Cercetări numismatice, XV, Bucureşti, 2009, p. 43-56

NUCLEAR METHODS AND LASER ABLATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY: HOW CAN THESE METHODS CONTRIBUTE TO THE STUDY OF ANCIENT COINAGE?

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Abstract

The Centre Ernest-Babelon developed and applied two different nuclear methods using a cyclotron for numismatic studies: Proton Activation Analysis (PAA) and Fast Neutron Activation Analysis (FNAA). At the beginning of the 1970s PAA was developed to study ancient gold coinage and in the 1980s FNAA was improved to determine non-destructively the contents of the major, minor and trace elements in silver and copper alloys coins. These two nuclear methods were successfully used to study numismatic and historical issues covering all periods and geographical areas. But they present some drawbacks. Therefore a complementary method was recently developed for the non-destructive analysis of archaeological gold and silver artefacts: Laser Ablation Inductively Coupled Mass Spectrometry (LA-ICP-MS). Basic quantitative analysis and depth profile analysis are performed. Comparison between these different methods are established. The capabilities of these methods are illustrated with numismatic examples: the provenance study of the Kushan minted gold, the Carolingian silver coinage, the identification of some bronze coins from the hoard of Olbia.

INTRODUCTION

After the pioneering work of Pieter Meyers at the end of the 1960s (Meyers 1969), the Centre Ernest-Babelon developed at the beginning of the 1970s Proton Activation Analysis (PAA) to study ancient gold coinage. The judicious choice of the particle's energy (11 MeV) permits a non-destructive multielemental analysis of these objects. In the 1980s Fast Neutron Activation Analysis (FNAA) was improved to determine with a bulk and non-destructively analysis the contents of the major, minor and trace elements in silver and copper alloy coins. And, last but not least, another method was recently and successfully developed for the non-destructive analysis of archaeological gold and silver artefacts: Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS).

This paper presents the whole analytical set of methods developed and available at the Centre Ernest-Babelon and emphasizes the last mentioned one, comparing these different methods. Their advantages are illustrated with numismatic examples.

THE METHODS DEVELOPED AT THE CENTRE ERNEST-BABELON

Proton Activation Analysis (PAA) and Fast Neutron Activation Analysis (FNAA)

PA and FNA are not explained in detail but only their characteristics are exposed (tables 1 and 2). The interested reader can find in previous publications further details (for a presentation of both methods see Guerra and Barrandon 1998; for PAA see Barrandon and Poirier 1985; for FNAA, see Beauchesne and Barrandon 1986, Beauchesne *et alii* 1988 or chapter II of Barrandon and Picard 2007 for an historical overview of the applied methods for copper based coins).

PAA makes possible non-destructive multielemental analysis of gold coins with low detection limits, ranging from about 10 ppm to 1 ppm. This method is suitable for silver coins, only if they have a high

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fineness of silver and if the silver surface enrichment that often affects these objects is negligible in comparison to the thickness analysed with this method. In fact, since the protons lose energy as they travel through the target and the probability of nuclear reactions (p,n) decreases with the energy of the incident protons, the thickness analysed with PAA does not exceed about 0.2 mm in silver and 0.1 mm in gold. PAA is not suitable for thin and small objects and for composite objects.

The radioactivity generated by the proton irradiation entails many constraints. PAA is a quite long method, because one month must pass by between the irradiation and the last measure of gamma emissions. Nevertheless PAA remains the analytical method of reference for gold coins for comparison purpose.

FNAA is also non-destructive and enables us to determine with a bulk analysis 11 elements among the most significant elements in silver and copper-based coins: antimony (Sb), arsenic (As), cobalt (Co), copper (Cu), gold (Au), iron (Fe), lead (Pb), nickel (Ni), silver (Ag), tin (Sn), zinc (Zn). The limits of detection can be as low as the fractions of ppm, in particular for the copper-based alloy coins.

The bulk analysis is especially useful for copper, copper alloys or billon coins. It is well-known that the surface of these coins has a composition that differs from the one of the core because of the corrosion (Condamin and Picon 1964 98-105, Condamin and Picon 1972 49-66). Moreover, lead forms inclusions in copper-based alloys. The bulk analysis ensures that the results obtained are representative of the average composition of the studied objects.

The drawbacks and restrictions of FNAA are related to the radioactivity and to the access to a cyclotron. But FNAA is the analytical method of reference for copper, copper alloys or for some billon coins, as no other method allows at the moment to determine their composition satisfactorily.

Table 1 — Proton Activation Analysis.

Name	PAA (Proton Activation Analysis)
Analysed struck alloys	Gold based alloys
Principle	Activation carried out by a beam of protons produced using a cyclotron; then gamma spectrometry measurements
Characteristics	Multielemental and non-destructive analysis; analysed weight of about 0.1 g (gold)
Determined elements	16 elements: antimony (Sb), arsenic (As), chrome (Cr), gallium (Ga), gold (Au), copper (Cu), iron (Fe), lead (Pb), mercury (Hg), palladium (Pd), platinum (Pt), ruthenium (Ru), silver (Ag), tellurium (Te), tin (Sn), zinc (Zn)
Limits of detection (lods)	1 ppm < lods < 10 ppm
Limits/ drawbacks	A cyclotron is necessary; not suitable for thin, small or composite objects (pieces of jewellery); long method

Table 2 — Fast Neutron Activation Analysis.

Name	FNAA (Fast Neutron Activation Analysis)
Analysed struck alloys	Copper-silver alloys; copper alloys
Principle	Activation carried out by a beam of fast neutrons produced using a cyclotron; then gamma spectrometry measurements
Characteristics	Multielemental, non-destructive and bulk analysis
Determined elements	11 elements: antimony (Sb), arsenic (As), cobalt (Co), copper (Cu), gold (Au), iron (Fe), lead (Pb), nickel (Ni), silver (Ag), tin (Sn), zinc (Zn)
Limits of detection (lods)	copper alloys: 0.1 ppm < lods < 50 ppm; copper-silver alloys: 5 ppm < lods < 0.2 %
Limits/ drawbacks	A cyclotron is necessary; long method

Table 3 — LA-ICP-MS and DPA-LA-ICP-MS.

Name	LA-ICP-MS (Laser Ablation Inductively Coupled Plasma Mass Spectrometry) and DPA-LA-ICP-MS (Depth Profile Analysis using LA-ICP-MS)
Analysed struck alloys	Copper-silver-gold; silver-gold
Principle	Micro-sampling using a laser and mass spectrometry performed on this sampling
Characteristics	Multielemental, almost non-destructive, single point analysis. It is possible to carry out depth profiles of the concentration of major and minor elements: DPA-LA-ICP-MS
Determined elements	Quasi all the elements ranging from Z=11 to Z=92
Limits of detection (lods)	Lods are generally inferior to 1 ppm for the basic quantitative analysis
Limits/ drawbacks	Matrix matched standards are required; not suitable for some alloys that appear to be heterogeneous

LA-ICP-MS for gold and silver alloys

On the one hand the constraints of radioactivity were emphasized and on the other hand our nuclear methods appeared to be not sensitive enough or even not able to measure some elements that could be interesting for provenance studies, such as some platinum group elements in gold or bismuth in silver coins.

Therefore a complementary method was recently and successfully developed for the non-destructive analysis of archaeological gold and then silver artefacts: Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) (Dussubieux and van Zelst 2004 353-356, Gratuze *et alii* 2004 163-169, Sarah *et alii* 2007 1163-1167).

LA-ICP-MS general principles

The objects to analyze are placed in an ablation cell flushed by argon carrier gas. The first step in LA-ICP-MS analysis is the micro-sampling using a laser ablation device. A high energy laser is focused onto the surface of the sample. The ablation rate can be adjusted from 1 to 15 Hz. The interaction between the laser and the sample causes the removal of matter that is transported by the argon flux to the ICP-MS. The ablated aerosol arrives then in the plasma torch where it is dissociated and ionized. The ions are extracted by the vacuum interface and separated depending on their mass to charge ratio. The ions are finally detected and the signal data are transmitted to a computer for the calculation of the concentrations. The laser ablation micro-sampling, whose diameter ranges from 20 to 80 micrometers, is invisible with the naked eyes, and is consequently suitable for the analysis of precious objects such as ancient coins.

Two types of analysis can be performed with LA-ICP-MS.

- The first type of analysis accumulates the signal of different isotopes during the laser ablation. It provides a basic quantitative analysis and the contents of 17 to 30 different elements (major, minor and trace elements) are determined. The concentrations are calculated from the mean signals measured on three different micro-samplings.

- The second type of analysis records the signals for each slice of time as the laser samples. It is called DPA-LA-ICP-MS (Depth Profile Analysis using DPA-LA-ICP-MS). Thus, it is possible to determine the variations of the contents of the major and minor constituents from the surface to a depth ranging between some tens of micrometers and more than 1 millimetre depending on the alloy, on the frequency of the laser shot, on the duration of the analysis and on the diameter of the sampling. This mode of analysis is particularly useful to study plated coins and enrichment phenomena that were intentionally made or that are consequences of corrosion and metallurgy.

Whatever the mode of analysis the calculation procedure involves matrix-matched standards whose composition is known and close to the objects to analyze. They are industrial alloys or archaeological alloys previously analysed using PAA or FNAA. Internal elements whose contents are assumed to be constant are used. And the sum of the concentrations of the detected elements is fixed to 100%.

The validation of the LA-ICP-MS analysis of gold coins

Celtic gold coins, Ecuadorian gold artefacts and French gold coins from the 18th century were analysed performing both methods PAA and LA-ICP-MS[1]. Most of the time a good agreement is achieved between these methods for the major elements gold, silver and copper (Figs 1, 2, 3). This means that the results obtained using LA-ICP-MS are reliable for large ranges of contents: from 30% to 100% for gold, from 0 to 50% for silver and from 0 to 60 % for copper.

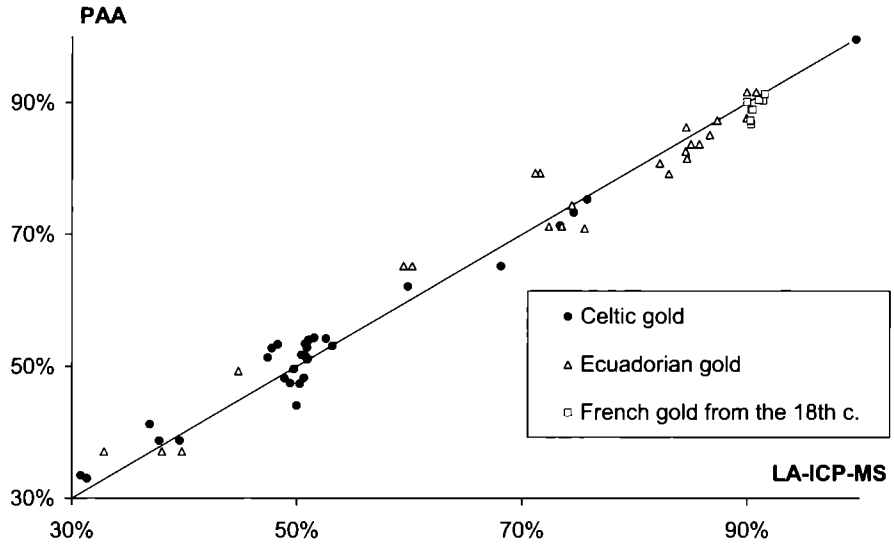

Figure 1 — Comparison between gold contents determined by LA-ICP-MS and PAA for different gold coinages or artefacts (Celtic, Ecuadorian, French).

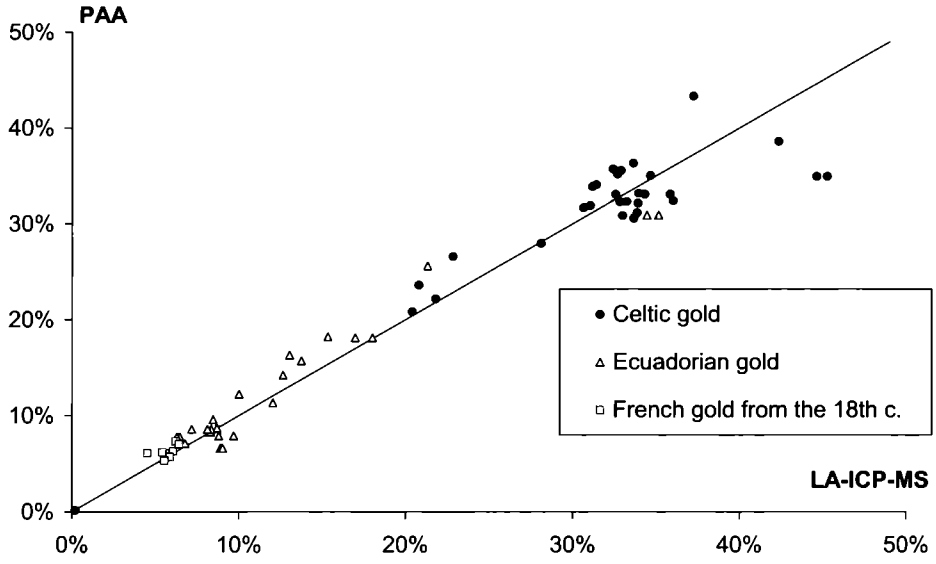

Figure 2 — Comparison between silver contents determined by LA-ICP-MS and PAA for different gold coinages or artefacts (Celtic, Ecuadorian, French).

[1] The analytical data obtained with the means of PAA for the Celtic gold coins are extracted from Nieto and Barrandon 2002 and from Nieto 2005; the study on Ecuadorian gold was carried out in collaboration with F. Valdez (Institut de Recherche pour le Développement) and Alexandra Yépez and Julio Hurtado (Museo del Banco Central del Ecuador), see Valdez *et alii* 2007 for further details.

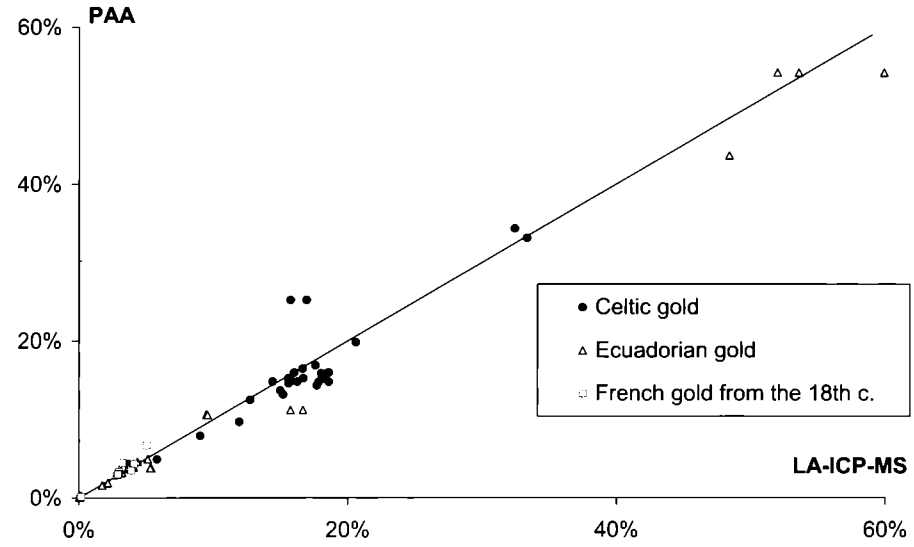

Figure 3 — Comparison between copper contents determined by LA-ICP-MS and PAA for different gold coinages or artefacts (Celtic, Ecuadorian, French).

The volume of analysed alloy using LA-ICP-MS is 50 to 100 times as small as the volume analysed performing PAA. It is necessary to check how it represents the mean composition of the alloy. This parameter is appraised as follows. The contents of each element are calculated from the mean value of three different micro-sampling. The relative standard deviation associated to this mean expresses how the archaeological alloy is homogeneous. It ranges from 3 to 5% for silver and copper contents determined for industrial alloys and for Arabic and French coins whereas it reaches 10% to 15% for some Celtic coins (Fig. 4). Celtic gold appears to be sometimes heterogeneous, especially for copper. The number of micro-samplings are then doubled in order to obtain a result that may be representative of the average composition.

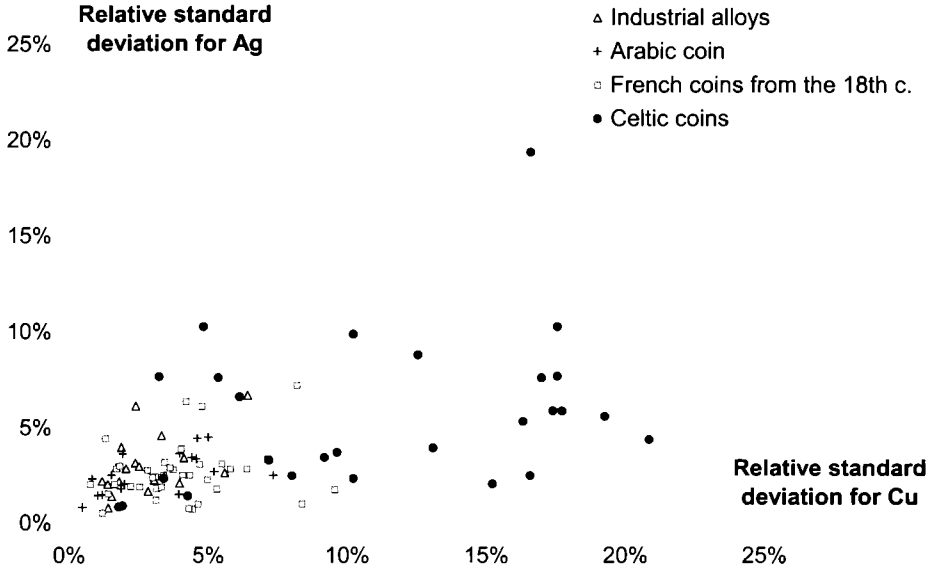

Figure 4 — Relative standard deviations calculated for the concentrations of silver *versus* this parameter calculated for copper, for industrial gold alloys and gold coins.

The comparison of the concentrations of trace elements obtained by PAA and LA-ICP-MS deals mainly with platinum and palladium. These elements are particularly relevant for a comparison because their concentrations vary in a large range for the analysed samples. Both methods are generally consistent (Figs 5 and 6).

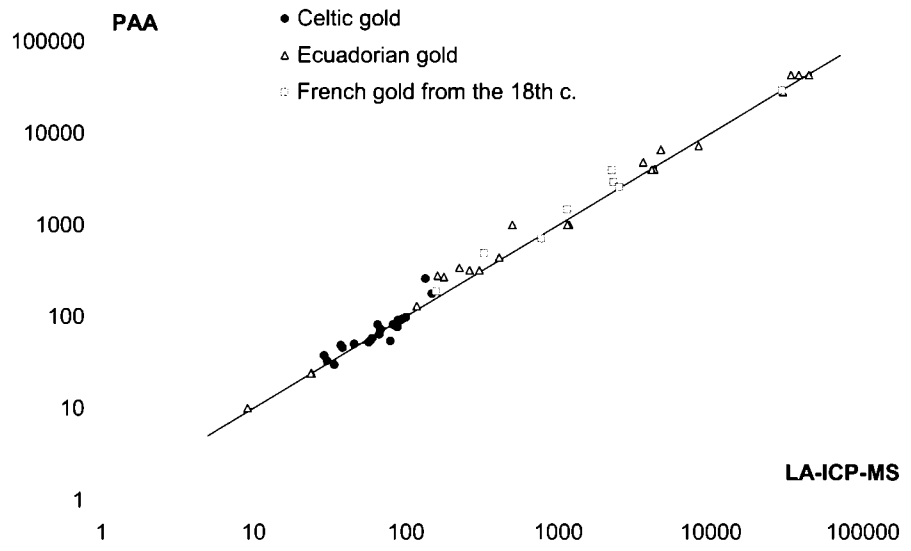

Figure 5 — Comparison between platinum contents determined by LA-ICP-MS and PAA for different gold coinages or artefacts (Celtic, Ecuadorian, French).

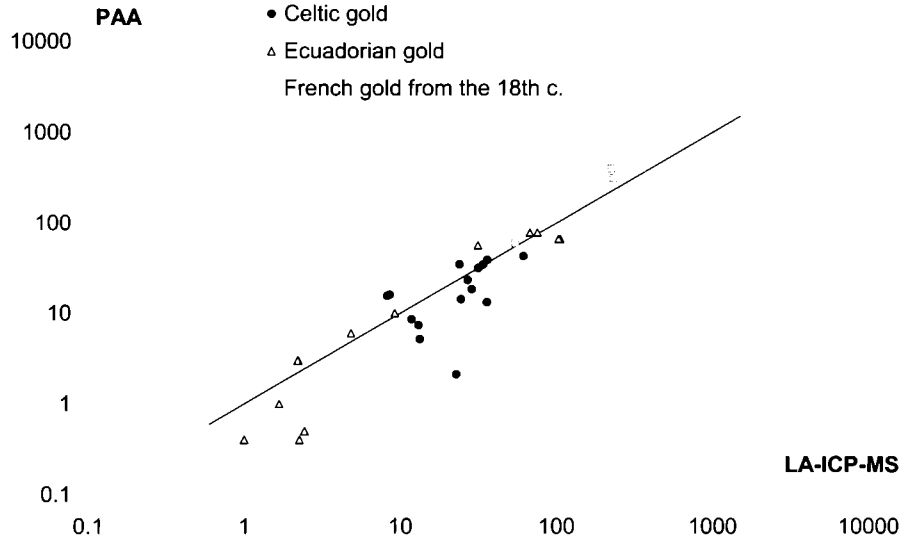

Figure 6 — Comparison between palladium contents determined by LA-ICP-MS and PAA for different gold coinages or artefacts (Celtic, Ecuadorian, French).

A good agreement is also achieved for numerous other impurities of gold based alloys (tin, antimony, arsenic). All of these trace elements seem to be quite homogeneously distributed in the alloy. The relative standard deviation associated with their content ranges from 5 to 15%. Lead, zinc, iridium, osmium, ruthenium and rhenium have on the contrary a rather heterogeneous distribution. The relative standard deviation associated with their concentration can reach 30 to 50% for these latter trace elements. It is well-known that the platinum group elements (*i.e.* ruthenium, rhodium, palladium, osmium, iridium and platinum) occur both as inclusions and in (homogeneous) solid solution in gold antiquities.

These limits are due to the fact that LA-ICP-MS performs a single point analysis. They only occur for some elements and some coinages. In spite of these drawbacks LA-ICP-MS is suitable to tackle every type of historical and numismatic problems dealing with gold coins, as PAA does.

Depth Profile Analysis using LA-ICP-MS for silver alloys

For the analyst the main characteristic of the ancient silver coins is the silver surface enrichment that often affects them. This enrichment is caused by segregation phenomena during the making of the blanks (Arles and Téreygeol 2011, Beck *et alii* 2004 153-162) and by the depletion of copper due to corrosion during the burying (Carter 1964 106-113, Condamin and Picon 1964 98-105, Condamin and Picon 1972 49-66).

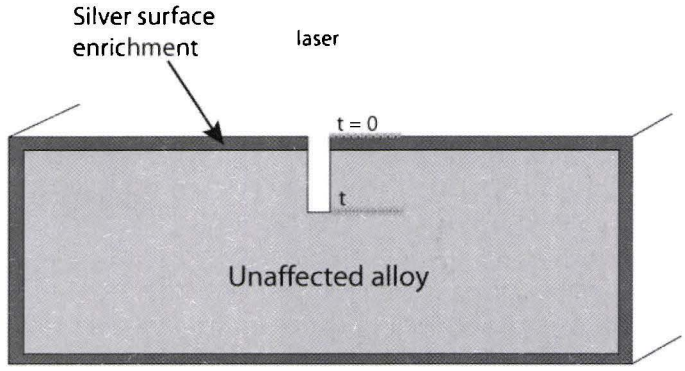

Figure 7 — Schematic cross-section of an ancient silver coin with a silver surface enrichment layer and representation of the progressive penetration of the laser into the sample.

As the penetration of the laser in the sample is progressive The Depth Profile Analysis using LA-ICP-MS allows obtaining concentration profiles (Fig. 7). The figure 8 shows the evolution of the silver and copper contents as a function of the time of ablation obtained for a silver Carolingian denarius: the surface enrichment can be observed and then a plateau of stability is visible. Thus, it is possible to determine the composition of the alloy that has not been disturbed by surface enrichment phenomena and that corresponds to the composition of the alloy at the time of the making of the coin.

Three depth profiles are carried out at different places on each silver coin and the composition of the major elements (silver and copper) and of five main minor elements (bismuth, gold, lead, tin and zinc) are calculated.

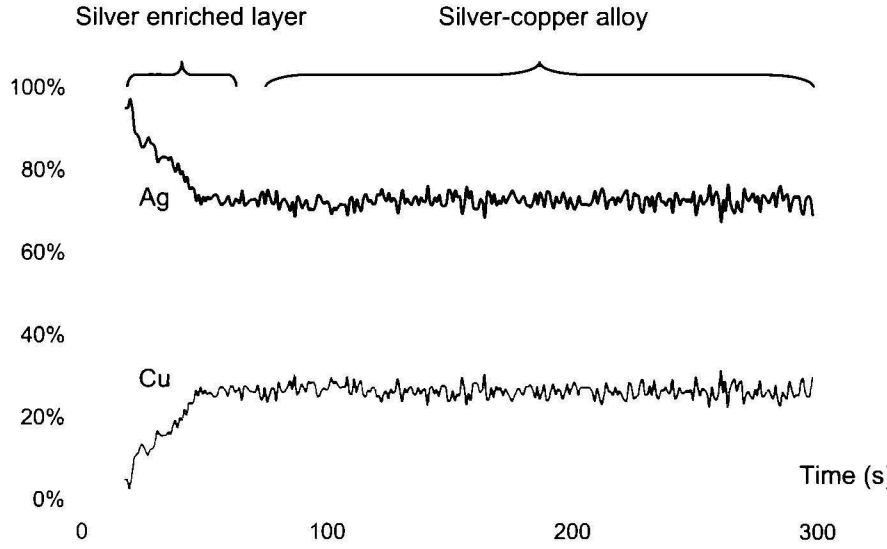

Figure 8 — Evolution of the silver and copper contents *versus* the time of the laser ablation obtained by DPA-LA-ICP-MS for a silver Carolingian denarius. The time scale can not be converted into the analysed depth (from Sarah *et alii* 2007 1163-1167).

The detection mode for the minor and trace elements is the basic quantitative mode in order to obtain the greatest sensitivity. Sixteen elements are determined in this minor and trace elements analysis. These elements have been chosen as they can be found in ancient silver coins, and might be used to distinguish different groups for the numismatic interpretation of the results.

The first point to verify is the reproducibility of the micro-sampling. The volume of the analysed alloy is about 3 times 0.0025 mm^3 that is negligible in comparison to the volume of a coin. It is primordial that the laser micro-ablations are representative of the entire alloy in order to obtain representative and thus reliable results. The standard deviation has been calculated on the three values determined for each element for 112 different Carolingian coins. For silver, this relative standard deviation is inferior to 1% for 79% of them. This shows that in most cases, the laser micro-ablations carried out on the same coin are reproducible and representative of the entire alloy. Consequently, the laser ablation is a suitable way of sampling for silver coins analysis.

Finally, the reliability of the developed protocol has been verified by a comparison between LA-ICP-MS and FNAA results (Fig. 9). The results obtained by both methods are in good agreement. The relative deviation for the silver contents above 90% is inferior to 2% in any case. For lower silver contents, this deviation can reach and sometimes exceed 5%. The coins corresponding to the points on figure 9 are Carolingian *denarii*. These coins are particularly thin: their average thickness is about 500 micrometers. The coins whose fineness is very high (above 90%) do not have a significant silver enriched layer at their surface, so the average content provided by FNAA corresponds to that of the unaffected alloy. But in the case of lower silver fineness, the surface enrichment of both sides of the coins might represent an important part of the coin, entailing an overestimation of the initial silver fineness by FNAA.

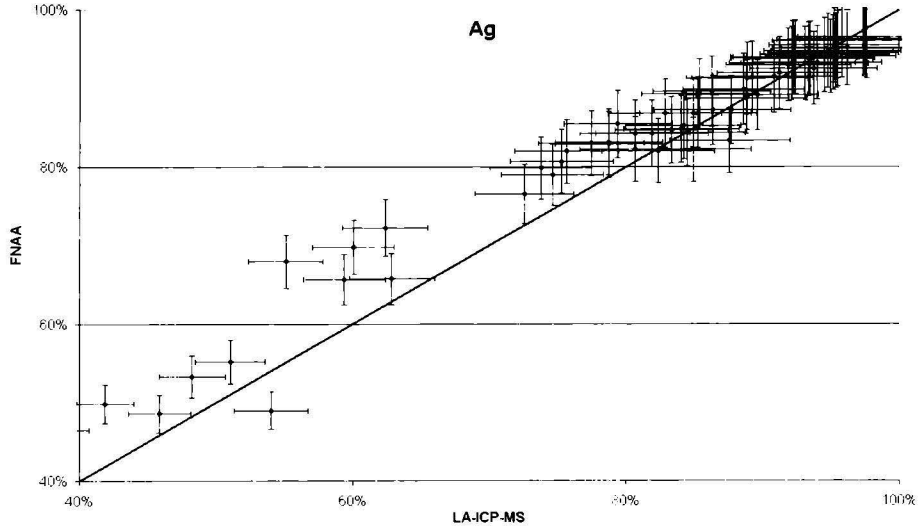

Figure 9 — Comparison between the silver contents determined by LA-ICP-MS and FNAA. Error bars fixed at 5% relative.

DPA using LA-ICP-MS and FNAA appear to complement each other. In most of the cases, LA-ICP-MS has to be preferred as this method is faster, more sensitive and allows the analysis of the alloy that has not been affected by surface enrichment phenomena. And as it has just been exposed, FNAA is susceptible of overestimating the initial fineness for thin coins. But FNAA is more suitable for heterogeneous samples for which LA-ICP-MS profiles are not representative.

Six minor and trace elements can be analyzed both by LA-ICP-MS and FNAA (antimony, arsenic, gold, lead, tin and zinc). The contents determined by the two methods in the Carolingian coins are compared in Sarah *et alii* 2007. For Zn, As, Sb and Au, the deviation is inferior to 10% in most of the cases, proving the good agreement between LA-ICP-MS and FNAA.

LA-ICP-MS permits to determine almost non-destructively and rapidly the concentration of many elements with very low detection limits in gold and silver alloys. This method is adapted to thin or composite objects such as gold foils and pieces of jewellery. The DPA mode allows studying plated coins and enrichment phenomena. The problem of the silver enrichment of copper-silver alloys coins can thus be overcome.

NUMISMATIC APPLICATIONS

The provenance study of the gold minted by the Kushanas

The provenance of the gold minted by the Kushanas is a controversial question. For some researchers, Robert Göbl for instance, Rome appears to be the most probable source, due to the direct trade relations between Romans and Kushanas (Göbl 1960 79).

The cataloguing of the Kushan coins from the Bibliothèque Nationale de France by Dr. Christine Sachs in collaboration with Professor Osmund Bopearachchi gave us the opportunity to analyze all the gold coins by PAA (Sachs and Blet-Lemarquand 2005 1659-1667). And to discuss the hypothesis on the provenance of the Kushan minted gold, we decided to analyse a sample of Roman Imperial gold coins minted from the 1st century and the beginning of the 2nd century A.D. by Augustus, Tiberius, Claudius I and Trajan (Blet-Lemarquand 2006 155-171). Coins were also selected following composition of hoards of Roman coins excavated in India. Two analytical methods were applied PAA and LA-ICP-MS.

It is well-known that Augustus and his successors maintained a high gold standard until the second half of the third century. (Callu *et alii* 1985 80). Our results confirmed this fact: the analysis showed that the Roman coins contain between 99.3 and 99.9% gold. In contrary to Roman aurei Kushanas and Late Kushanas gold was successively debased by adding about twice as much silver as copper; its fineness ranges from 99.9% to 84.1% (Sachs and Blet-Lemarquand 2005 1659-1667). But this comparison on the fineness is not sufficient to prove that both golds are different. It could be hypothesized that Kushans remelted down Roman gold coins adding silver and copper. The concentration of platinum and palladium that are characteristic trace elements of gold[2] bring decisive arguments to rule out this hypothesis and to conclude that both gold are different (Fig. 10).

Roman gold of Augustus, Tiberius, Claudius I and Trajan can be distinguished from Kushanas and Late Kushanas gold regarding the platinum contents: Roman gold contain 2 to 150 ppm, whereas the contents of this element range from 200 to 1000 ppm in the other gold coins.

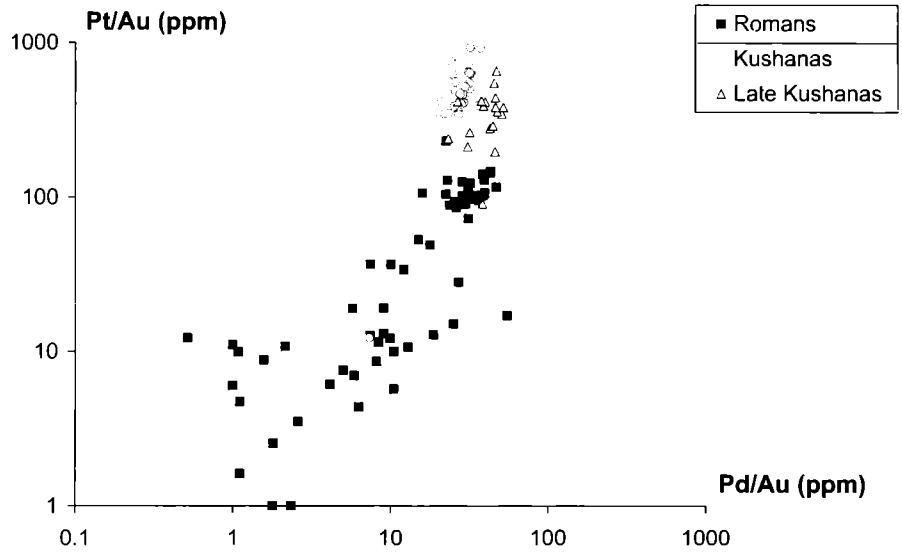

Figure 10 — Normalized platinum contents *versus* normalized palladium contents for Kushanas, Late Kushanas and Roman gold coins. Logarithmic scale.

Consequently the hypothesis of a Roman provenance for the gold minted by the Kushanas can be definitely rejected. Other provenances for the Kushan gold should be explored. The study of the gold medallion of Alexander gave the occasion to re-examine this issue. (M. Blet-Lemarquand forthcoming).

[2] These elements are not affected when the native gold is refined: their contents normalized to that of the gold (platinum/gold and palladium/gold ratios) remain constant from the ore to the coin. Thus, platinum and palladium are susceptible of characterizing the origin of the noble metal.

The Carolingian coinage

The first coins that benefited the improvements allowed by the development of silver alloys analysis by LA-ICP-MS are Carolingian denarii struck in the names of Charlemagne and Louis the Pious. More than 250 of these coins struck between 771 and 840 have been investigated. They were all lent by the Cabinet des Médailles of the Bibliothèque Nationale de France. These coins are silver-copper alloys and are supposed to be of a high silver fineness. Nevertheless, the analyses of similar coins previously published are too few and obtained by different analytical methods, so it was not sufficient to allow an overview of the composition of the coins minted by the first Carolingian rulers.

Four main classes of coins have been investigated. The two main classes of Charlemagne, struck respectively from 771 to 793/4 and from 793/4 to 812, that is before and after the general weights and measurements reform of this ruler, has been first studied (named C2 and C3 on fig. 11). Then, the two first Classes of coins of his son and heir Louis the Pious minted from 814 to 818 and from 818 to 822 (L1 and L2) have also been exhaustively investigated.

First, the evolution of the silver fineness of the coin between 771 and 822 has been considered (Fig. 11). The study of the results reveals a noticeable increase in the silver fineness from Charlemagne's Class 2 to Louis the Pious' Class 2. The most important increase coincides with the general reform of weights of Charlemagne in 793/4: the average silver content of the coins rises from 87.6% to 92.8% at this time. There was thus not only a standardization in the design and weight of the coins, but also a significant increase in the fineness of the coins, showing the growing authority of Charlemagne over the mints.

Then, under Louis the Pious, the average silver fineness of the coins stabilizes first.[3] The value determined for Louis's Class 1 coins is 92.9%, that is similar to Charlemagne's post-reform coins. There is finally a slight increase for Class 2 coins of Louis the Pious: these denarii contain 93.7% of silver on average. It is noticeable that a few of these coins have silver contents lower than 90%; such values have not been observed for the preceding period.

The points corresponding to the Venetian coins of Louis the Pious's Class 2 have been dissociated from the ones corresponding to similar denarii struck in other mints. The coins of Venice bearing the name of this ruler contain actually only 83.5 % of silver on average whereas this value is 93.7% for contemporary issues bearing other mint names. Moreover, the dispersal of the fineness in Venice (a single mint) is much more important than for all the other mints from any part of the empire. These observations have to be linked with the very particular situation of Venice in the beginning of the ninth century: at this time, the lagoon town is under theoretical Byzantine rule, but is in fact independent. The proximity of Venice with Northern Italy and the prohibition of the importation of foreign coins into the boarders of the Carolingian empire probably encouraged the Venetian minters to undertake the coinage of denarii in their own name to trade with cities located in Caroligian Italy, or even more remote market places. But as Venice was not under Carolingian rule, we can imagine that the control exercised but the authority was not as tight in the Venetian mint as it seems to have been in the other ones. This might explain the average lower fineness of the coins of Louis the Pious bearing the name of Venice.

The study of the contents of some minor and trace elements also differentiate the Venetian coins of Louis the Pious's Class 2 from the other ones. In this point of view, two elements are of particular interest: gold and bismuth. In a general trend, the Venetian coins contain much bismuth and few gold, whereas the contrary is observed for the coins from other mints (Fig. 12). These two elements are particularly useful in provenance studies as they might characterize different sources of precious metals. In our case, the discrepancy between the gold and bismuth contents could show that the silver used for coin minting under Louis the Pious in Venice and in Carolingian cities located into the boarders of the empire comes from different mines. The well-known role of the Venetian merchants as trading middlemen between Western and Eastern Mediterranean during early Middle Ages might be a clue for a Byzantine or Abbasid origin of the silver struck in Venice. Further investigations are planned for a better understanding of this issue.[4]

[3] The coins of Louis the Pious bearing the name of Melle have not been considered neither on fig. 11 nor in the calculation of the average silver contents for the corresponding Classes of coins. For further information about the coinage of Melle under Louis the Pious see: G. Sarah, *Analyses élémentaires de monnaies de Charlemagne et de Louis le Pieux du Cabinet des Médailles: le cas de Melle,* in *Proceedings of the Conference of the Société d'Etudes Numismatiques et Archéologiques «Numismatique et Archéologie en Poitou-Charentes»*, in press.

[4] The complete interpretation of the differentiation of the Venetian coins regarding their composition and the historical implications of these results can be found in Sarah *et alii* 2008.

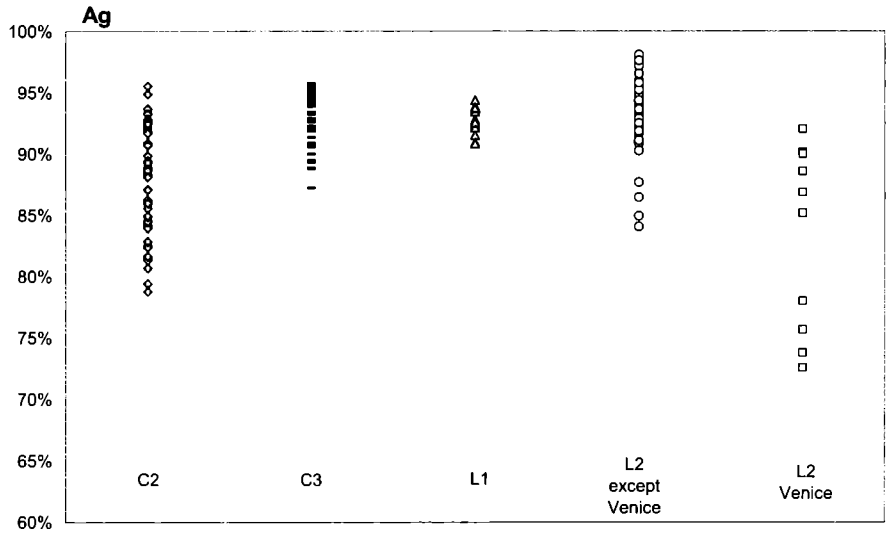

Figure 11 — Evolution of the silver fineness of the Carolingian coins for the four Classes studied.

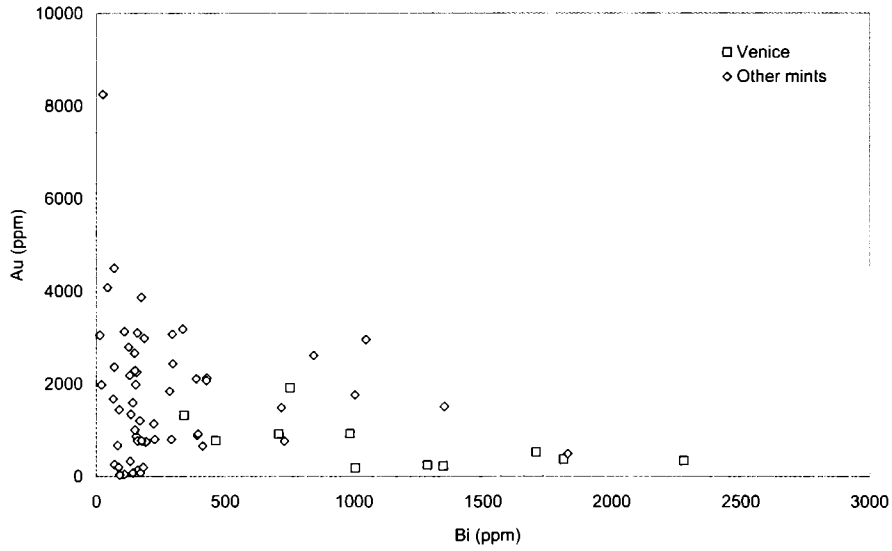

Figure 12 — Gold contents as a function of bismuth contents for the coins of Louis the Pious's Class 2 (818-822) from Venice on the one hand and from other mints on the other hand.

Identification of some coins coming from the hoard of Olbia

The hoard of Olbia (Hyères, Var, France) was discovered in 1967 during the excavations of the trading outpost (*emporion*) of Marseille directed by Professor Jacques Coupry. It was studied and published by Claude Brenot and Daniel Nony (Brenot and Nony 1978, 1987). It is composed of 102 "large bronze" coins from Marseille minted from the third century BC onwards. Some coins are very worn off and oxidised entailing difficulties to identify them. Only one third of them could be identified by Cl. Brenot and D. Nony whereas the two other thirds could only be partially identified or could not even be read at all.

A large study has been carried out on the bronze coinage of Marseille including typological, metrological and elemental data (Barrandon and Picard 2007). About 500 coins have been investigated by the means of FNAA. For instance three different groups can be distinguished among the "large bronzes" with the control marks. And there appears to be trends for the elemental composition for the different typological

series of the "large bronzes" (table 4). The first coins classified into groups 1, 2 and 3a are made up in bronze without lead; lead has been added in the last issues 3b and 3c and its content increases from 3b to 3c. Iron can be found in various proportions in the "large bronzes" (Barrandon and Picard 2007 50) and these contents are often consistent with the typological classification (Fig. 13).

Table 4 — The three different typological groups of the "large bronzes" of Marseille and their elemental composition.

Typological groups	Elemental compositions
Group 1: control mark on the obverse	Bronze without lead (Sn 2-6 %)
Group 2: control mark on the reverse	Bronze without lead (Sn 2.8-8.4 %)
Group 3: control marks on the obverse and on the reverse	3a) Bronze without lead
	3b) Lead bronze (Pb < 3 %)
	3c) Lead bronze (Pb 10-30 %)

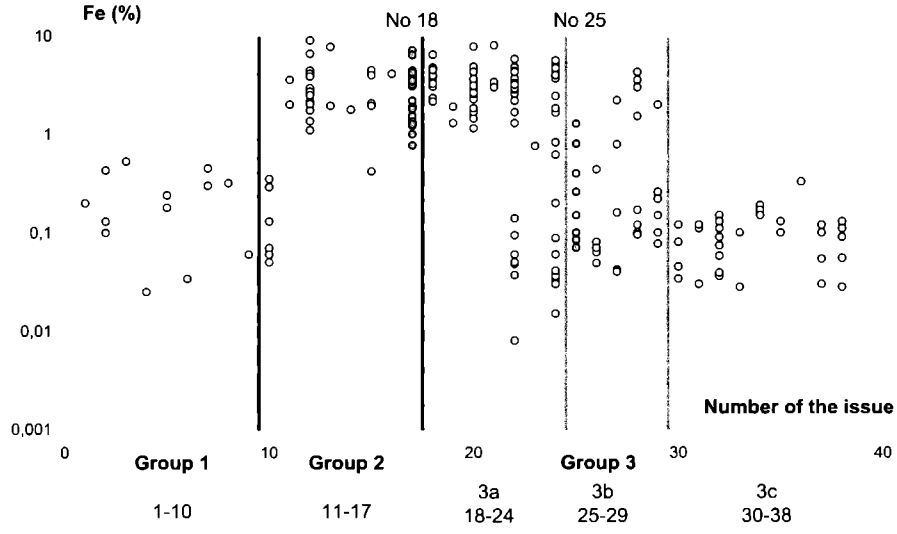

Figure 13 — Evolution of the iron content for the "large bronzes" of Marseille classified into groups and issues (the issues 18 and 25 are differently represented because the figure 14 refers to them).

A metrological study undertaken on the coins from Olbia proves that all the coins of the hoard could belong to the groups 2, 3a or 3b (Barrandon and Picard 2007 54). How can the elemental analysis of these coins help to go further in the identification? The coins whose number ranges from 5 to 11 are convincing examples of the relevance of the methodology. They bear a victory on their reverse and their obverse can not be read. They can be classified into two different issues: whether victory on the reverse (group 2, issue No 17) or torch on the obverse and victory on the reverse (group 3b, issue No 25). The iron and lead contents determined for Olbia Nos 5 to 11 coins are compared to the contents determined for the coins belonging to the issues 17 and 25 (Fig. 14). This group of 7 coins splits into two different compositional areas: two coins tally with the issue victory on the reverse whereas five of them have a composition that is consistent with the torch and victory issue. Therefore the elemental analysis gives conclusive argument to classify the Olbia Nos 5 to 11 coins.

In fact, most of the coins from Olbia on which only one control mark could be read can be connected to a particular issue interpreting the analytical data.

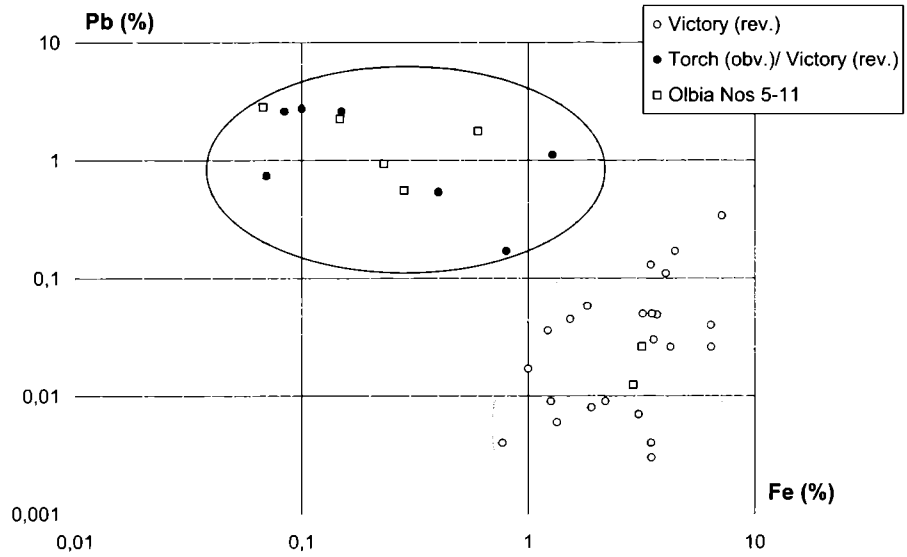

Figure 14 — Iron contents *versus* lead contents for the coins Nos 5 to 11 of the Hoard of Olbia compared to the coins with a victory on their reverse.

CONCLUSION

As shown by the examples developed above the analytical methods developed in the Centre Ernest-Babelon since the beginning of the 1970s for the numismatic studied proved their efficiency and contribute successfully to the numismatic studies. The elemental analysis appears to be of prime importance. It brings new information for the history of the coinages and can also help to correct misattributions. It allows tackling the difficult problem of the provenance of the minted metals studying the trace element fingerprints.

ACKNOWLEDGMENTS

The authors are grateful to the museums, especially the Cabinet des Médailles of the Bibliothèque Nationale de France, for permission to analyse their coins. We thank the cyclotron of Orléans (CNRS-CEMHTI) for the irradiation facilities and are indebted to the Region Centre for its financial support.

Bibliography

Arles and Téreygeol 2011 – A. Arles and F. Téreygeol, *Études des structures et des objets liés à la fabrication de la monnaie*, in *L'atelier monétaire de La Rochelle: Fouille de la place de Verdun*, ed P. Mille, Rennes, 2011.

Barrandon and Picard 2007 – J.-N. Barrandon and O. Picard, *Monnaies de bronze de Marseille. Analyses, classement, politique monétaire*, CNRS Editions, 2007 [Cahiers Ernest-Babelon, n° 10].

Barrandon and Poirier 1985 – J.-N. Barrandon and J. Poirier, *Les méthodes d'analyse des monnaies d'or*, in *L'or monnayé I. Purification de l'or et altération de Rome à Byzance*, eds. Morrisson, C. Brenot, J.-P. Callu, J.-N. Barrandon, J. Poirier and R. Halleux, CNRS Editions, 1985 [Cahiers Ernest-Babelon, n° 2], 17-38.

Beauchesne *et alii* 1988 – F. Beauchesne, J.-N. Barrandon, L. Alves, F.B. Gil, M.F. Guerra, *Ion beam analysis of copper and copper alloy coins*, in Archaeometry, 30-2, 1988, 187-197.

Beauchesne and Barrandon 1986 – F. Beauchesne, J.-N. Barrandon, *Analyse globale et non destructive des objets archéologiques cuivreux par activation avec des neutrons rapides de cyclotron*, in Revue d'Archéométrie, 10, 1986, 75-85.

Beck *et alii* 2004 – L. Beck, S. Bosonnet, S. Réveillon, D. Eliot and F. Pilon, *Silver surface enrichment of silver-copper alloys: a limitation for the analysis of ancient silver coins by surface techniques*, in Nuclear Instruments and Methods in Physics Research Section B 226 1-2, 2004, 153-162.

Blet-Lemarquand 2006 – M. Blet-Lemarquand, *Analysis of Kushana Gold coins: Debasement and Provenance Study*, in *Dal* denarius *al dinar: l'Oriente e la moneta Romana, Atti dell'Incontro di Studio,*

Roma 16-18 Settembre 2004, eds F. De Romanis and Sara Sorda, Roma 2006 [Studi E Materiali, 12], 155-171.

Blet-Lemarquand forthcoming – *The Gold Medallion of Alexander: How Can the Elemental Analysis Contribute to its Study?*, in *Proceedings of the Round Table Discussion on the Medallion of Alexander the Great from the Mir Zakah Deposit*, 26 mars 2007, ENS, Paris, ed O. Bopearachchi, published by the University of Texas, Austin, forthcoming.

Brenot and Nony 1978 – Cl. Brenot and D. Nony, *Trésor de drachmes légères de Marseille à Olbia (Hyères, Var)*. In Revue Numismatique 6 20, 1978, pp. 56-62.

Brenot and Nony 1987 – Cl. Brenot and D. Nony, trésor d'Olbia, *Trésor des monnaies de Marseille (bronzes lourds au taureau) découverts à Olbia (Hyères, Var)*, in *Mélanges offerts au docteur Jean-Baptiste Colbert de Beaulieu*, Le Léopard d'or, 1987, 121-132.

Callu *et alii* 1985 – J.-P. Callu, C. Brenot J.-N. Barrandon and J. Poirier, *«Aureus obryziacus»*, in *L'or monnayé I. Purification de l'or et altération de Rome à Byzance*, eds. C. Morrisson, C. Brenot, J.-P. Callu, J.-N. Barrandon, J. Poirier and R. Halleux, CNRS Editions, 1985 [Cahiers Ernest-Babelon, n° 2], 80-111.

Carter 1964 – G. F. Carter, *Preparation of Ancient Coins for Accurate X-Ray Fluorescence Analysis*, in Archaeometry, 7, 1964, pp. 106-113.

Condamin and Picon 1964 – J. Condamin, M. Picon, *The Influence of Corrosion and Diffusion on the Percentage of Silver in Roman Denarii*, in Archaeometry, 7, 1964, 98-105.

Condamin and Picon 1972 – *Changes Suffered by Coins in the Course of Time and the Influence of these on the Results of Different Methods of Analysis*, in *Methods of chemical and metallurgical investigation of ancient coinage*, eds E.T. Hall and D.M. Metcalf, London, 1972 [Royal Numismatic Society Special Publication, No. 8], 49-66.

Dussubieux and van Zelst 2004 – L. Dussubieux and L. van Zelst, *LA-ICP-MS analysis of platinum-group elements and other elements of interest in ancient gold*, in Applied Physics A, 79, 2004, 353-356.

Göbl 1960 – R. Göbl, *Roman patterns for Kushana coins*, in Journal of the Numismatic Society of India, XXII, 1960, pp. 75-96.

Gratuze *et alii* 2004 – B. Gratuze, M. Blet-Lemarquand and J.-N. Barrandon, *Caractérisation des alliages monétaires à base d'or*, in BSFN, 6, 2004, 163-169.

Guerra and Barrandon 1998 – M.F. Guerra and J.-N. Barrandon, *Ion Beam Activation Analysis with a cyclotron*, in *Metallurgy in Numismatics*, 4, eds A. Oddy and M. Cowell, London, 1998, 15-34.

Meyers 1969 – P. Meyers, *Non-destructive activation analysis of ancient coins using charged particles and fast neutrons*, in Archaeometry, 11, 1969, 67-85.

Nieto 2005 – S. Nieto, *La place du monnayage arverne dans les monnayages gaulois du centre et du sud de la Gaule aux IIe et Ier siècles av. J.-C.: étude numismatique et analytique*, in *XII Congreso Internacional de Numismática Madrid 2003*, Madrid, 2005 459-468.

Nieto and Barrandon 2002 – S. Nieto, J.-N. Barrandon, *Le monnayage en or arverne: essai de chronologie relative à partir des données typologiques et analytiques*, in Revue Numismatique, 158, 2002, 37-91, pl. IV.

Sachs and Blet-Lemarquand 2005 – C. Sachs and M. Blet-Lemarquand, *Le monnayage d'or kouchan: altération et chronologie*, in *XII Congreso Internacional de Numismática Madrid 2003*, t. II, Madrid, 2005, 1659-1667.

Sarah *et alii* 2007 – G. Sarah, B. Gratuze and J.-N. Barrandon, *Application of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) for the investigation of ancient silver coin*, in JAAS, 22, 2007, 1163-1167.

Sarah *et alii* 2008 – G. Sarah, M. Bompaire, M. McCormick, A. Rovelli and C. Guerrot, *Analyses élémentaires de monnaies de Charlemagne et de Louis le Pieux du Cabinet des Médailles: l'Italie et Venise*, in Revue Numismatique, 2008.

Valdez *et alii* 2007 – F. Valdez, J.-N. Barrandon, P. Estévez, *Mucho ruido y pocas nueces. Epilogo de la controversia del origen de los soles de oro del Ecuador*, in *Metalurgia en la América Antigua. Teoría, arqueología, simbología y tecnología de los metales prehispánicos*, ed Roberto Lleras Pérez, Bogotá, 2007, 501-520.