germanium detectors was determined by means of the escape peaks phenomena.[21] Figure 1 shows for bronze and brass certified standards that
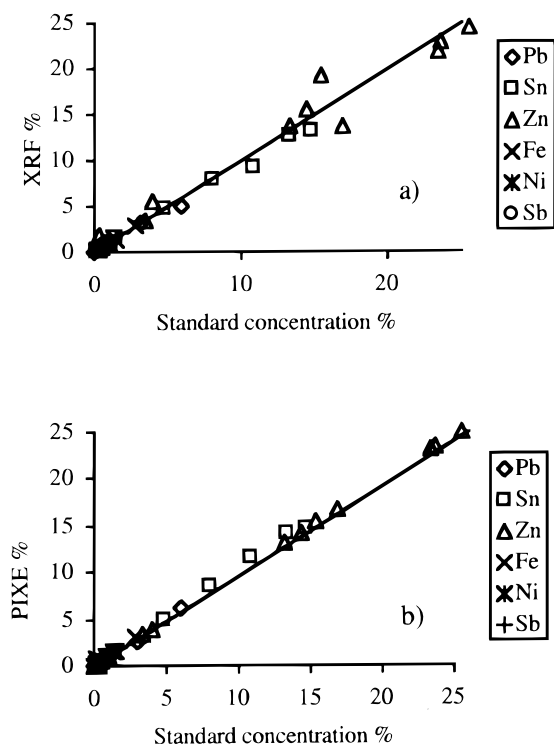
good agreement is obtained for measured and certified concentrations[21,26,27] (zinc interferes with copper).

The limits of detection (LOD) for thin targets are generally better for PIXE than for EDXRF. The detection limits for protons from 1 to 4 MeV can attain the ppm level for $15 < Z < 45$ and about 5 ppm for $Z > 45$.[28] Suitable filters can be used for selective absorption and secondary x-rays are formed at lower rates. However, interferences seriously affect the sensitivity and self-absorption of emerging x-rays in thick samples.

For some special thick samples, such as the determination of heavy metals in low-Z alloys,[29] the LOD for EDXRF may reach 10 ppm for lead in bronze (it is possible to measure 20 ppm on bronze alloy using EDXRF and R/C ratios[30]) and about 1 ppm for the lanthanide series (note that for archaeological metals, lanthanide elements suffer oxidation and evaporation during smelting). We know the differences in the empirical LODs of trace elements in copper and iron archaeological matrices for PIXE.[31] For example arsenic, tin and lead have LODs of about 160, 70 and 110 ppm, respectively, in copper and about 10, 110 and 40 ppm in iron. Several papers discuss the comparison between PIXE and XRF.[22,32,33] Most workers agree that they are complementary techniques, depending on the kind of matrix and the atomic number of the determined elements. This is evident from the comparison between the Kα x-ray production cross-section as a function of the target atomic number for irradiation with ^{55}Fe, ^{109}Cd, ^{241}Am and 1–3 MeV protons.[34]

One of the rare papers on the comparison of PIXE and XRF in the archaeology and the arts was published by Malmqvist,[33] who, like the others, concluded that the techniques are complementary. During the last 10 years, archaeological sciences has seen major developments mainly in micro-beams for XRF and PIXE, XRF portable systems[35,36] and PIXE external beams; for the analysis of small samples, techniques such as ICP-MS now provide LODs at the ng ml^{-1} level.[37]

In our opinion, for archaeological metals and considering budget problems, EDXRF allows a good compromise for the elemental analysis of archaeological metals. Low-Z elements are of little importance for the main historical questions and the use of small beams allows one to choose 'flat' regions of analysis. The background is of the same order of magnitude for both techniques in the most important x-ray region and the sensitivities can reach very good levels when using secondary targets or a combination of several radioactive sources. Also, there is a much better penetration of the matrix than for protons, which may avoid some patina effects, and the quantitative evaluations are easier than for PIXE as there is no loss of energy during penetration.

PIXE can be equipped with a microbeam system[38,39] and EDXRF beams can be collimated even if the large decrease in intensity precludes the analysis of samples with as large diameters as in PIXE.[35] The advantages of PIXE concern, however, the micro-beams for some special cases, the association with Rutherford backscattering (RBS) for the study of thin layers, particle-induced gamma-ray emission (PIGME) to carry out depth profiles and particle and gamma-ray detection for

Figure 1. Comparison between certified values and (a) PIXE and (b) XRF results for certified bronze and brass standards from the Centre Technique des Industries de Fonderie.

Table 1. Results (%) obtained for five Roman copper alloy coins by PIXE, PAA and FNAA

Coin	Method	Fe	Ni	Zn	As	Ag	Sn	Sb	Au	Pb
1	PIXE (face)	0.17	0.01	0.13	—	0.07	0.08	0.1	—	0.19
	PAA	0.14	<0.01	0.11	0.044	<0.3	0.056	0.08	<0.05	0.09
	FNAA	0.14	0.008	0.11	0.045	0.03	0.055	0.115	<0.0002	0.065
2	PIXE (face)	0.99	0.02	9.3	—	—	1.4	0.83	—	0.15
	PIXE (slice)	0.46	0.016	11.0	—	0.04	0.63	0.15	—	0.31
	PAA	0.7	<0.02	10.8	0.038	<0.03	0.68	0.1	<0.1	0.3
	FNAA	0.55	0.015	10.5	0.032	0.04	0.6	0.11	0.07	0.31
3	PIXE (face)	0.85	0.02	8.8	—	—	1.2	0.28	—	1.17
	PIXE (slice)	0.21	0.035	13.8	0.1	—	0.26	0.22	—	0.1
	PAA	0.36	<0.05	12.0	0.051	<0.3	0.26	0.16	<0.05	0.2
	FNAA	0.21	0.026	12.3	0.052	0.04	0.25	0.24	0.00005	0.17
4	PIXE (face)	0.45	0.04	0.22	0.95	—	21.5	0.85	—	9.6
	PIXE (slice)	0.08	0.04	0.16	0.09	—	8.2	0.6	—	7
	PAA	0.12	<0.1	0.14	0.08	<0.3	9.4	0.1	0.003	12.6
	FNAA	0.09	0.03	0.37	0.8	0.07	4.5	0.1	0.003	12.6
5	PIXE (face)	0.16	0.073	0.12	0.15	—	5.2	0.26	—	22
	PIXE (slice)	0.1	0.04	0.39	0.12	—	5.9	0.13	—	10.3
	PAA	0.11	<0.1	0.35	0.12	<0.3	5.6	0.11	<0.05	15.4
	FNAA	0.14	0.035	0.35	0.12	0.07	3.1	0.11	0.027	16.2

the determination of complementary elements (in the case of archaeology and the arts see Ref. 14).

HISTORICAL QUESTIONS

The main questions in the field of archaeological metals concern the manufacturing technology of the artefact and the provenance of the ore. From the archaeological scientist's point of view, some questions may be simple such as the fineness of a certain coinage (determination of gold for gold coins and silver for silver coins) or the type of alloy (e.g. arsenical copper or bronze), which only need the determination of the major elements; however, more elaborate questions concerning possible re-melting and changes in ore supply may be posed, needing the determination of trace elements[40,41] (e.g., are the copies of the Philips II of Macedonia stater found in Gaul made with Greek gold ?).

Although in recent years we have been able to answer some of the historian's questions on manufacturing technologies, the origin of the metals remains a very difficult question. In fact, two cases exist: either we know the mine exploited to obtain the ore used for the manufacture of a group of artefacts or, which arises much more often, we do not know the mine. Whereas for the first case only one trace element may be enough to follow the metal, for the second only the determination of a group of trace elements (often at very low concentrations) or/and the determination of lead isotope ratios may identify the sources of raw material. For the first case some examples have been successful,[42,43] but very few examples are known for the latter situation,[44,45] even for native metals that suffer less processing.

Although the determination of lead isotope ratios[44] and of trace elements at very low concentrations is a difficult analytical problem for any type of sample,[46] for

archaeological objects other problems exist concerning non-destructive analysis, heterogeneity and surface enrichments as well as surface treatments.

HETEROGENEITY OF ALLOYS

Gold, silver and their alloys do not generally present corrosion and oxidation layers and heterogeneities. However, we have to consider some surface enrichments[47] and surface treatments[40] such as blanching, gilding, preferential removal of more reactive metals and plating (manufacturing technology or forgery).

Surface enrichments for archaeological gold have been treated by several workers,[22,47] showing that surface techniques may give a 20% relative error in gold content. Also for silver alloys we have the same problem. Oxidations are responsible for variations of the surface composition, e.g. for an object containing 71% silver, the result obtained for the surface was 81%.[48] Tate[15] states, '. . . all the artefacts made of precious metal alloys . . . have shown, to a greater or lesser extent, surface depletion of the less noble metal,' depending on burial conditions, alloy composition, fabrication technique, etc. He analysed three Viking silver ring coins by EDXRF using four stages of abrasion and measured for silver 80, 80 and 75%, respectively, on the surface and 76, 55 and 60%, respectively, in the last stage. SEM showed a copper-rich phase of 150–200 µm.

Copper alloys (including copper–silver alloys, the so-called billion of numismatists) are used for the manufacture of all kind of objects. Unfortunately, they are subject to all types of phenomena: surface enrichments, corrosion, heterogeneity, etc. Considerable work has been done on corrosion and surface enrichments since the first papers at the beginning of the 1960s.[49–51] Brass alloys analysed by seven different techniques present

disparities between the surface and the bulk composi-tions.[52] Methods using drilling are susceptible to being unrepresentative of the entire object. We analysed five Roman coins covering the most common copper alloys[27] by PIXE (surface: a few μm), 12 MeV proton activation (PAA, semi-global: 300–400 μm), fast neutron activation (FNAA, bulk) and SEM (profiles). The difference in the composition as a function of the technique (and so of the depth of analysis, note coins 3 and 4 for tin, lead and zinc) is shown in Table 1. PIXE results on the slice correspond better to the bulk ones than on the face.

Figure 2 shows the SEM profiles on the slice of lead bronze coin 4 and explains the differences observed for the three techniques. It shows that for certain coins the patina may attain 100 μm thickness; although in some cases the patina may be removed, for lead bronzes the lead and tin precipitates may be present all over the coin, giving random concentrations.

These results demonstrate how important the choice of the technique is: the type of alloy and the conserva-tion of the object must always be considered. Surface techniques may give wrong historical conclusions, as illustrated by the following example for a group of arsenical copper artefacts from the Iberian Copper Age.[53] When we plot the concentration of arsenic obtained on 23 artefacts by EDXRF and FNAA (see Fig. 3), we see that EDXRF shows that for some arte-facts, contrary to the results obtained by FNAA, there
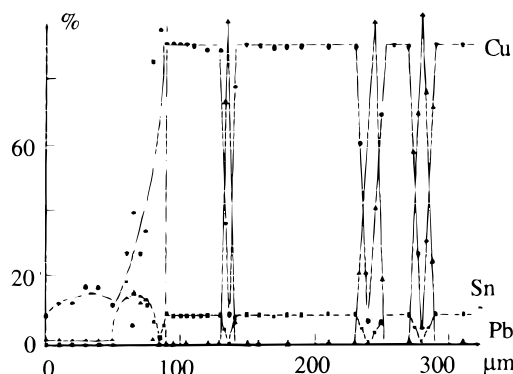
was a deliberate addition of As (>5%) to improve hardness, with the advantage of lowering the melting point.

Two artefacts were cleaned by mechanical abrasion and the concentrations of As measured by XRF and PIXE on the cleaned face agreed. In fact, the As profile obtained by LA-ICP-MS (inductively coupled plasma mass spectrometry with laser ablation[46]) on one of the artefacts slice showed the migration of this element into the surface.

It is evident that XRF and PIXE give good results when there is no patina. In fact, archaeological samples bring new difficulties to the archaeological scientist. It is evident that the use of Carter's technique of surface mechanical abrasion gives the bulk composition even if errors are sometimes unavoidable.[53] However, for pre-cious objects, for which cleaning cannot be carried out, and lead bronze alloys only the use of bulk techniques avoids the risk of a wrong historical conclusion.

SOLVING HISTORICAL QUESTIONS

Manufacturing technology

One of the most important advantages of XRF and PIXE in art and archaeology is the use of microbeams and external beams, as shown by the study by PIXE of the jewels from the Eauze treasure (Gers, France), a typical ensemble from the 3rd century. The use of an external beam allows the analysis of every object and a small beam that of every soldering. The composition of the jewels' alloys explains the manufacturing technol-ogies of the goldsmiths.

Most of the jewels are made of an average alloy: 91.5% Au, 7.5% Ag and 1% Cu (ranges: 85–99%, 1–14% and 0.2–2.3%, respectively) and Fig. 4 shows the double distribution of compositions: a horizontal on the silver axis around 0.75% Cu and a vertical in the
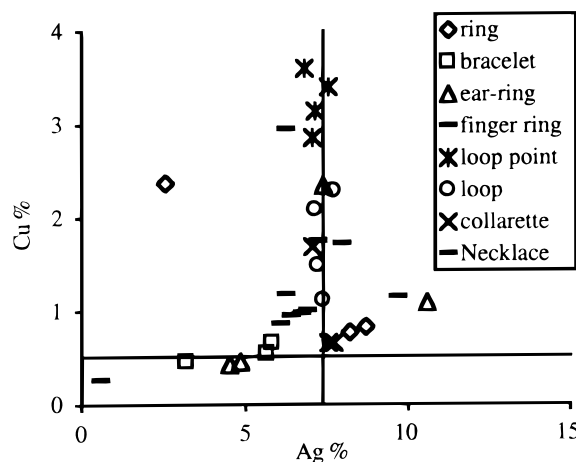

Figure 2. Pb, Sn and Cu SEM profiles for lead bronze coin 4.

Figure 3. As concentration obtained by XRF and FNAA for Copper Age artefacts.

Figure 4. Distribution of the composition for the jewels from the Eauze treasure.

copper axis around 7.5% Ag. This distribution shows that most of the objects are made with native gold (3–12% Ag and <1% Cu) and the same typological groups do not have the same composition, and so not the same origin. Certain parts of the objects have a higher concentration of copper, such as the loop points: deliberate addition of copper increases the hardness and lowers the melting point.

The analysis of the soldering on all objects shows a small increase in copper with the silver concentration remaining constant. This is a typical case of soldering by copper diffusion (addition of copper compounds instead of pure metals to gold and silver).

The variation of the energy of the incident beam for PIXE may be used for depth profile analysis for the study of surface technologies (e.g. silver and gold surface treatments), as shown by a recent study of surface gold treatment (tumbaga) in pre-Colombian objects and fakes;[54] it may be associated with the use of the L line/K line ratio[55] for some elements by EDXRF.[56] However, the depth of analysis in gold is short owing to the high absorption rate for x-rays and so for plated objects (thicker surface layer) depth profile proton-induced gamma-ray emission (DP-PIGE)[57] is an excellent technique for determining the composition of both surface and substrate.[58]

The analysis of Roman (4th century) and Merovingian (5th–7th century) gilded brooches[59] by PIXE and RBS showed that for the surface layer, the silver and copper concentrations are very varied for each typological group and the Hg/Au ratio is the same for both periods. This means that there is no change in technology. However, the analysis of the substrate by PIGE (plating thickness reaching 11 μm) shows that the bronze used by the Romans is replaced for the Merovingian jewels by a copper–silver alloy rich in silver (except for one typological group). This manufacture change corresponds, contrary to the complete gilding of Romans, to a silver–gold colouring effect by partial gilding.

Both XRF and PIXE are good techniques for the analysis of major elements used in the manufacture of artefacts and coins and so solve many of the existing historical problems; XRF has the advantage of *in situ* measurements (museums and archaeological sites) by means of portable systems. For other questions these techniques may be only a first approach and so be used as complementary techniques, as shown by the following example.

A group of blanched (silvering technique common in the Middle Ages) billion dinheiros from the first dynasty of Portugal (1128–1383) were analysed by EDXRF to determine the debasement.[60] Figure 5 shows that the fineness corresponds to the legal one except for the troubled reign of Fernando I (F) and that two groups are formed in the second reign (Sancho I). Two questions are posed: which is the composition of the surface layer and why are there two groups for the second reign? As XRF does not give any answer to these questions, coins from all the typological groups were analysed by FNAA for trace elements and two coins were analysed by SEM.

SEM analysis shows that blanching was done by preferential removal of copper, leaving a 1–2 μm silver
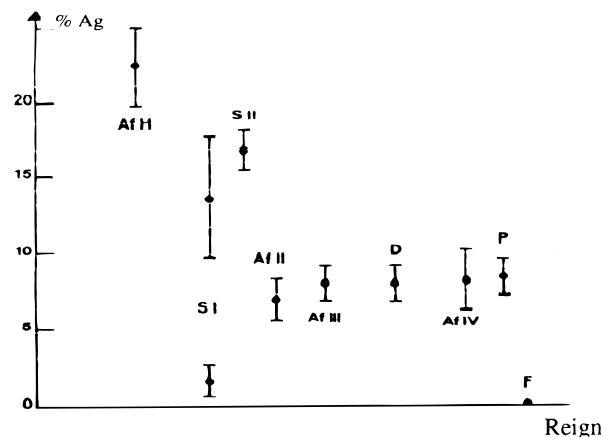

Figure 5. Fineness evolution of the dinheiros from all the first dynasty of Potuguese reigns.

layer. The As/Cu ratio determined by FNAA indicates the existence of two copper supplies (see Fig. 6), one to the north mint (low As/Cu) and another to the centre and south mints (high As/Cu). A new chronology is proposed: the group HSII which was typologically attributed to Sancho I corresponds, in fact, to the coins minted during the troubled period of Sancho II's reign.[61]

Although we were able to determine the manufacturing technologies of the coins, to propose a new chronology and find different ore supplies, trace elements were insufficient to attribute a provenance to the copper ores.

Provenance

Most provenance studies are done on ceramics and stone materials, as with metals the smelting processes change the composition of the original ore and re-melting and re-use complicate the problem. Hence it is very difficult to find a metal–ore correlation.

Tracing to source is very important for detecting forgeries[62] and for solving historical questions. A general view over all the archaeological matrices was
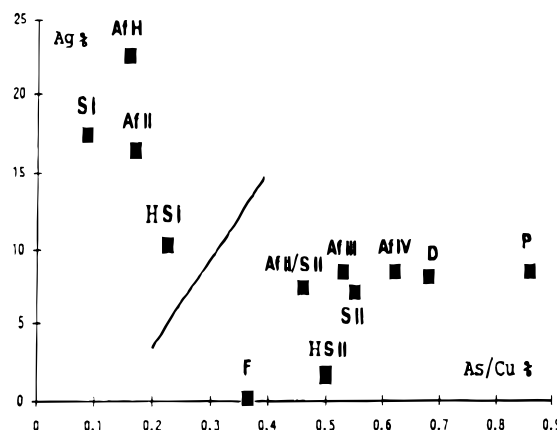

Figure 6. As/Cu ratio as a function of Ag content for all typological groups.
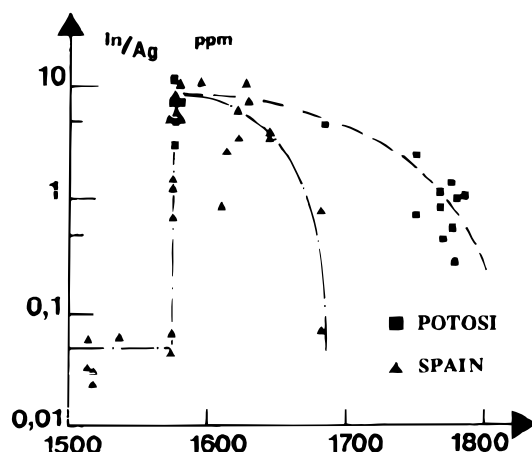
Figure 7. Evolution of the In/Ag ratio with time for Spanish and Potosi silver coinages.

Table 2. Comparison between the limits of detection (ppm) for PAA and LA-ICP-MS

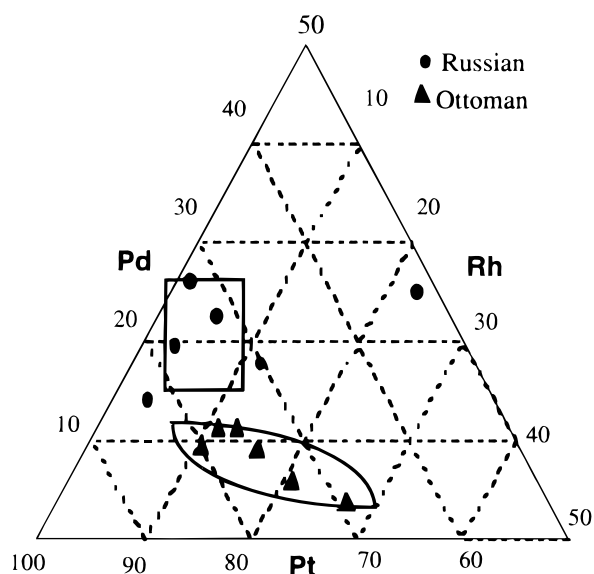| Element	PAA	LA-ICP-MS
Ti	1	0.20
Fe	1	0.50
Zn	5	0.03
Ga	10	0.02
As	1	0.06
Ru	2	0.04
Rh	1000	0.09
Pd	2	0.03
Cd	5	0.03
Sn	1.5	0.04
Sb	1	0.01
Te	1	0.02
Os	20	0.04
Ir	20	0.01
Pt	1	0.01
Hg	3	0.03
Pb	1	0.05

Figure 8. LA-ICP-MS PGE results for Russian and Ottoman gold coins.

given by Hughes.[63] A paper concerning the provenance questions for metal artefacts was published by Pernicka.[64] For provenance enquiries, only techniques having LODs at the $\mu g\ g^{-1}$ level may be used. A 'fingerprint' of the ore deposit must be formed either by trace elements or by lead isotope ratios; these elements and isotopes must not be affected by weathering and oxidation or by metallurgical processes. One of the rare examples of provenance research concerns Sassanian silver[45] by NAA with chemical separation: of the 17 elements determined only gold and iridium concentrations (1–1000 ppb) give criteria to distinguish different origins of silver ores. Also, the high concentration of certain trace elements together with geochemical data and written documents may give some identification of the ore's source,[63] e.g. the high concentration of arsenic in copper.

Among others, the most important elements for the determination of precious metals' provenance are the platinum group elements (PGE); a description of the characteristic elements of metal matrices is given in Refs 6 and 64. To cite Pernicka,[64] PIXE is a powerful analytical tool for the identification of technology, but for provenance studies, PAA for gold and NAA for silver and lead offer the best sensitivities and must be combined with lead isotope ratios determination. In fact, after the publication of his work, only NAA for silver, lead isotope ratios for copper and silver and PAA for gold have solved a very few questions.

We have already seen that for provenance studies we have two situations: either we know the mine and one trace element may be enough to follow the metal, or we do not know the mine and trace elements and/or lead isotope ratios must be determined. For the first situation we were able to determine the arrival of some of the New World precious metals in Europe between the 16th and 18th centuries and to estimate the amount arriving in France.[42,43] We used In to follow the silver from Potosi and palladium to follow the gold from Brazil.

For silver from Potosi, several historical documents refer to the arrival of South American silver in Europe and also to the inflation observed during the 16th century.[65] During the 1970s, Gordus et al.[66] tried in vain to date the arrival of the silver from Potosi in European coinages by using NAA. We made a new attempt making use of geochemical data on the silver ores from the Andean region. These data revealed that Andean silver ores contain rare elements such as germanium and indium. These elements do not occur in Mexican and European ores (Spanish, French, Italian, etc.). We developed a non-destructive global technique based on the moderation in graphite of a fast neutron beam from the cyclotron especially to measure, among others, indium and gold with an LOD of about 50 ppb in the silver coins.[67] The global technique guarantees the amount of silver measured in the coin (In/Ag ratio).

Figure 7 shows the evolution of the In/Ag ratio as a function of the date of issue of the Spanish and South American coins. The dilution of silver from Potosi in another silver ore (Mexico and Europe) makes the gold content vary from 2.3 to 5235 ppm and indium from 0.03 to 10.2 ppm. We can note the appearance of indium in the Spanish coins struck under Philip II,

Table 3. Concentrations of some PGE elements in the analysed coins[a]

Coin	Reign	Rh (ppm)	Pd (ppm)	Ir (ppm)	Pt (ppm)	Au (%)
Russian						
BN632	Alexis	13	8	4	65	98
BN673	Ivan Pierre and Sofia	30	4	3	75	98
BN764	Pierre I	20	18	5	120	93
BN803	Pierre I	17	15	6	130	97
BN840	Pierre I	595	175	32	2090	81
BN865	Anne	18	18	4	125	93
BN958	Elisabeth I	135	110	10	315	93
BN1013	Catherine II	160	—	—	2	92
BN1070	Catherine II	—	7	4	690	99
Ottoman						
BN920	Mohamed I	36	55	11	215	99
BNV1616	Abdulhimal I	15	60	4	195	93
BN830	Suleyman	—	2	—	11	96
BN	Ahmed II	1	3	—	13	95
BN2361	Mustafa III	—	6	6	17	98
BN1075	Selim III	30	35	16	70	96

[a] BN = Bibliothèque Nationale de Paris.

which means that Potosian silver crossed the Atlantic and was then quickly diluted in another silver ore. The arrival of Potosi silver corresponds to the introduction of the more productive silver extraction by the mercury amalgam method in Peru, following the opening of the mercury mines in the Huancavelica region in 1563–64.

As we have already indicated, the origin of archaeological ores remains a very difficult analytical problem. For example, for South American silver and gold, we were unable to differentiate Mexican from European silver and to determine the origin of the gold in which Brazilian gold was diluted in France and England.

The most difficult analytical cases concern pure and native gold (lead level < 100 ppm), as a theoretical minimum of 100 ng of lead is needed for lead isotope ratio analysis.[43] Therefore, archaeological scientists turned to the determination of trace elements such as the PGE to characterize gold. ICP-MS is becoming one of the most powerful multielement techniques for the characterization of materials owing to its low LOD and broad linear dynamic range. When associated with laser ablation, LA-ICP-MS becomes a virtually non-destructive technique (craters of about 40 μm diameter and 130 μm depth for an Nd:YAG laser used in the UV region and operated in the Q-switched mode[68]).

The improvement in LOD for LA-ICP-MS for the group of elements determined by PAA in gold is shown in Table 2.[68] With this very recent technique we were able to differentiate several gold ores.[69] To illustrate its potential we present in Fig. 8 the Pd–Pt–Rh diagram forming two distinct groups for Russian and Ottoman gold minted during the 18th century. The concentrations of these elements are given in Table 3.

CONCLUSION

As the major elements are strongly activated by thermal neutrons and as chemical separation is difficult and tends to reduce the number of studied artefacts, XRF, AAS, PIXE and other IBA techniques, epithermal and fast neutrons as well as proton activation have been mostly used to analyse archaeological metals.

To determine the metal manufacturing technology, major, minor and some trace elements are the most significant, so XRF and PIXE solve an important number of historical questions. Although for some samples they are influenced by the surface corrosion and the heterogeneity of the alloys, they have the advantage of processing microanalysis and using inexpensive portable systems. The use of complementary techniques on a sample gives maximum information.

Although we are now able to solve most of the manufacturing technology questions and follow some ores, the provenance of metals is still a difficult question for archaeological scientists and very little is known in this field. The development of new techniques is opening up new possibilities of research.

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