# Neutron Resonance Capture Analysis (NRCA), elemental compositions of bronze age objects

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**Abstract:** Neutron resonance capture analysis (NRCA) has been applied to determine the elemental compositions of three valuable, precious and very well preserved ancient bronze objects from the National Museum of Antiquities in Leiden (NL). For this study it was not allowed to use analytical methods, for which samples should be taken from objects. For this reason they were studied by NRCA using epithermal neutron beams from the pulsed neutron source of the GELINA facility of the EC-JRC-IRMM in Geel (Belgium). Neutrons can penetrate thick layers of materials, and therefore this method provides bulk compositions. NRCA is a fully non-destructive method. Since thermal neutrons are removed from the beam, the activation of the objects is low already directly after the measurement and fully negligible after a short waiting period. This research is part of the European ANCIENT CHARM project.

**Keywords:** neutron capture; resonances; elemental composition; non-destructive analysis; Bronze Age objects

## Introduction

The underlying physical phenomenon for neutron resonance-capture analysis (NRCA) is that absorption (capture) of neutrons by nuclei as a function of neutron energy shows sharp peaks (resonances). These resonances are specific for nuclear isotopes and therefore suitable to identify and to quantify elements in materials and objects. That is, an element can be recognized on the basis of the energies of one or more of its neutron resonances. The areas of resonance peaks provide information about the amounts of elements. Capture can be observed by detecting the prompt emission of gamma rays, which are emitted during capture processes in most elements and with a total gamma radiation energy of the order of 5 to 8 MeV. The energy of a captured neutron can be determined from the time ($t$) the neutron needs to travel over the distance ($L$) between the neutron source and the object in which the neutron is captured. This information gives the velocity $V = L/t$ of the captured neutron and thus, in the non-relativistic, low-energy realm, the neutron energy is $E = {}^1/_2 m(L/t)^2$, where $m$ is the neutron mass. With a pulsed neutron source the time-of-flight $t$ can be determined from the start pulse from this source and the stop pulse obtained from the detection of the prompt gamma-radiation. Since it is not necessary to have a good energy resolution for the gamma rays, one can use large scintillation detectors for this purpose. Consequently the efficiency for detecting capture

events is high. With a relatively simple detection system this efficiency can easily be something like 10 - 20% or even more.

Pulsed neutron sources can be realized with certain types of accelerators. The results described in this paper are obtained with the pulsed-neutron source of the GELINA facility of the EC-JRC Institute of Reference Materials and Measurements (IRMM) in Geel (B). Its basic unit is a 150-MV electron accelerator, which produces bursts of electrons as short as 1 nanosecond with a maximum repetition rate of 800 Hz. Stopping the accelerated electrons inside a target of heavy metal generates hard gamma radiation known as Bremsstrahlung. In the case of GELINA the target is a rotating disk of uranium. Bremsstrahlung in turn produces high-energy neutrons inside the uranium disk. A part of the neutrons escaping from this target enters two 4-cm thick containers located just above and below the disk and filled with water. These neutrons are slowed down and in this way a neutron spectrum is obtained from thermal energy up into the MeV region. In the epithermal range the energy of the neutrons is roughly inversely proportional with energy. For the reported experiments the useful range of neutron energies is from about 1 to 5000 eV.

In a paper by Mondelaers and Schillebeeckx (2006) more details about this pulsed-neutron source and time-of-flight (TOF) systems at GELINA are given. A typical resonance spectrum obtained with this facility is shown in figure 1.

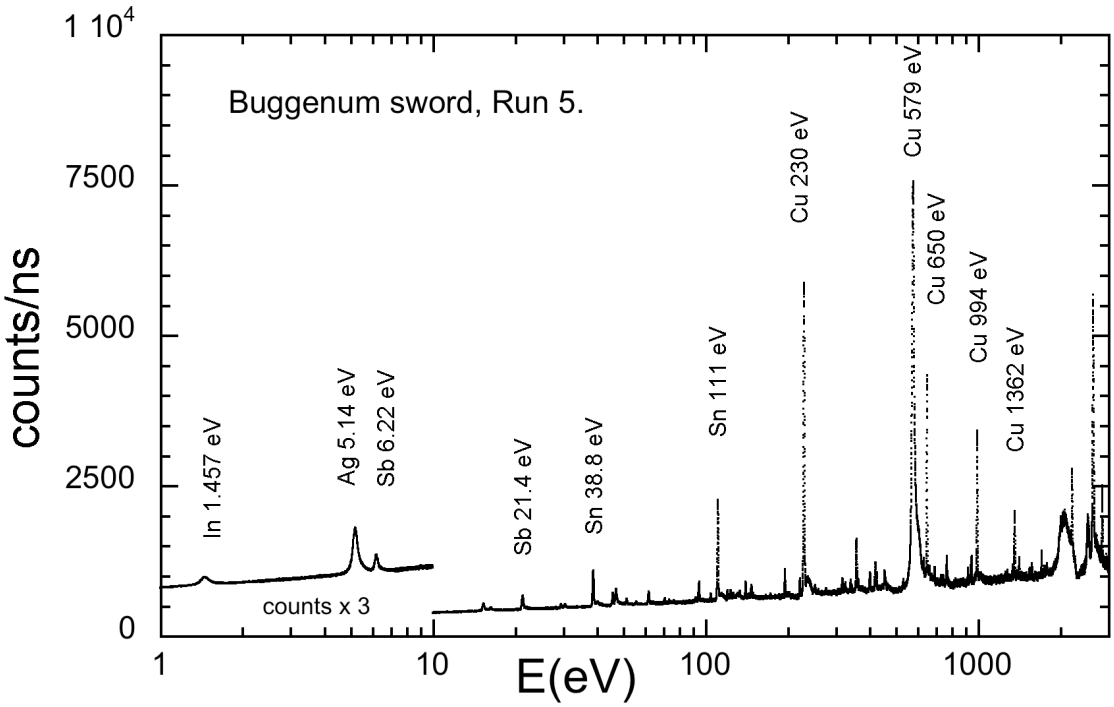


Fig. 1 – A typical resonance spectrum obtained with the Buggenum sword from the National Museum of Antiquities (NMA) in Leiden (NL). Some resonances, important for NRCA, are indicated with their element and energy.

In this paper the results of some NRCA measurements are presented as examples about what can be obtained concerning elemental compositions of objects. These measurements have been carried out with three bronze objects on loan from the National Museum of Antiquities (NMA) in Leiden (the Netherlands). All three objects are precious and very well conserved objects. NMA showed great interest in the determination

of the compositions of these artifacts, however only non-destructive analytical methods were acceptable for these objects. Therefore NRCA has been applied to these objects.

## Some details of NRCA

There are basically two ways to analyze NRC spectra; that is:

A) Absolute method to determine the amounts of elements based on knowledge of resonance parameters, detection efficiencies for capture events, neutron flux data, and size and shape of the object.

B) Relative method to determine the ratio of elements based on the comparison with calibration samples. In this method it is not necessary to know resonance parameters, detection efficiencies and the absolute flux. It requires calibration measurements carried out under the same conditions as the measurements with the artifacts.

Most of our analyses of ancient artifacts are carried out with the relative method, in our case comparing elements of the bronze objects to copper as the main component. Since it is based on the ratio of areas of two resonances, one from copper and the other from another element, for the object as well as for a calibration sample with known composition, one is in fact dealing with a double ratio method. In this way problems due to irregular shapes of objects and to the often insufficiently known properties of resonances are circumvented. The weight ratios of elements with respect to copper can be converted into absolute values (e.g. in weight %) if it can reasonably be assumed that all elements are known, maybe with the exceptions of a few weak components. Actually this is a general problem also for other methods, which are not able to determine all elements of an object.

The basic information for determining elemental amounts are the numbers of captures (counts) in the chosen resonances. The number of counts in a resonance peak is obtained as a sum of the channel contents of the peak after background subtraction. The latter requires some care.

Apart from capture there is always scattering, which can be followed by capture inside the object. These scattering-followed-by-capture (SC) events add to the TOF spectrum. Since neutrons lose energy in the scattering process each resonance peak may show a broad structure at its high-energy side. Part of this SC structure is underneath the capture peak. This must be subtracted from the spectrum to get the correct number of events of a capture peak. This can be done for instance by a parametric fitting procedure. For very low energy resonances a larger part of the SC structure is underneath the capture peak as compared to higher energy resonances.

Another important correction concerns the fact that the neutron flux diminishes during penetration of the object due to capture and scattering. Notably this occurs at resonance energies, which therefore reduces the number of capture events in resonance peaks. This is known as the resonance self-shielding effect. It is a factor to be taken into account in the analysis. It can be calculated in most cases sufficiently accurately on the basis of the total Doppler-broadened neutron resonance cross section.

For several elements it is possible to choose more than one resonance for the analysis. For copper suitable resonances are at the 230, 650, 994 and 1362 eV and for tin resonances at 38.8, 45.75 and 111 eV can be used; see figure 1. That means twelve pairs of Cu- and Sn-resonances can be used to calculate the Sn/Cu weight ratio. If one is dealing with a thin object (in which therefore self-shielding does not play a role) of a tin-

bronze the twelve pairs of resonances should give the same weight ratio. However, for thick artifacts the count rates in the resonance peaks are diminished by self-shielding factors, and since these resonances have different strengths count-rates are affected in different ways. Without correcting for self-shielding the experimental weight ratios are therefore different. Hence correction for self-shielding can be important, and since self-shielding depends on the thickness, an effective thickness can be found at which the corrected weight ratios for the twelve pairs of resonances are equal. This provides a simultaneous determination of the Sn/Cu weight ratio and an effective thickness (areal weight in g/cm$^2$). More details of this and other aspects of NRCA can be found in Postma et al (2004), Schut et al (2008), and Postma and Schillebeeckx (2009).

## The artifacts

The three artifacts on loan from the National Museum of Antiquities in Leiden (NL) are:

a) the Buggenum sword, which was found during the dredging of a lateral canal of the river Meuse in a village near Roermond (NL) It is dated from about 1300 – 1100 BC,
b) The Jutphaas sword, which was accidentally found near the river Rhine. It is one of five very similar swords without a hilt. It is a thin, skillfully crafted blade without provisions for attaching a hilt, a non-utilitarian, ceremonial object dated from 1500 – 1400 BC.
c) The double axe from Escharen, a small village on the Raam a tributary of the Meuse and near Grave (NL). It is dated 2100 – 1800 BC.

The main results of NRCA measurements obtained with these artifacts will be reported with some discussions of the objects.

### The Buggenum sword

All-metal swords with very similar decorations as the Buggenum sword are known from upper-Danube and its tributaries north of the Alps. Therefore the Buggenum sword is thought to be from this region and since it was found in the Netherlands, it must have traveled a long distance. This sword is considered to be a ceremonial object and it is dated to the Hallstatt A1 Middle Bronze Age period (13$^{th}$ -11$^{th}$ c.BC). (Butler, Fontijn 2007) It does not show any sign that it has been used as a weapon. The blade and the hilt are of different casts of tin-bronze with 12% respectively 13% tin. They contain the minor elements Sb, As, Ag and In with diminishing amounts in this order, constant over the blade, however, with slightly different values for antimony and arsenic in the hilt. More details of the NRCA measurements and results of the Buggenum sword are given by Postma et al (2009) together with results from neutron diffraction at ISIS (UK). From the latter results it is argued that the Buggenum sword has actually been made as a functional weapon.

### The Jutphaas sword

This artifact is one of a group of five very similar swords with sizes from 42 to 70 cm. The Jutphaas sword is the shortest one of them. They are found in the United Kingdom, France and the Netherlands and are known as the Plougrescant-Ommerschans type of swords. None of them are equipped with a hilt or have remains indicating how hilts could have been fastened to these swords. They are clearly useless as weapons. It is assumed that they are meant to be ceremonial or impressive objects for their owners. (Buttler, Safratij, 1970/1971), (Fontijn 2001) They are considered to be from the Middle Bronze Age (1500 – 1400 BC).

Two NRCA-measurements have been carried out with the Jutphaas sword; a long run at the top and a shorter one at the tip. It is shown to be a 13 wt% tin-bronze with the minor elements Sb, As, Ag, Zn, Co, In, Fe and Ni; the latter two showed up only in the longer measurement at the top section. Lead could not be detected in both runs with an upper limit of about 2 wt%. The compositions deduced from the two runs of the Jutphaas sword are very similar and in addition also similar to the compositions measured for two other swords of this series, namely the Beaune and Oxborough swords, and similar to the composition of a related, but not identical sword found in Kimberley. (Needham 1990) The Kimberley sword has a slightly different shape and is not considered to belong to the Plougrescant-Ommerschans type. Figure 2 shows the composition of the Jutphaas sword as a bar plot on a log-scale.

**The Escharen double axe**

This metal artifact is a strange object and certainly not useful as an axe. It is considered to be a Zabitsch type axe of which there exists only a very limited number. (Butler 1995/6, Fontijn 2002) It has a hole in the middle too narrow to be securely hafted. NRCA showed that it is a fairly pure copper object with a very small amount of tin and the minor elements Sb, As, Ag, Co and In. For zinc an upper limit is given. Figure 2 shows its composition as a bar plot on a log scale. The largest amount concerns arsenicum. This composition resembles closely the Singen composition. (Butler, 1995/6) The Escharen double axe is considered to be from the early Bronze Age (2100-1800 BC).

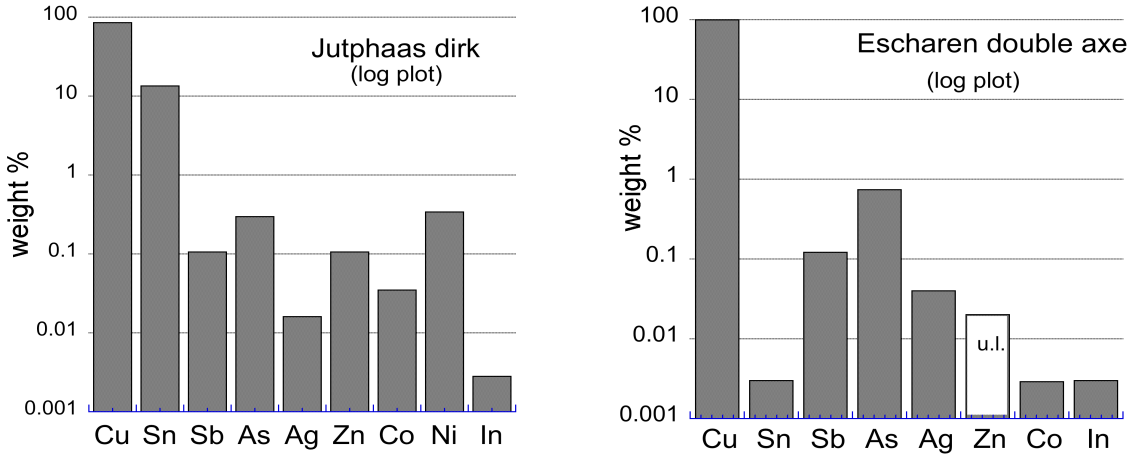


Fig. 2 – Bar plots on a log scale of the compositions of the Jutphaas sword and the Escharen double axe in weight %.

## Activation by neutrons

Capture of neutrons may lead to activation of an object since part of the isotopes produced by capture can be unstable. In many cases the half-lives are short and the produced activation may already partly disappear during the NRCA runs, or otherwise during short waiting periods after the measurements at the GELINA facility. Some long-living isotopes can be produced but that has never been a problem at the GELINA facility due to the low neutron fluence and the removal of thermal neutrons by either a cadmium sheet of 1 mm thickness or a disk containing $^{10}B$. This reduces activation by thermal neutron by a very large factor. Activation may still occur by resonance capture, but this leads at most to a very low activation at the GELINA

facility. As a consequence objects studied by NRCA can be returned to their owners after a short waiting period, normally less than one day.

## Advantages and limitations

NRCA determines the composition of the bulk matter of an object. It is not necessary to do any preparation. Removal of the patina is not necessary since this is normally thin compared to the bulk, and thus it has little or no influence on the result. NRCA is a non-destructive method and can be applied to irregular and fragile objects. By removing thermal neutrons, which are not of interest to NRCA, from the beam reduces the activation to a very low level and activation is negligible after a short waiting time.
A disadvantage is that the NRCA method can only be carried out at a limited number of accelerators; in Europe at the GELINA facility of the EC-JCR Institute for Reference Materials and Measurements in Geel in Belgium and at the ISIS facility of the Rutherford-Appleton Laboratory in the UK.
The GELINA facility should therefore be used mainly for cases of expensive or rare objects. The ISIS facility with its much higher neutron flux could be an interesting future facility for NRCA measurements of large series of objects. Even very small objects can be measured within a short time as has been shown by test experiments in the ANCIENT CHARM collaboration; see the paper by Gorini (2009) presented during this conference.

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