IL NUOVO CIMENTO Vol. 30 C, N. 1 Gennaio-Febbraio 2007
DOI 10.1393/ncc/i2006-10036-8

Neutron resonance capture applied to some prehistoric bronze axes(*)

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(ricevuto il 31 Ottobre 2006; pubblicato online il 13 Febbraio 2007)

Summary. — The elemental analysis of materials and objects on the basis of neutron resonance capture by nuclei as a function of neutron energy is briefly explained. The feasibility of neutron resonance capture analysis (NRCA) is demonstrated with five prehistoric "bronze" axes of different kinds and complex elemental compositions. Attention is paid to the occurrence of indium as a trace element in these artefacts.

PACS 25.40.Lw – Radiative capture.
PACS 29.30.Hs – Neutron spectroscopy.
PACS 81.70.Jb – Chemical composition analysis, chemical depth and dopant profiling.
PACS 82.80.Jp – Activation analysis and other radiochemical methods.

1. – Introduction

The capture of neutrons by nuclei as a function of neutron energy shows peaks, known as resonances, which are related to states of the compound nucleus just above the neutron binding energy. Neutron resonances are isotope specific and therefore suitable to recognize elements. They can be adequately detected in a time-of-flight (TOF) system using a pulsed, "white" source of neutrons. In this way a resonance spectrum can be obtained as a function of TOF. Knowing the length (L) of the flight path the resonance spectrum can also be plotted as a function of neutron energy (E) using the expression $E = 5227 \times (L/T)^2$, where T is the TOF in μs, L is in m and E in eV. The strengths of the peaks in a resonance spectrum can be used to determine the amounts of elements in an object. We determine ratios of elements from ratios of resonance areas using calibrations with samples of known compositions. Since these calibration samples (40×40 mm

(*) Paper presented at the Workshop "RICH—Research Infrastructures for Cultural Heritage", Trieste, December 12-13, 2005.
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and 3–5 mm thick) differ in shape (and also in composition) from the studied objects it is necessary to apply corrections. These corrections are large for strong resonances of major elements. Such resonances are therefore avoided. More details are given in sect. **4**.

We like to call this neutron-based analytical method "neutron resonance capture analysis" (NRCA). It has been successfully applied for instance in an authenticity study of Etruscan statuettes [1]. In this paper a pilot study with five prehistoric bronze axes will be reported. It is known that prehistoric objects may have considerable amounts of arsenic, antimony and silver [2]. Therefore, their resonance spectra are expected to be much more complicated compared to normal tin-bronzes.

2. – Experimental set-up

For the experiments reported in this paper, we could use a TOF system at the GELINA facility of the Institute for Reference Materials and Measurements (IRMM) in Geel (Be). The basic instrument is a linear electron accelerator, which produces electrons up to 150 MeV bunched to pulses of 1 ns. By stopping these electrons in a rotating disk of uranium a strong flash of Bremsstrahlung is produced. Subsequently photonuclear reactions and partly fission produce a pulse of fast neutrons. These neutrons are moderated by water in two 4 cm thick beryllium containers close to and positioned on both sides of the uranium disk. The energy distribution of the neutrons emerging from these containers has a thermal part and a part of which the flux decreases roughly proportional with energy. The containers are viewed through evacuated beam tubes with collimators. The accelerator is normally running at 7 kW power and a repetition rate of 800 Hz maximum. The TOF of each captured neutron is determined with the aid of the start signal, given by the accelerator, and the stop signal generated by detecting the prompt neutron capture γ-rays with a set of scintillation detectors. In the reported measurements two C_6D_6 detectors were used. These detectors are $3''$ thick and $5''$ in diameter, and mounted opposite to each other with respect to the object and close to the beam. On the basis of known resonance energies the length of the flight path, which we used, was determined to be 14.33 m.

The time resolution of the TOF system is excellent, but varies with energy mainly due to the moderation of the neutrons in the small water tanks. Advantages of the C_6D_6 detectors are their very small detection efficiencies for neutrons and short decay time of about 3 ns. However, their energy resolution is poor. But this is not a disadvantage for NRCA, since we accept all capture γ-rays in a wide energy range, typically between 0.3 to 10 MeV. The beam is collimated to about 6 cm using a number of collimators along the flight path. We do not apply shielding around these detectors since this is in our condition not necessary, even contra-productive. For most elements neutron capture is followed by γ-cascades, which may consist of 3 to 5 steps. This multiple γ-emission increases the detection efficiency for capture considerably. For the described detector system this efficiency is of the order of 15%.

In the case of bronze objects the practical energy range is from about 1 eV to about 3 keV depending on the complexity of the resonance spectrum. For other materials, for instance marble, the practical maximum neutron energy can be much higher, of order of 50 keV using the same, 14 m, flight path.

The TOF is recorded using a special time-coder with basic frequency of 2 GHz. The first 4096 channels were 4 ns wide, the next group of 4096 channels 8 ns, etc. covering a total time of 1073 μs.

Fig. 1. – A selection of bronze axes from the Groningen Institute of Archaeology, University of Groningen (the Netherlands).

A 15 mm Bi-plate was installed in the beam to prevent the Bremsstrahlung flash from the accelerator to reach and overload the detectors during some time. To avoid overlap of neutrons from subsequent machine pulses, also a 0.75 mm thick Cd-sheet was placed in the beam; its cut-off energy is about 0.7 eV.

3. – Prehistoric bronze axes

In the West Europe Bronze Age, various types and forms of bronze axes were developed in the course of roughly 1000 years. There are many regional variations in shape and compositions. Figure 1 shows five axes of different forms, provenance, and stages of the Bronze Age from the study collection of the Groningen Institute of Archaeology (GIA), University of Groningen, the Netherlands.

The *flanged axe* (No. 4 on fig. 1) is of unknown provenance; it was obtained in 1920 as a present from the Hungarian National Museum. It has a black peat patina. It is virtually identical to a flanged axe from a rich tumulus burial of the end of the Early Bronze Age from Wohlde-Roxhüllen, Stadt Bergen (Kr. Celle) on the Lünenburger Heide (see [3], p. 59, No. 178, Taf. 91D). These two flanged axes may well be imports from the Central European area. Similar axes, with varied details, are common in South Germany and Switzerland [4].

The broken *palstave* (No. 2 on fig. 1) is also of unknown provenance and has a peat patina; the break is also patinated and therefore ancient. In form it is common and characteristic for the North European area in the Middle Bronze Age, c. 1350 BC. It was required in 1922 from the Lüneburg Museum as coming from a private collection and found on or near the Lüneburger Heide.

Three *socketed axes* are shown on fig. 1. Number 1 is small, only 6 cm long. It is of a type very common in the North European area, especially Schleswig-Holstein, Denmark and South Sweden, from the Late Bronze Age, Northern periods V and VI (see [5], pp. 16, 23-24, 181-186, Taf. 6). It is found on or near the Lüneburger Heide. The socketed axe

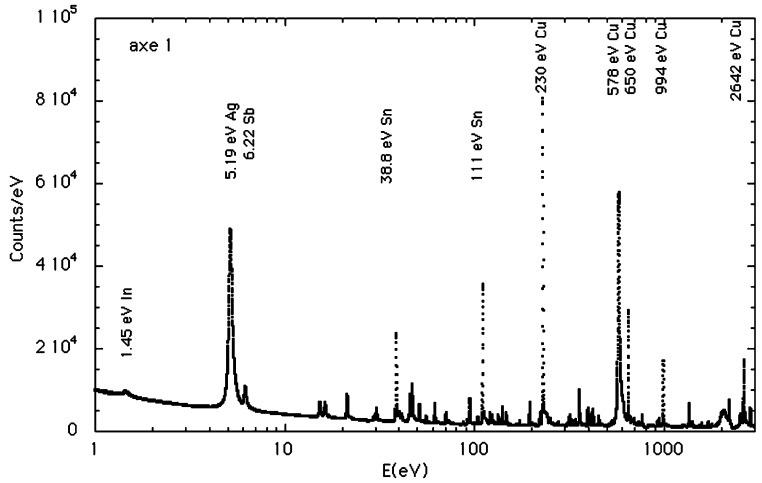

Fig. 2. – Neutron resonance spectrum of the small socketed axe No. 1 (1922/XII.35). The accumulated number of capture events (counts/eV) is corrected for the energy dependence of the neutron flux.

(No. 3 on fig. 1) is probably a product of local industry in the Late Bronze Age (c. 900-700 BC) in the north or east of the Netherlands, or the adjacent North German area (see [6], p. 259, No. 700).

The long socketed axe (No. 5 on fig. 1, length 14.8 cm), is well cast, but unusually thin-walled; apparently too thin to be suitable for chopping. It may have been intended for some ritual purpose. It was found together with another, very similar axe and bronze knife of Central European Urnfield type. The findspot is given as Caberg near Maastricht in Limburg in the Netherlands. Similar socketed axes, so similar that they probably come from the same workshop, have been found in some numbers, sometimes in pairs, on both sides of the Dutch-German border, and along the Meuse in Belgium and the Netherlands. A hoard of 26 such axes has been found at Geistingen close to the Meuse, near Maaseik in Belgium, from which these axes are known under the name "Type Geistingen". There are no datable associations, but on typological grounds they are presumed to belong to the end of the Bronze Age or transition to the pre-Roman Iron Age, c. 900-700 BC (see [7], pp. 166-168, 214, Nos. 787-804, Taf. 77, No. 1007, and [8], pp. 303-309, Nos. 550-562, p. 304, map 6).

4. – Experimental results

The axes have been subjected to 5 to 27 hours of beam time. The Cd-sheet mentioned in sect. **2** removes neutrons below 0.7 eV, which is the main source of activation, from the beam. Therefore the activation of the objects is low. It was not necessary to store them for radiation safety, and when returned to Groningen a few days later the residual activation due to the longer living isotopes, mainly ^{64}Cu with decay time of 12.7 h, was negligible. Only 0.6% of the decay of this isotope concerns γ-radiation.

Figure 2 shows as an example the neutron resonance spectrum of the palstave fragment plotted as a function of neutron energy. This measurement took 16 hours. Since the neutron flux of the beam is proportional with $E^{-0.92}$, the capture rate plotted in

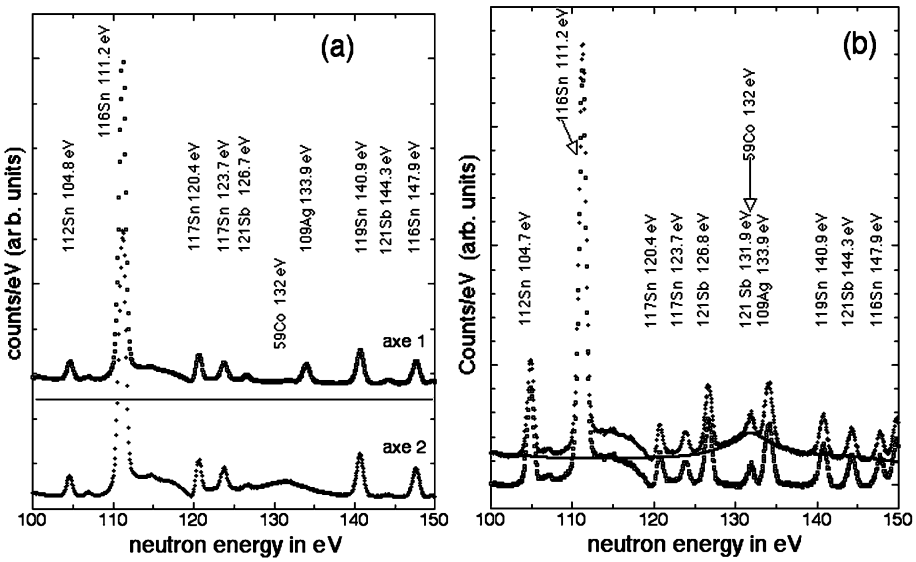

Fig. 3. – a) Sections of the resonance spectra of the small socketed axe No. 1 (1922/XII.35), and the palstave No. 2 (1922/XII.46) between 100 and 150 eV. Axe 2 shows the broad 132 eV resonance of cobalt. b) The upper resonance spectrum concerns socketed axe No. 3 (1938/IV.5). Background and Co-resonance at 132 eV are indicated by the solid curve. The lower spectrum shows the background and Co-resonance subtracted. The broad structure at the higher side of the Sn-resonance at 111 eV is due to scattering followed by capture.

this figure is divided by this factor. The spectrum shows a large number of resonance peaks. Some of the resonances used for the analysis are indicated with their energies and elements.

The Lorentzian-shaped resonances are broadened by the Doppler effect and due to the time resolution of the TOF system. Both effects are closely Gaussian. Consequently the peaks can often be described by the Voigt function. That is, Gaussian shaped in the middle and Lorentzian at the wings. The neutron flux is reduced during penetration of the object. This reduction is stronger at resonance energies. This self-shielding effect, which is not the same for all resonances, requires a correction for the number of observed capture events. To avoid large corrections we prefer to use the weaker resonances of elements in larger quantities. For instance for copper in bronze we do not use the strongest resonance at 578 eV, but the weaker resonances at 230, 650, 994 and 1362 eV. For tin, resonances at 38.8, 45.0, 62 and 111 eV are suitable. For minor and trace elements normally the strongest resonances are used in the analysis. The occurrence of several resonances makes it possible to calculate ratios for pairs of resonances. In a proper analysis the calculated ratios for two elements (for instance tin and copper) should be the same. Details of the analysis can be found in earlier papers [1, 9, 10].

Figures 3a and b show sections of the resonance spectra of axes Nos. 1, 2 and 3 between 100 and 150 eV. The peak at 111 eV is due to ^{116}Sn. It has a broad bump at the higher energy side, which is due to (multiple) scattering followed by capture in this resonance. There are several weaker peaks of tin, antimony and silver in these spectra. The spectrum of axe No. 2 in fig. 3a shows clearly the broad resonance of cobalt at

TABLE I. – *Ratios of elements of five bronze axes from the Groningen Institute of Archaeology (GIA) in weight % with respect to copper, except for indium, which is in ppm. The numbers of the axes in column* 1 *are also given on fig.* 1 *and are used in this paper.*

Axe	Sn/Cu	As/Cu	Sb/Cu	Ag/Cu	Fe/Cu	Co/Cu	Zn/Cu	Pb/Cu	In/Cu
1	9.42 ±0.11	0.0774 ±0.0011	0.0736 ±0.0095	0.1004 ±0.0009	≤ 0.32	n.o.	0.100 ±0.011	≤ 1.3	17.4 ppm ±0.3
2	15.68 ±0.19	0.292 ±0.004	0.0727 ±0.0009	0.0143 ±0.0005	0.50 ±0.02	0.067 ±0.002	0.224 ±0.014	≤ 1.2	23.2 ppm ±0.4
3	4.96 ±0.06	0.183 ±0.004	0.355 ±0.005	0.153 ±0.002	≤ 0.03	0.052 ±0.003	≤ 0.05	≤ 2.4	7.5 ppm ±0.4
4	3.79 ±0.06	0.189 ±0.027	0.0395 ±0.0008	0.0076 ±0.0007	≤ 0.03	n.o.	≤ 0.09	≤ 2.3	4.1 ppm ±0.7
5	0.082 ±0.015	1.012 ±0.018	2.225 ±0.045	0.662 ±0.005	≤ 0.08	n.o.	≤ 0.29	≤ 2.2	4.4 ppm ±1.0

1) Small socketed axe (1922/XII.35), 2) palstave, lower part (1922/XII.46), 3) Socketed axe (1938/IV.5), 4) Flanged axe (1920/5.53), 5) Socketed axe, Geistingen type (1938/X4). n.o. = not observed.

132 eV. Also the spectrum of axe No. 3 in fig. 3b contains this resonance, but it is covered by resonances of antimony and silver. This makes the analysis somewhat more difficult, but with the peak parameters obtained from spectrum of axe No. 2, it was possible to retrieve the cobalt content of axe No. 3.

We have determined weight ratios of the elements with respect to copper. These ratios are quoted in table I in wt% except for indium, for which the weight with respect to copper is given in ppm. In this way of presenting the data it is possible to quote their individual errors, which are basically statistical.

5. – Discussion

The patina layers of these axes are thin and since neutrons penetrate deeply into the material NRCA will give bulk compositions. As table I shows there are considerable differences in the compositions of the five axes. All five contain tin, the largest amount (Sn/Cu ratio = 0.16) in the palstave (No. 2) and the smallest amount (Sn/Cu ratio = 0.0008) in the Geistingen type socketed axe (No. 5). Thus, the material of four of them (No. 1 to 4) are regular tin-bronzes though some with fairly large amounts of the minor elements As, Sb and Ag. For these axes the sum of these three minor elements ranges from 0.24 to 0.69% with respect to copper.

In the case of the Geistingen socketed axe the sum of As, Sb and Ag is 3.9% with respect to copper. These elements may compensate for the lack of tin in this object. That is, to lower the melting point, and may be to get good casting and hardness properties for this thin-walled object. As and Sb components of the Geistingen axe fall into the As/Sb-clusterplot of Ösenring coppers given by Junk, Krause and Pernicka [11].

In table I five other elements, iron, cobalt, zinc, lead and indium are quoted, all of them detected in small amounts except lead for which upper limits of about 1.2 to 2.4% are given. Detection of lead is difficult because it has resonances only in the keV region; suitable lead resonances are at 3057 and 3163 eV. Apart from the lower neutron flux,

there are resonances of As, Sb and Ag, which can make the analysis of lead resonances difficult. The most promising resonance for analysing nickel is at 2250 eV, but it is in a region where neutrons are removed from the beam by the Bi-filter due to its broad resonance at 2310 eV. Hence, we could not detect nickel in this experiment.

All five axes contain very small amounts of indium ranging from about 4 to 23 ppm with respect to copper. Since indium has a strong resonance at 1.45 eV it can be easily detected. There appears to be a correlation between the indium and tin data with linear correlation factor 0.96, which means that the probability of no correlation is about 1% for this small set of five objects. The indium may have come into bronze as an impurity of tin minerals. With the small number of studied objects, the suggested correlation should be considered as preliminary. There appears to be no correlation of indium with As, Sb and Ag in our data.

6. – Conclusions

This pilot experiment shows considerably different compositions within a small series of bronze axes. Large amounts of arsenic, antimony and silver have been reported earlier, for instance in Ösenring and Singen metals [11, 12].

The observation of indium in bronze artefacts is remarkable and probably new. We have seen indium in a few other ancient bronzes [9, 10]. Little information about the occurrence of indium is available in the archaeological literature. An important question is whether the occurrence of indium is a local phenomenon related to the north-west and central regions of Europe, or that it is more widespread and that its detection has been missed in earlier analyses by other methods. If indeed indium correlates more generally with tin it is of interest to look into the occurrence of indium in tin minerals of various mining areas.

To detect nickel and other elements with resonances in the high-energy region, say above 2000 eV, it is important to improve the resolution by using a longer flight path, and to avoid the use of filters like lead and bismuth. A longer flight path of 30 m is available at the GELINA facility.

The NRCA results might be of interest for furthering the interpretation of prehistoric objects, their origins, production methods, or trade and social connections within Europe.

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We very much like to thank W. Mondelaers and his staff for the dedicated and skilful operation of the linac at the EC Joint Research Centre, IRMM, in Geel. HP likes to memorize the kind hospitality experienced at IRMM during many years. Professor Reinders of the GIA in Groningen has been helpful in making objects available to us. We like to express our appreciation to Hannie Steegstra and Jan Lanting for arranging the axes for this study and for searching the GIA records for information about these objects.

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