Daggers, Rings, Axes or Fibulae Have Different Composition? A Multivariate Study on Central Italy Bronzes from Eneolithic to Early Iron Age

G. Visco¹, S.H. Plattner¹, G. Guida², S. Ridolfi³ and G.E. Gigante¹
¹University “La Sapienza”, Rome, Italy; ²National Institute for Conservation and Restoration, Rome, Italy; ³Ars Mensurae, Rome, Italy

Abstract
Since the early 1900s, the composition of ancient bronzes has interested researchers from every corner of the world. The elemental composition is studied by chemists in order to check for correlation with the usage of objects; a question raised by archeologists. An initial response has been given in our previous work [1] where we analysed by EDXRF a sample composed by 14000 bronze fragments of commonly used objects excavated more than 130 years ago in Bologna [2], the so-called "Ripostiglio di San Francesco" (St. Francesco hoard).

The sample of the present study instead consists of 133 bronze objects, found in Central Italy and dating back from the Eneolithic period to the end of Bronze Age including the Early Iron Age. As, Zn, Fe, Ag, Sb, Pb, Sn and Cu contents were measured.

Introduction
A huge number of small bronze object fragments can be found in Italy. One of the oldest finds, an axe of pure copper used by Ötzi the Iceman was found in the Alps of Ötztal, at the boundary of Italy and Austria in 1991; it dates back to about 3300 B.C. as stated by archeologists and denotes the overcomp of the final Bronze and copper Ages. The origin of the objects described in this paper are from the Italian Abruzzo region. Contrarily to the previous work [1] objects destination of use was easily recognizable and information provided by Italian archeologists is summarized in table 1 (usage classification and number of samples).

The 133 objects were analysed by EDXRF, a widely used non-destructive technique for a total of 200 measurements depending on object dimensions. Analysts (among authors), preferred abrad ing spots of the oxidation patina with an abrasive systems before measurements in order to obtain data closer to bulk composition. Although micro-invasive, this technique allowed measurements on many objects and produced a large number of element-concentration% data. As stated in literature this method does not provide absolute, quantitative values but only relative percentages, but the use of reference materials with the same (identical?) alloy composition can produce semi-quantitative data acceptable for interpretation.

Materials & Methods
Objects are stored in various museums of central Italy and measurements were conducted under the auspices of a CNR project started in 1997 with the aim to ameliorate the scientific knowledge on the immense inheritance of...
objects. After studying the variety (type and age) of the conserved objects we selected a *probability proportionate to size* sampling design. A data set should contain a certain level of redundancy to allow calculation of method’s precision (and/or homogeneity of alloy); in this case a third of the objects were measured twice or more.

The EDXRF instrument assembled by two of the authors [3] was equipped with a Xray tube (W anode, 40-50 kV, 0.3 - 1 mA, Al filter window) focalized on a 0.6 mm spot and a cryogenically cooled Ge detector, HPGe type with Be window, with a 195eV resolution at Fe line (EG&G Ortec, Oak Ridge, Tennessee, USA). For abrasion a spherical diamond wheel of a famous brand was used (2mm, code7103).

**Results**

In Tab. 2 the statistic values of the detected elements are shown. The average value of the 132 objects is in accordance with the typical composition for the middle and late Bronze Age in Italy and France [4]. The objects were divided into homogeneous groups following three different classification criteria: age, shape and usage.

A first attempt to separate groups can be obtained by a scatter plot-matrix, after column centring, showing all possible var-var combinations; this graph enhances that bronze objects are studied because only the Cu-Sn scatterplot shows correlation.

One of the problems with XRF methods is the closure to 100 of the matrix rows, as, for instance, an erroneously overestimated element depresses the concentration of all others. Various methods of scaling have been suggested [5] to circumvent this problem and we have used the logratio-centered one.

The chemometric analysis was performed attempting to visualise classes through PCA (MVSP software) using all elements and leaving out one group. In fig.1 the 3D representation with all objects and “usage groups” is shown. Weak separation of only one group is evident, composed by Fe rich, objects. A small group on the far left of the chart may be evidenced, but probably recalulation without the Fe objects can produce better separation.

**Conclusions**

Multivariate analysis of EDXRF data on ancient bronze objects did not allow identification of homogeneous classes. Experimental evidence shows that already during the Bronze Age it was common practise to recast broken or damaged items [1]; expert foundry-men had already discovered convenience of recycling broken objects compared with metal extraction starting from minerals.

**References**

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