Feasibility study for a non-destructive investigation by non-invasive large-scale techniques of Roman metal archaeological objects from the Municipium Tifernum Mataurense area (S. Angelo in Vado, Italy).

TIFERNUM MATAURENSE: HISTORICAL AND ARCHAEOLOGICAL OUTLINE

Over the last fifteen years the University of Macerata, working in synergy with the Superintendence for Archaeological Heritage of the Marche Region and other local authorities, has been carrying out continuous historical and archaeological research at Tifernum Mataurense with periodical area surveys and annual excavations (Sant’Angelo in Vado -PU-Marche, Italia. Coord. GPS: Lat. 43.666392; Long. 12.416167; IGM F. 115, I NE); these activities were decisive in the rediscovery of this Roman municipality, of Umbrian origin, belonging to the Augustan sexta regio, situated between the high Metauro valley and the central Italian Apennine range, near the via Flaminia (Stortoni 2004; Tornatore, 2006; Catani 2012; Catani, Monacchi 2010; Catani, Monacchi & Stortoni 2014; Catani-Stortoni 2009; Stortoni 2010; 2013; 2013-2014; 2014 a-b; c.d.s.c.). According to scholars, the ancient centre passed through a protohistorical period between the high Metauro valley and the central Italian Apennine range, belonging to the Augustan sexta regio, situated on the Metauro valley. Further research has lead to the rediscovery of the Roman municipality, of Umbrian origin, belonging to the Augustan sexta regio, situated between the high Metauro valley and the central Italian Apennine range, near the via Flaminia (Stortoni 2004; Tornatore, 2006; Catani 2012; Catani, Monacchi 2010; Catani, Monacchi & Stortoni 2014; Catani-Stortoni 2009; Stortoni 2010; 2013; 2013-2014; 2014 a-b; c.d.s.c.).

According to scholars, the ancient centre passed through a protohistorical phase and then took the status of municipium during the years of the Social War (90-89 B.C.), in the late Republican and Augustan age it saw the initial stages of urbanization, followed, in the period of Hadrian and the Antonines, by a phase of monumentalisation. The area appeared to have experienced a brief resurgence under the Constantinian empire, then to be abandoned by as soon as the middle of the 6th century A.D.

The municipium covers a wide area, mainly hilly and mountainous. Road access is concentrated in three different directions: in the East towards Pitinum Mergens and the Flaminia; in the South towards Tiferinum Tiberinum; in the West towards Sestinum.

In the urban area, spread out between the present Campo della Pieve and the locality of Colombaro (previously property of Monti and Graziani Pinzauci, now State-owned: Land Register of the Municipality of Sant’Angelo in Vado, record 1295, Page 47, land parcels 106, 408, 410, 914), records exist of long stretches of road relating to cardines and decumani, efficient infrastructure systems and remains of important private residences also with sumptuous polychrome mosaic decoration, such as the so-called Nord-West domus and the so-called domus of the myth. Furthermore, large and detailed sections of the thermae have been conserved, unfortunately seriously damaged by modern interventions; of these, conspicuous traces have survived of a cold setting in polychrome mosaic showing a marine scene, part of the calidarium system with relative hypocaustum and praefurnium, remains of the natatio.

Such well-finished monuments and works are testimony to a social and economic context, characterised by wealthy and cultivated clients, who were close to the heart of central power, who, particularly in the period of the middle Empire, employed master craftsmen, working on the two sides of central Italy (Paci 2004; de Marinis-Quiriri 2005; 2006; Stortoni 2014 b). Its establishment along an important network of rivers and roads (Luni 2002), not far from the Apennine passes, forming an early contact with the Roman state to the North of the Esino already in the 3rd century B.C., may have for some time contributed to the process of Romanisation and thus creating favourable conditions for lasting socio-cultural development with inevitable economic repercussions. Indeed, a dense exchange network must have been created right from the start between the Umbrian mountain area and the hills and coastline of Ager Gallicus. This appears to be confirmed by studies carried out of the epigraphical and archaeological materials sporadically discovered over time (Monacchi 1997, 24-62; Catani-Monacchi 2004; Paci 2004; Catani-Monacchi 2010) o in stratigraphic context (Palermo 2006; Monacchi-Stortoni 2000-2014).

Of particular significance is the fine ceramic tableware, the study of which has shown how from the last centuries of the Republic to the end of the middle Empire the Municipium Tiferinum along with its bordering centres, such as Sestinum, Urvinum Mataurense, Pitinum Pisaurense, Forum Sempronii and Suasa Senonum, entered intense trade relations with workshops in the central Apennine region, in the central-northern Adriatic coast and on the Tyrrhenian coast (Monacchi 1995, 50-51; Mazzeo Saracino 1991; Monacchi 1997; Ermeti 2002; Gori 2003; Monacchi 2004 b; 2010 b; Palermo 2006). The hypothesis that Tiferinum Mataurense occupied what was by no means a marginal status among the central Apennine communities especially in the middle Empire age is also demonstrated by the existence of local figilae for the production of fine tableware.

The centrality of the municipium Tiferinum in the central Apennine region, compared to the great trading routes that mainly ran from east to west, seems, furthermore, to be supported by the analysis of other categories of materials; indeed, it is almost certain that the same trans-Apennine
The IRATMA Project  E.S.

A decisive contribution towards an improved understanding of these issues could come from archaeometric research, based on the application of sophisticated scientific technology archaeological investigation (Rogante 2011; Olcese 2009). It was in this context and upon these assumptions that the IRATMA (nips, tof-nd and pixe Investigation of Roman metal Archaeological objects from the municipium Tifernum Mataurense Area, italy) Project was created, and this paper sets out to illustrate its content and feasibility. The Project plans to carry out an investigation on a small group of bronze items from Tifernum by applying neutron techniques - Prompt Gamma Activation Analysis, PGAA (Glascow-Spalding-Biers-Cornman 1984, 96-103; Rogante 2006). The method, which is non-destructive and non-invasive, and which was recognised in the eighties as a powerful research tool for cultural heritage, has only been actively and systematically applied during the last fifteen years; on several occasions this technique has been used for the archaeological heritage of the Marche Region by the Rogante Engineering Office, of which Dr. M. Rogante is the Italian Member of the International Scientific Advisory Council of the Budapest Neutron Centre and co-author of this project. Investigations were successfully carried out in the past on a number of Picenian and Roman bronzes from Matelica, Fabriano and Treia (Rogante 2006; Rogante et al. 2007; Rogante et al. 2010a; Rogante 2011; Manni 2008). The IRATMA Project, created in the ambit of the CHARISMA EU FP7 programme and thus of international value, was authorised by the General Directorate for Antiquities of the Ministry for Cultural Heritage and Activities. As explained later, different non-invasive large-scale techniques have been considered in this study, including neutron induced gamma spectroscopy, neutron diffraction and proton induced X-ray emission.

The crafted items, selected with the help of our colleague Monacchi, who collected them and has already published them (1997, nos. 50 c, 56, 57, 59, 76, 86), were discovered outside stratigraphic context and are now kept in the local deposit of S. Maria extra muros. There are six numismatic and toreutic items in total, archaeologically datable between the early and late Empire: a scalpel, a capsella, a fragment of gilded statue, a decorative metal sheet, the toe of a statue and a small coin.

The expected results could provide useful information on the structure and composition of the metal cast in the creation of the items, namely bronze and iron. Bronze can include a wide variety of alloys with different internal proportions of copper, lead, tin and zinc; the varying combination of elements was influenced by the greater or lesser availability of the individual components and/or by the particular characteristics required by the specific use of the item. Iron, however, was generally chosen for its lower cost and for its versatility in relation to the use of the tool. Easily obtainable and very tough, iron could be tempered using a process of carburisation in order to produce extremely solid and/or sharp instruments; always hand cast and never smelted, it also enabled the production of unique and personalized objects (Cigada-Pastore 2012; Giardino 1998; Luni 2001, 69, 74-77; Jackson 2009, 74). Knowledge of the nature and state of the metals could be of assistance in gaining information about the relative mineral deposits, the conservation setting, the production and function technology and about the authenticity of each individual item. The data obtained, put alongside the archaeological study of the objects, could prove to be useful in shedding new light on the trade and craft circuits and on possible workshops for on-site production. Figures 1-7 show the analysed archaeological object.
Table 1 reports the summarizing description of these objects. Chemical analysis of archaeological artefacts has become an important tool for source identification, provenance analysis based on the determination of major- and trace elements. The most usual analytical methods (e.g., X-Ray Fluorescence Spectroscopy, Instrumental Neutron Activation Analysis and Inductively Coupled Plasma-Mass Spectroscopy) require partial or total destruction of the samples, which often is impossible in case of valuable whole or fragmental artefacts. Neutron investigations have become an increasingly significant probe for materials across a wide range of disciplines, and they are becoming ever more useful in the non-destructive characterisation of materials and components of industrial interest or belonging to the Cultural Heritage (Rogante 2008). This feasibility study aims to propose a non-destructive investigation of the considered objects by non-invasive large-scale methods, including neutron techniques.

**EXPERIMENTAL METHODS AND EXPECTED RESULTS M.R.**

Composition of an artefact is constantly associated with its function, and the key step in planning a conservation action or preservation measures is also to identify the component materials. Suitable analyses methods to get accurate information on composition, thus, are essential to archaeological research, since they identify the constitutive metals gives a substantial help in identify the object (Horváth et al.). In the present feasibility study, a possible multistage process at macroscopic, microscopic and large-scale analytical levels has been considered, by linking the following complementary non-destructive and non-invasive large-scale investigation techniques: PIXE, PGAA, NIPS and TOF-ND. PIXE is a powerful non-destructive analysis technique adopted to assess the elemental composition of a material or object. This method was initially proposed in 1970 by S. Johansson, who developed it successively together with his colleagues R. Akselsson and T.B. Johansson (Johansson et al. 1970). Atomic interactions occur, when a material is exposed to an ion beam, giving off electromagnetic (EM) radiation of wavelengths in the X-ray part of the EM spectrum specific to an element. The object investigated by PIXE is excited by a proton beam with typical 1 - 3 MeV energy. The atoms in the sample, in collisions with the protons, become ionized and excited. The inner electron holes, subsequently, are relaxed by the emission of X-rays whose energy is characteristic of a given atom. PIXE is based mainly on the detection of K-shell transitions in lighter and L-shell transitions in the heavier atoms. The characteristic energies of these transitions are well adequately separated, to discern contributions of different atoms in the spectra, which are recorded by a typical semiconductor X-ray detector - e.g., a Si(Li) semiconductor counter (Rogante et al. 2010 b). The analytical quality of the PIXE technique depends somewhat on the precision of the deconvolution of the X-ray spectra. Nearly all of the deconvolution programs adopted for this scope rely on awareness about the response function of the measuring detector (Maxwell et al. 1995). After measuring the PIXE spectrum, photon yield has to be normalized to the total proton dose, received by the investigated object during the measurement. The number of photons under the specific line in the spectrum is then proportional to the hole creation cross section, of the experimental geometry and, naturally, to the concentration of a given element in the specimen. The sensitivity of the PIXE technique varies with Z and amounts to 1 ppm (µg/g) for light elements (from Na to Cl) below 0.1 ppm for transition metals and close to 10 ppm for heavier elements. A PIXE experiment can produce three types of spectra, i.e. X-ray emission, Rutherford backscattering and proton transmission. Only elements heavier than F can be detected. The lower detection limit, for this technique, depends on the capability of the X-rays to pass across the window between the chamber and the X-ray detector. The upper limit, on the other hand, depends on the ionisation cross section, the probability of the K electron shell ionisation: this is highest as the proton velocity equals the electron velocity (10% of the light’s speed), consequently 3 MeV proton beams are ideal. PIXE is adoptable in the archaeology, art conservation and geology, to support answer questions of authenticity, dating and provenance, as well as in various other fields such as life sciences (Szökefalvi-Nagy 1994).
Neutron analytical methods have been considered to explore the compositional or microstructural characteristics of the investigated artefacts. The bulk elemental concentrations of the alloying components can be identified by using neutron capture γ-ray facilities PGAA and NIPS. PGAA is based on the detection of characteristic prompt gamma photons that originate in \((n,\gamma)\) nuclear reactions, and it allows the analysis of elemental composition by observing neutron-capture prompt γ-rays. For the analysis, a selected part of an object is irradiated with a collimated beam of cold neutrons, and the emitted characteristic gamma photons are detected simultaneously. The quantitative analysis is based on the following considerations. The detected gamma-ray intensity \(A_\gamma\) is directly proportional to the mass of a given element, the analytical sensitivity \(S\) and the measurement time \(t\), such that

\[
A_\gamma = m \cdot S \cdot t
\]

The detected count rate \(\frac{dN_\gamma}{dt}\) in a given gamma peak is proportional to the number of nuclei emitting the gamma photons of a given energy. It can be calculated, as in the following equation:

\[
\frac{dN_\gamma}{dt} = \int_{A_\gamma}^{\infty} \frac{\mu(r)N_\gamma}{M} \sigma_{n}(E_\gamma) \Phi(E_\gamma) \epsilon(E_\gamma, r) dE_\gamma dr
\]

where \(N_\gamma\) is the peak area, \(\mu(r)\) is the density of the element of interest in the point \(r\), \(N_A\) is the Avogadro number, \(M\) is the atomic mass of the element, \(\Phi(E_\gamma)\) is the local neutron flux and \(\epsilon(E_\gamma, r)\) is the detector efficiency.

A few simplifications, in practice, can be introduced. For example, \(\epsilon\) is the partial gamma ray production cross section, and can be defined as:

\[
\sigma_{\gamma} = \sigma_{0\gamma} \cdot I_y \cdot \theta
\]

where \(\sigma_{0\gamma}\) is the thermal neutron absorption cross section, \(I_y\) is the probability of gamma ray emission and \(\theta\) is the isotopic abundance.

If it is supposed that we have a small, thin and homogeneous sample, and that the detector efficiency is independent of the sample position (it is in a fixed position), then the thermal equivalent flux \((q_0)\) is defined so as to have the same reaction rate, as below:

\[
R = N \int_{E_\gamma}^{\infty} \Phi(E_\gamma) \sigma_{n}(E_\gamma) dE_\gamma = N \int_{E_\gamma}^{\infty} \nu \cdot n(E_\gamma) \sigma_{0\gamma} \epsilon(E_\gamma) dE_\gamma =
\]

\[
= N \cdot \sigma_{0\gamma} \int_{E_\gamma}^{\infty} \nu \cdot n(E_\gamma) dE_\gamma = N \cdot \sigma_{0\gamma} \cdot \Phi_{\epsilon}
\]

Such that the peak area may be calculated from the equation:

\[
N_{\gamma} = \rho \cdot t_m = m \cdot S \cdot t_m = \frac{m \cdot N_A}{M} \cdot \Phi_0 \cdot \sigma_{0\gamma} \cdot \epsilon(E_\gamma) \cdot t_m
\]

And hence the sensitivity may be given by:

\[
S = \frac{N_A}{M} \cdot \theta \cdot \sigma_{0\gamma} \cdot I_y \cdot \Phi_0 \cdot \epsilon(E_\gamma)
\]

The analytical sensitivity \(S\) is expressed in units of counts×s⁻¹, as seen in eq. (5), and is proportional to the neutron capture cross-section of the following nuclear constants, the nucleus \(0\), the isotopic abundance \(\theta\), and the gamma yield \(\gamma\), as well as to the neutron flux \(\Phi_0\) and the detector efficiency \(\epsilon(E_\gamma)\), which are characteristics of the measuring system. According to eq. (3), lower energy (cold) neutrons mean higher thermal equivalent flux, which according to eq. (5) means better sensitivities.

Other symbols in eq. (5) are Avogadro’s number \(N_A\), and the atomic mass \(M\) of any given element. The mass ratios, or equivalently the weight-percentage ratios of arbitrary elements “X” and “Y” are independent of both the actual amount of each sample and of the exact neutron flux, and can be calculated from peak area ratios and sensitivity ratios as follows:

\[
\frac{w_X}{w_Y} = \frac{S_{X,\gamma}}{S_{Y,\gamma}} \cdot \frac{A_X}{A_Y}
\]

All the chemical elements can be determined by internal standardisation measurements. At the Budapest Neutron Centre (BNC), e.g., they are collected in a new gamma-ray spectrum catalogue for PGAA (Révay et al. 2001). For a detailed treatment of the theoretical bases, see (Révay 2009; Révay et al. 2004; Molnár et al. 1997; Molnár et al. 1998; Révay et al. 2006; Révay-Molnár 2003; Rogante 2006).

The NIPS instrument serves for different nuclear spectroscopic measurements analysing the prompt gamma radiation of material activated in neutron beam. The NIPS-NORMA station of the Budapest Neutron Centre, e.g., has been designed for investigation of objects of dimensions up to 20×20×20 cm³ and for a wide variety of experiments involving neutron capture induced prompt and delayed gamma radiation, including γ-γ-coincidences; γ-rays as low as 14 keV can be also observed. NIPS technique would allow determining the bulk composition, even if the surface of the investigated objects is corroded. Furthermore, it would be possible to analyse different parts of the considered bronze objects. The most important chemical elements to be measured by NIPS in these objects are Cu, Sn and Pb alloying components. The main purpose is to compare the obtained data related to these elements with those achieved in the PGAA investigation carried out by the Rogante Engineering.
Office on the Picenan bronzes from Matelica and Fabriano necropolis (Rogante et al. 2007; Rogante et al. 2010) and also on other (e.g., Aenean) objects. Additionally to the bulk composition measurements, the set-up can make possible to perform NR of selected parts, and to combine imaging methods with elemental analysis based on (n,γ) reaction (Belgya et al. 2008). Materials and technological traits have been already studied by using the TOF-ND (Rogante 2008; Káli et al. 2007). The penetration depth of neutrons in copper can be in the order of 1 cm, consequently real bulk average results could be obtained. The TOF-ND analysis would aim the quantitative bulk characterisation of the phase composition and the structural properties of the metallic constituents of the alloy. Also possible traces of the past treatment (mechanical or thermal) can be observed in the eventual crystallographic texture. To eliminate the effect of the possible preferred orientation and the background from the corrosion and crust, the positions of the valuable peaks can be determined by multiple peak fit and the lattice parameters of the hcp system (a and c) can be fitted for the set of peak data, taking into account the uncertainties in the weighting. The investigation by the TOF-ND technique would consent a qualitative and quantitative assessment of the sample phase composition and the structural properties of the constituents as averaged in finite macroscopic volumes of the bulk. Multiple data points would be collected across the investigated objects. The TOF-ND technique, in addition, would permit studying by means of atomic scale the dynamic behaviour of the material and eventual texture or grain orientation, helping to indicate possible manufacturing techniques. TOF-ND is completely non-invasive and would not mark, heat, or alter the investigated object. Moreover, there isn’t any long-term activation as a result of the investigation.

All the considered methods need no sample preparation. The expected results would supply helpful information in order to verify composition, possible manufacture technologies, origin of the metals used and other problems, as well as considerable scientific contributions to understand the origin context of the investigated objects. These results compared with archaeological and contextual data could supply useful knowledge also of a more precise dating of the life phases of this interesting - but still little well-known - mountain centre of the Roman Italy. Contextually, it would be enhanced the modest regional database currently available, which is based essentially on the investigations in recent times performed, e.g., by PGAA on comparable Picenan objects coming in particular from Matelica and Fabriano necropolis. These works remarkably sustained the local source of the manufactured objects (Rogante et al 2010; Rogante et al. 2007; Parrini 2008). These data are very useful to better interpret the possible geographical origins. The mentioned techniques, moreover, will allow obtaining possible indications to create replicas of the major element compositions and in accordance with the supposed manufacturing process, and also to analyse that as a standard to compare with the original objects.

The progress of research and the formation of a rich and more reliable database would allow to the researchers, finally, gathering interesting and original features, with potential inestimable scientific effects.

CONCLUSIONS (M. R. AND E.S.)
The application of a possible multistage process at macroscopic, microscopic and large-scale analytical levels has been considered to develop the study of the archaeological heritage of Marche Region, Italy. The traditional archaeological research would be helped, in this way, to find answers to the historical-archaeological questions that the usual sources do not succeed by now to get ahead into focus. The expected results could give also a contribution in obtaining indications to create replicas of the major element compositions and in accordance with the supposed manufacturing process, as well as to analyse that as a standard to compare with the original objects.

The progress of this research and the formation of an increasingly rich and reliable database would allow researchers gathering more and more interesting and original features, with potential precious scientific effects.