Some Applications of Neutron Resonance Capture Analysis

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Abstract. The probability for nuclei to capture neutrons reveals sharp peaks, so-called “resonances,” which occur at neutron energies specific for each element. These resonances are very suitable for identifying and quantifying elements in objects and materials. They are the basis of an analytical method called “Neutron-Resonance-Capture-Analysis” (NRCA). This is a fully non-destructive method applicable to almost all stable isotopes, which determines the bulk elemental composition, and does not require any sample preparation and results in negligible residual activity. Up to now NRCA has been mostly applied for archaeological applications. In this paper we review the technique and discuss the applicability of the technique in the biomedical field and in material science.

INTRODUCTION

There are three aspects of the neutron-capture process, which can be used to analyse the elemental composition of objects and materials [1]. The first aspect concerns the radioactivity induced by neutron capture. Usually small samples are taken from an object and irradiated inside a reactor. After a suitable waiting time, the energy and intensity of the gamma rays following the radioactive decay are determined with a high-resolution detector to identify and quantify the elements of the sample. This is known as instrumental-neutron-activation-analysis (INAA). The second aspect concerns the energy and intensity of prompt gamma rays emitted directly after neutron capture and again detected with a high-resolution detector. This method, known as prompt-gamma-neutron-activation-analysis (PGNAA), has found many applications and has already reached a high degree of sophistication. The third aspect of neutron capture relevant to the analysis of objects relates to the resonances occurring in the energy differential capture cross section. The resonances occur at energies typical for each nucleus. They are the basis of an analytical method, “Neutron-Resonance-Capture-Analysis” (NRCA), which has been developed in a joint project of IRI (Delft, NL) and IRMM (Geel, B). NRCA is a non-destructive method that is applicable to almost all stable isotopes, determines the bulk elemental composition, does not require any sample taking or surface cleaning, and results in a negligible residual radioactivity.

EXPERIMENTAL SET-UP

The NRCA technique has been developed at the neutron Time-of-Flight (TOF) facility GELINA of the Institute for Reference Materials and Measurements (IRMM) in Geel, Belgium. This facility has been designed and built especially for high-resolution neutron cross-section measurements [2]. It is a multi-user time-of-flight facility, providing a pulsed white neutron source, with a neutron energy range between 1 meV and 20 MeV. The linear electron accelerator provides very short electron pulses on the order of 1 ns, which produce neutrons by hitting a piece of uranium metal. To produce a neutron spectrum in the low-energy region, two water-filled Be containers, 4 cm thick, are used as moderators. The moderated spectrum shows a Maxwellian distribution plus a tail of partially moderated neutrons with an approximate 1/E behavior. The energy differential neutron fluence rate \( \varphi(E_n) \) at a distance L from the production target for neutron energies \( E_n > 1 \text{ eV} \) is in first approximation [3]:

\[ \varphi(E_n) \approx \frac{C}{E_n} \]
\[
\phi(E_n) = \frac{1.16 \times 10^6}{L^2 E_n^{0.92}}
\]  

(1)

where \(\phi(E_n)\) is in \(\text{cm}^{-2}\text{s}^{-1}\text{eV}^{-1}\), \(E_n\) in eV, and \(L\) in m.

The resonance structure can be observed by the time-of-flight (TOF) technique using a set of high-efficiency \(\gamma\)-ray detectors. The TOF of a neutron is determined by the time between the start signal, given at each electron burst, and the stop signal from the capture detectors. These pulses are sent to a Fast Time Coder with a 0.5-ns time resolution, designed at the IRMM [4]. The TOF together with the pulse height of the detected events are recorded in list mode using a data-acquisition system developed at the IRMM [5]. The list mode allows off-line analysis of the data. Close to the target hall a set of BF3 proportional counters monitors the stability of the accelerator and their output is employed to normalise the spectra to the same total neutron intensity. In the capture measurement stations the shape of the neutron spectrum is also measured with an ionisation chamber placed 80 cm before the capture detection system. The chamber has a cathode loaded with a thin \(^{10}\text{B}\) layer.

NRCA measurements have been performed at two measurement stations with flight paths of 14 and 30 m. We compared the performance of a detection system based on \(\text{C}_6\text{D}_6\) detectors with the one based on BGO detectors and used different shielding configurations. The main conclusions were [6]:

- Shielding around the detection system does not improve the peak-to-background ratio. However, we need improved shielding against neighboring flight paths.
- Above about 1 keV the performance of \(\text{C}_6\text{D}_6\) detectors is much better compared to BGO detectors. This is due to the lower neutron sensitivity and better time resolution. We prefer to use \(\text{C}_6\text{D}_6\) detectors.
- To detect high-energy resonances in the keV region, good resolution is required. When the resonances are isolated measurements at a short flight path are preferred. The loss in neutron fluence, at a longer distance, is not compensated by the improved resolution.
- We do not observe a substantial improvement by a selection of specific \(\gamma\)-ray energies using BGO. One needs detectors with better energy resolution.

We designed an improved detection system and optimised shielding in the measurement station at 14 m.

### DATA ANALYSIS

For a regular object with thickness \(d\) the number of capture events \(Y_c\) resulting from an isolated resonance of nuclide \(k\) can be expressed as [7]:

\[
Y_c \propto (1-e^{-n_k \sigma_{\gamma,k} d}) \mu \frac{\sigma_{\gamma,k}}{\sigma_{t,k}} \phi(E_n)
\]  

(2)

The total and capture cross section for a nuclide \(k\) are expressed as \(\sigma_{t,k}\) and \(\sigma_{\gamma,k}\), respectively. The number density of the element \(k\) is denoted by \(n_k\). The term in brackets accounts for the self-shielding effect and \(\mu\) for the multiple scattering correction. For a correct treatment of the self-shielding the total cross section should be Doppler broadened. The observed count rate \(N\) also depends on the efficiency to detect a capture event \(\epsilon_c\). The line shape is a convolution of Eq. (2) with the time resolution of the spectrometer.

In an ideal detection system the efficiency to detect a capture event should be independent of the capture \(\gamma\) cascade [7]. This can be achieved by using total absorption detectors, which have an almost 100% detection efficiency for all \(\gamma\) rays regardless of their energy. An alternative is the total-energy detection principle, which is based on a low-efficiency detection system with a \(\gamma\)-detection efficiency, \(\epsilon_\gamma\), that is proportional to the \(\gamma\)-ray energy. The Pulse Height Weighting Technique [7] (PHWT) can be applied to the detector output pulses in order to render the detection efficiency proportional to the \(\gamma\) energy. If \(\epsilon_\gamma\) is very small, the efficiency for detecting a capture event is directly proportional to the total energy released in the capture event. In principle, both BGO and \(\text{C}_6\text{D}_6\) detection systems can be used together with the PHWT to apply the total-energy detection principle. It is shown that the weighting function depends strongly on the characteristics of the object under investigation [7]. Up to now we have not yet applied the PHWT. The determination of the detection efficiency for a capture event is included in our calibration procedure.

For a weak resonance and/or a thin sample, such that \(n_k \sigma_{\gamma,k} d \ll 1\), we can neglect the self-shielding in Eq. (2) and the capture yield becomes a simple function of the resonance parameters. When the weak resonance/thin sample approximation is not valid, the self-shielding and multiple scattering play an important role. Resonance shape analysis codes, such as REFIT and SAMMY, could be used to account for the resolution and Doppler broadening, and the self-shielding and multiple scattering in the object.
So far we have preferred to determine weight ratios of elements of the object (or material under study) by comparing with standard samples of known elemental ratios. That is, we use the expression:

\[
\frac{w_k}{w_m} = A_c \cdot R(E_{r,k}, E_{r,m}) \frac{N(E_{r,k})}{N(E_{r,m})}
\]  

(3)

The weights of the elements k and m are defined by \(w_k\) and \(w_m\), respectively, and the integrated areas of the resonances by \(N(E_{r,k})\) and \(N(E_{r,m})\). The factor \(R\) accounts for the self-shielding correction and \(A_c\) is a constant, which is determined by a measurement of a calibration sample with a known elemental composition. The correction for self-shielding is based on Eq. (2). The effective thickness of the object can be deduced from the ratio of the integrated areas of two resonances with a different strength [8]. This is illustrated in Fig. 1 where we plot the ratio of the integrated area of the 230- and 578-keV resonance of Cu as a function of the thickness of the object. The full line through the data points is based on Eq. (2), employing the resonance parameters listed in the evaluated data files, and only adjusting a normalisation factor to account for the difference in detection efficiency per capture event for the two resonances.

![Figure 1: The ratio of count rates of two copper resonances at 230 and 578 eV, respectively, as a function of the Cu thickness in g/cm².](image1.png)

To verify the consistency of the data, we also try to use several resonances per element to determine the elemental composition [9]. In Fig. 2 we compare the Sn/Cu weight ratio of an object deduced from the 230-, 650-, 994-, and 1631-eV resonances of Cu and the 33.8- and 111-eV resonances of Sn. This provides eight values for the Sn/Cu weight. Without self-shielding correction some of the Sn/Cu weight ratios differ by more than 50%. After a proper analysis of the self-shielding effect, the resulting weight ratios agree within the statistical uncertainty.

![Figure 2: The Sn/Cu ratio of a prehistoric bronze axe determined from eight pairs of resonances without and with self-shielding corrections.](image2.png)

The elemental composition of a bronze arrowhead obtained by NRCA has been verified with INAA. For all elements the agreement between the relative abundance was within the uncertainties due to counting statistics only [10]. It has also been verified that the residual radioactivity of objects investigated with NRCA can be neglected. In [11] we compare the performance of NRCA with PGAA, and show that they are related and complementary analytical methods. PGAA is very suitable for the lighter elements, which have no resonances at sufficiently low energies to make NRCA applicable for light elements. But NRCA is more sensitive for most of the heavier elements with very high sensitivities for elements with resonances of a few eV. Due to the high detection efficiency for capture events, NRCA needs a much lower neutron fluence to get results comparable or even better than PGAA. A difference is that in PGAA elements compete for the same neutrons, while in the case of NRCA elements use neutrons of different energies of a “white” beam.

**APPLICATIONS**

NRCA has been proven useful for the non-destructive quantitative elemental analysis of bronze archaeological artifacts and similar valuable objects. In bronze objects, apart from copper and tin, other elements, such as In, Au, Ag, Sb, As, Co, and Fe, might be present as impurities, and lead is often added...
as a component. The presence and concentration of various impurities is helpful in assessing the origin of the ores, the smelting techniques, and the fabrication of objects. NRCA was successful in determining the elements indicated above, most of them having resonances in the low-energy range. NRCA could be employed to verify the authenticity of Etruscan bronze artifacts based on the Zn/Sn ratio [1]. However, in the case of lead, with resonances only in the keV range, the detection was not satisfying. In addition the background at this energy was high. Recently, the experimental set-up has been improved, allowing detection of resonances at higher energies, and thus improving the determination of the Pb/Cu ratio.

The improvements allowed broadening of the NRCA applications. In particular, new applications in the biomedical field and in construction material science have been tested. The first involves measurements for the determination of calcium and phosphorus in the frame of osteoporosis related studies. It has been proposed that the Ca/P ratio might be a parameter for the assessment of bone-related diseases [12]. NRCA is used for the determination of elemental ratios and, in this respect, it could be a suitable technique for the determination of the Ca/P ratio in vivo. The application in vivo requires dosimetric considerations. This goes beyond the scope of this paper. Preliminary experiments have been performed both on bone-like synthetic materials (hydroxyapatite) and on bovine ribs to determine the Ca/P ratio. The results obtained for hydroxyapatite agreed with data from chemical analysis, whereas the results on bone ribs agreed with the INAA data [12].

The second field of application regards the determination of chlorine in marble matrices. The combined effect of weathering and salts, such as chlorides and sulphates, results in embrittlement and stone decay of marble structures [13]. NRCA offers a tool to determine chlorine relative amounts in the sample without need of treating the sample prior to analysis. As both the neutrons and prompt gammas have high penetrating power, measurements of chlorine concentrations deep into the marble are feasible. Measurements have been performed on pure marble samples loaded with small quantities of chlorides. The Cl/Ca ratio was determined both with NRCA and INAA and the results agreed within the experimental errors. Recently, experiments on weathered marbles of different provenance have been performed. The data reveal that the detection of sulphur is possible with NRCA. Table 1 illustrates the results discussed above by showing some elemental ratios determined with NRCA, together with comparison data, either from literature or measured.

**CONCLUSION**

We have demonstrated that NRCA can be applied as a non-destructive tool for various applications such as archaeology, material research, and in the biomedical field.

**TABLE 1.** Elemental ratios of samples analysed with NRCA compared with results of other methods.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elemental Ratio (g/g)</th>
<th>NRCA</th>
<th>Other Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxyapatite</td>
<td>Ca/P</td>
<td>2.0</td>
<td>2.05 (0.02) Chemical Analysis [14]</td>
</tr>
<tr>
<td>Cow Rib</td>
<td>Ca/P</td>
<td>2.2</td>
<td>2.13 (0.32) INAA [12]</td>
</tr>
<tr>
<td>Marble-Cl</td>
<td>Cl/Ca</td>
<td>0.0018</td>
<td>0.00171 (0.00006) INAA</td>
</tr>
</tbody>
</table>

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5. J. Gonzalez, C. Bastian, S. de Jonge, and K. Hofmans, Internal Rep. GE/R/INF/06/97, IRMM, Geel
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