IL NUOVO CIMENTO Vol. 31 C, N. 2 Marzo-Aprile 2008
DOI 10.1393/ncc/i2008-10292-6

Prompt gamma activation studies on archaeological objects at a pulsed neutron source

Zs. Kasztovszky([1]), W. A. Kockelmann([2]), E. Perelli Cippo([3]), G. Gorini([3]) and M. Tardocchi([3])

([1]) *Institute of Isotopes Hungarian Academy of Sciences - POB 77, H-1525 Budapest Hungary*
([2]) *STFC, ISIS Facility, Rutherford-Appleton Laboratory - Chilton, Didcot OX11 0QX, UK*
([3]) *Dipartimento di Fisica "Giuseppe Occhialini", Università di Milano-Bicocca Piazza della Scienza 3, I-20126 Milano, Italy*

(ricevuto il 15 Aprile 2008; revisionato il 29 Luglio 2008; approvato l' 1 Agosto 2008; pubblicato online il 28 Ottobre 2008)

Summary. — The potential of Prompt Gamma Activation Analysis (PGAA) for non-destructive quantitative investigation of archaeological objects at a pulsed neutron spallation source was studied. Experiments were performed on the ROTAX time-of-flight diffractometer of the ISIS neutron source on a chalcolithic copper axe, a limestone sample from the ancient Quarry of Masarah (Egypt), a Roman bronze fibula and two fragments of glass from the Roman Villa Adriana. For reference and comparison, measurements were also performed at the PGAA station of the Budapest research reactor. It is found that the performance of a PGAA analysis at a pulsed source, with a make-shift set-up on an instrument designed for diffraction studies, cannot match the achievable results at a dedicated PGAA facility at a reactor source. However, the possibility of performing different investigations, *e.g.*, neutron diffraction for structure analysis and PGAA for elemental analysis, at a single facility on one and the same object remains attractive and offers useful applications in the field of cultural heritage.

PACS 28.20.Np – Neutron capture γ-rays.
PACS 61.05.fm – Neutron diffraction.

1. – Introduction

A variety of chemical and physical probes are currently available for non-destructive analysis on cultural-heritage objects. Among others, X-rays and electrons are widely used as laboratory probes for providing information on the chemical composition and structure of artefacts. The use of neutron-induced activation analysis techniques is, on the other hand, limited to a few specialized centres. Neutron analyses are motivated by the deep penetration range of neutrons in materials (*e.g.*, metals) compared to X-rays, which allows for bulk analyses of samples.

Prompt Gamma Activation Analysis (PGAA) [1] makes use of the fact that many nuclei de-excite with the prompt emission of γ radiation after neutron capture. The prompt γ spectrum is detected by high-resolution gamma-ray spectrometers, and the intensities of the emission peaks provide quantitative identification of the emitting nucleus. PGAA is to be distinguished from Instrumental Neutron Activation Analysis (INAA) [2], because for the former the γ emission is measured during sample irradiation. Since the emission is measured at the time of irradiation, prompt emission signals are stronger than in INAA for the vast majority of nuclei. Moreover, some nuclei do not have delayed emission at all. However, the neutron fluxes on PGAA instruments are typically orders of magnitudes lower compared to INAA irradiation facilities. The typical number of elements in a sample is about 10 for PGAA, compared to 20 for INAA. The major advantage of PGAA for cultural-heritage materials is the possibility of performing completely non-destructive studies on objects, without the need to take samples, or to remove patina from a metallic object. For PGAA analysis, the intact object is just placed in front of the neutron beam. In the past, the number of PGAA applications have been limited by the need of a dedicated station at a neutron source like the PGAA facility at the Budapest Research Reactor. Moreover, high-resolution germanium detectors are needed, which in turn have the disadvantage of limited detection efficiencies and of radiation damage by high neutron fluxes required for these types of measurements.

This paper reports on the first investigations of the PGAA technique at the ISIS neutron spallation source using a high-purity germanium detector. The pilot study was motivated by the fact that, at present, there are no PGAA analysis facilities operated at pulsed neutron sources. The studies were also motivated by the limitations of neutron diffraction analyses which are performed on a regular basis at ISIS [3]. Time-of-flight neutron diffraction is a non-invasive tool for obtaining structural information from ceramic and metal objects. Diffraction is very strong in separating out corrosion phases and secondary phases, allowing an unobstructed view onto the original ceramic or alloy components of the object. Diffraction analysis, however, only provides indirect information of the chemical compositions, for example via lattice parameter measurements and application of Vegard's rule [4]. The two methods, PGAA and neutron diffraction, yield different aspects of the materials in terms of element and phase concentrations, respectively. The prospect of obtaining information on the element contents for exactly the same sample volume that is illuminated for neutron diffraction has several advantages: i) elemental contents are indispensable to unambiguously interpret the diffraction data; ii) there is an ideal correspondence of the irradiated sample bulk volume; iii) an object is only irradiated once in the neutron beam.

The experience and first results of a make-shift PGAA set-up on the neutron diffractometer ROTAX at ISIS are reported. The PGAA results obtained on ROTAX are compared with PGAA results obtained at the Budapest PGAA facility. The recently upgraded PGAA facility is currently unique in Europe and dedicated to perform non-destructive multi-elemental or isotopic analyses on various samples, such as archaeological objects up to tens of a centimetre in diameter, and on geological rocks. The measurements at the Budapest Facility provided benchmark and reference data for the set-up at ISIS. Since the Budapest (PGAA) station is standardised for quantitative analysis, and also checked on various standard reference materials (geological, industrial, environmental), the results of archaeological samples can be regarded as PGAA-references within the uncertainty of the data.

2. – Choice of artefacts

The samples selected for PGAA at ISIS are representative of the diversity of artefacts currently investigated by different neutron techniques. The first object was a Levantine chalcolithic copper axe, dated about 4000 BC of dimensions of approximately 100 mm × 4 mm × 10 mm: its surface does not show evidence of significant oxidation or corrosion. A neutron diffraction study of the copper axe has found cuprite in addition to the copper phase [5]. Another analyzed object was a fragment of white limestone from the Egyptian quarry of Masarah. Limestone from this quarry, used over a wide time period for producing monuments and sculptures, was considered amongst the highest quality stones in ancient Egypt [6]. Finally, two glass fragments from the mosaics of the Roman Villa Adriana and a Roman bronze fibula were also investigated. Diffraction data obtained on ROTAX and PGAA data obtained on the Budapest PGAA station on the copper alloy fibula were reported earlier [7].

3. – Experimental

3˙1. *Principles of PGAA.* – PGAA is based on the capture of a neutron by a target nucleus, via the reaction

$$(1) \qquad {}^{Z}_{A}X + {}^{0}_{1}n \rightarrow {}_{A+1}{}^{Z}X^{*},$$

where the * symbol indicates a nucleus left in an excited state. The excited nucleus decays with the prompt emission of one or more γ photons. General expressions for the activation and decay rates can be found in refs. [8, 9]; here we just recall the formalism for the special case of a mono-elemental target.

The activation rate of a sample exposed to a neutron flux ϕ is

$$(2) \qquad \left[\frac{\mathrm{d}N}{\mathrm{d}t}\right]_{\text{activ.}} = \sigma\phi n,$$

where σ is the capture probability (expressed as a cross-section area) and n is the number of target nuclei in the sample. The transmutation rate is so low that n can be considered as a constant for the entire duration of the activation experiments (usually of the order of up to a few hours).

The decay rate is

$$(3) \qquad \left[\frac{\mathrm{d}N}{\mathrm{d}t}\right]_{\text{decay}} = -\lambda N,$$

where λ is the inverse of the decay time and is unique for each nucleus. Finally, the total activity rate is

$$(4) \qquad \frac{\mathrm{d}N}{\mathrm{d}t} = \sigma\phi n - \lambda N$$

and the number of the emitting atoms at time t is thus

$$(5) \qquad N(t) = \frac{\sigma\phi n}{\lambda}(1 - e^{-\lambda t}).$$

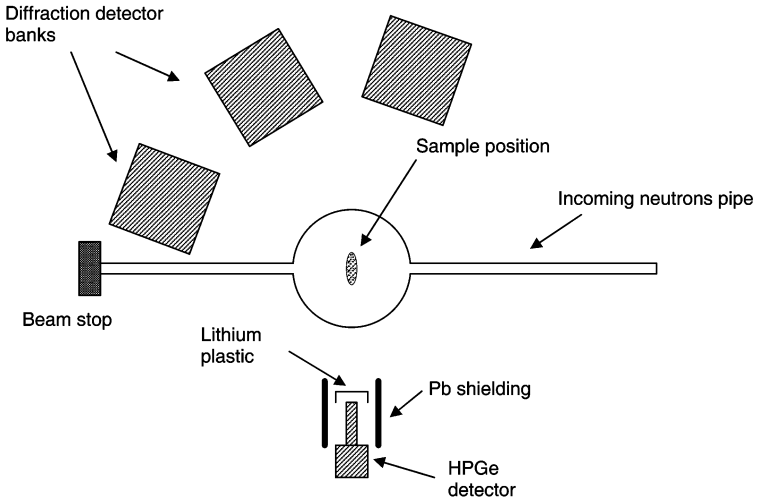

Fig. 1. – Sketch of the ROTAX beamline at ISIS, with the HPGe detector used for PGAA measurements, and the standard ROTAX diffraction detector banks.

In the case of prompt emission, the value of λ is very large, and eq. (5) reduces to

$$N(t) \approx \frac{\sigma \phi n}{\lambda} . \tag{6}$$

Thus the activity induced by the neutron flux is independent of time during the measurement period.

3˙2. *The ROTAX beamline at ISIS*. – The ROTAX beamline was selected as the most suitable for PGAA at the ISIS spallation neutron source [10]. ROTAX has been used for many years as a neutron diffractometer, also for diffraction analyses of cultural-heritage artefacts. It is now used as a test beamline, providing a flux of about 10^6 neutrons $\cdot s^{-1} \cdot cm^{-2}$ in the thermal energy range 5–200 meV. The instrument makes use of three position-sensitive ^{6}Li-glass detector banks covering the angular range from 10° to 170°. These detectors are positioned on one side of the sample chamber (fig. 1). Other detection systems can be installed on the other side of the sample position providing an opportunity for simultaneous measurements of PGAA spectra and diffraction patterns.

The PGAA experiments were performed with a High Purity Germanium (HPGe) detector. The HPGe was used to record the γ spectra emitted by the samples irradiated by the relatively high flux of thermal neutrons coming from the ISIS liquid methane moderator. The HPGe detector was positioned at about 90° relative to the incoming neutron beam direction, and looking at the sample through a 1 mm thick aluminium window (see fig. 1). The position of the HPGe detector was adjusted in order to be as far as possible from the neutron beam-dump which was recognised as a source of significant γ background. The detector was enclosed in a double shielding, made of a lead (Pb) brick wall and a lithium-enriched plastic sheet of about 1 mm thickness. The latter is a ^{6}Li fluoride loaded polymer matrix (Ing Stronciwilk, Berlin) which is characterised by a very low secondary radiation emission. The lead reduced the gamma-ray background while

the lithium plastic was used to shield the HPGe crystal from the neutrons scattered by the sample.

3˙3. *Background reduction.* – Gamma background radiation, *i.e.* prompt or delayed gamma photons that are not originating from the nuclei in the sample and thus does not contribute to the elemental analysis of the sample, can be due to irradiation of ancillary components on the instrument by primary neutrons from the source or by scattered neutrons. Background radiation may originate from previous activation of materials around the sample area, or from neighbouring neutron beamlines.

The main technical difference between PGAA and the more commonly used INAA technique is that the former is performed simultaneously with the sample irradiation. This implies that the gamma-ray detectors are subject to neutron-induced prompt and delayed gamma-ray background, that poses severe limitations for PGAA measurements.

Several background sources have been identified, including the ISIS target, the moderator, the neutron beam-dump and the neutron collimators of ROTAX. Further sources of γ background are the vacuum sample tank surrounding the sample and other mechanical structures of the instrument. These are sample dependent, because these components are exposed to neutrons scattered from the sample and produce prompt and delayed γ radiation. One of the major effects concerns the scattering of neutrons in the sample, which can remove a significant fraction of neutrons from the beam. Hence, there is a sample-dependent component by the neutron beam-dump because different amounts of neutrons are removed by different sample sizes and compositions. These latter sample-dependent background contributions are more difficult to take into account. Even samples of similar size can produce different background spectra. A thick and heavy sample like a bulky copper axe strongly attenuates the intensity of the primary beam, thus causing a reduction of the background component from the beam-dump. This can be observed in the copper axe spectrum (fig. 2) by a reduction of the 477 keV peak intensity which is due to ^{10}B, and which is present in large quantities in the beam-stop, compared to the no-sample spectrum of fig. 3. On the other hand, strong scattering of neutrons in the sample causes a high level of the overall neutron and gamma background originating from the sample chamber, pipes and surrounding walls.

Background reductions were attempted in several ways. First of all, the HPGe detector was gated applying a gating time of 10 ms, synchronized with the ISIS accelerator with a delay time of 1.4 ms (the overall duty cycle of the ISIS accelerator is 20 ms). This was done in order to both reduce the effect of the γ flash from the neutron target and minimize the delayed γ component. Moreover, the detector was protected by the aforementioned lead and ^{6}LiF enriched polymer shielding. A further neutron shield made of the same ^{6}LiF plastic material (see fig. 4) was positioned around the sample holder. Since the ^{6}Li neutron absorption reaction does not produce photons, it is not a source of background for PGAA. Such a shielding was particularly effective in reducing the background induced by scattered neutrons, as can be seen from fig. 5, which shows gamma spectra obtained from the bronze fibula with (lower curve) and without (upper curve) the lithium plastic screen. On the other hand, some lines due to neutron capture in the detector itself and in its lead shielding (like the germanium and bismuth lines visible in fig. 5) are not influenced by the lithium shielding.

The methods of background suppression resulted in a six-fold reduction of the overall background.

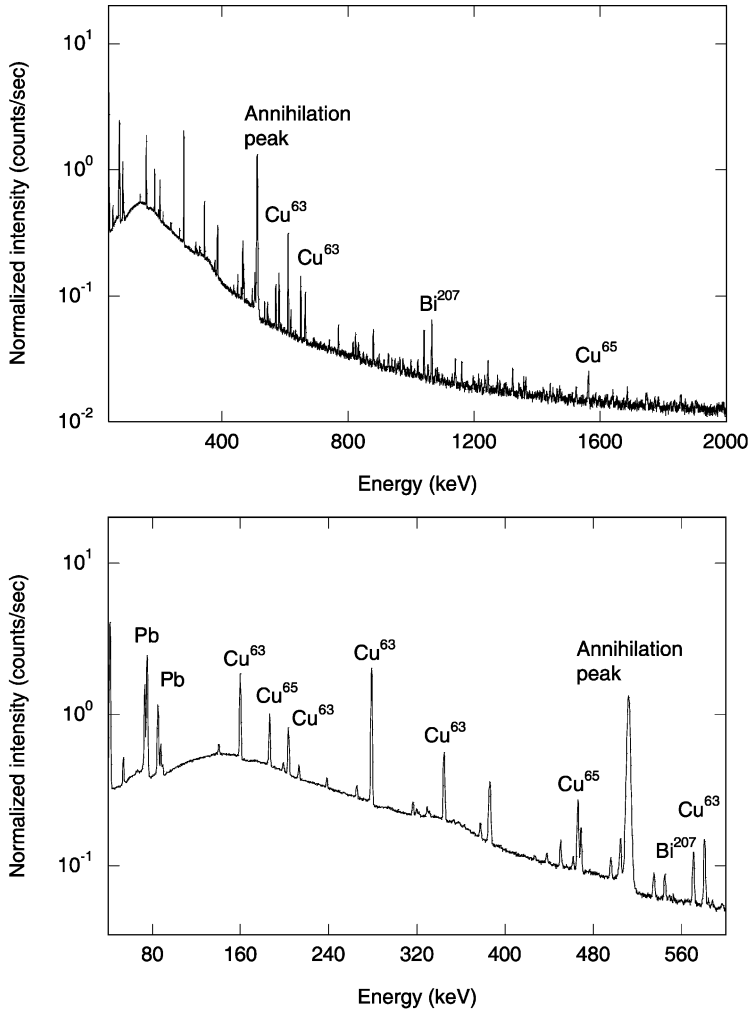

Fig. 2. – PGAA spectrum recorded from the copper axe at ISIS (run time $\sim$ 15 h). Top: full spectrum up to 2 MeV photon energy. Bottom: zoom of the same spectrum in the region up to 600 keV. Some identified peaks are shown as an indication.

3˙4. *The Budapest PGAA facility.* – For reference and comparison, some of the samples were also measured at the PGAA facility in Budapest. The standard PGAA instrument at the Budapest Research Reactor [11] is a dedicated station for prompt activation analysis of archaeological objects. It can be considered as an example of a state of the art beamline for PGAA. It operates on a horizontal cold neutron beam, guided 30 m away from the core of the 10 MW Budapest Research Reactor. Since 2007, the upgraded neutron guide produces a cold beam of $1.08 \times 10^8\,\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$. The samples can be irradiated in vacuum or in air in a fixed position of the sample holder. The cross-section of the beam is usually $2 \times 2\,\mathrm{cm}^2$ or $1 \times 1\,\mathrm{cm}^2$, but, if necessary, it can be reduced down to a smaller spot with the help of ^{6}Li-containing collimators.

The prompt- and delayed gamma photons are detected with a specially designed detector system, containing an HPGe surrounded by 8 BGO anti-coincident scintillator

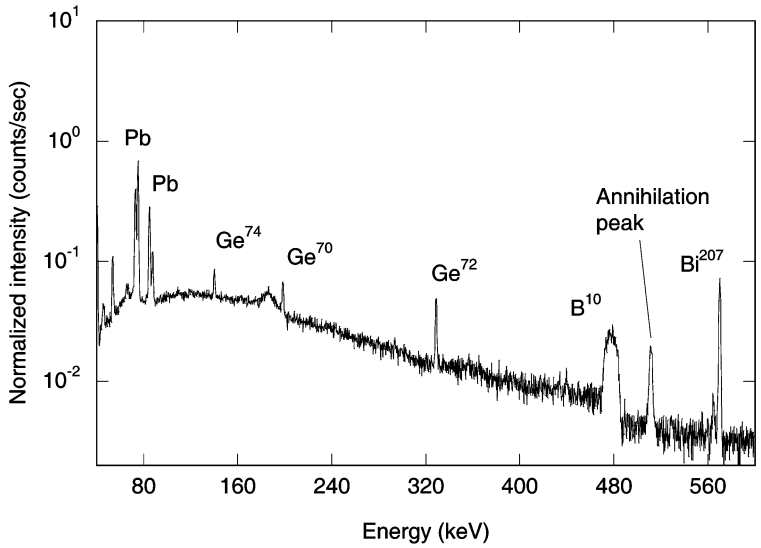

Fig. 3. – Reference background spectrum in the energy region 40–600 keV. This spectrum was taken without sample (run time ~ 2 h). Some identified peaks are shown as an indication.

detectors. This arrangement allows performing a significant Compton suppression of the spectrum baseline. The inner shielding of the sample holder chamber with ^{6}Li-containing polymer sheets, and the lead shielding of the detector system result in a low spectral background of 5 cps. Another experimental station, called NIPS, is designed to the lower part of the same beamline. This is a much simpler arrangement, without BGO

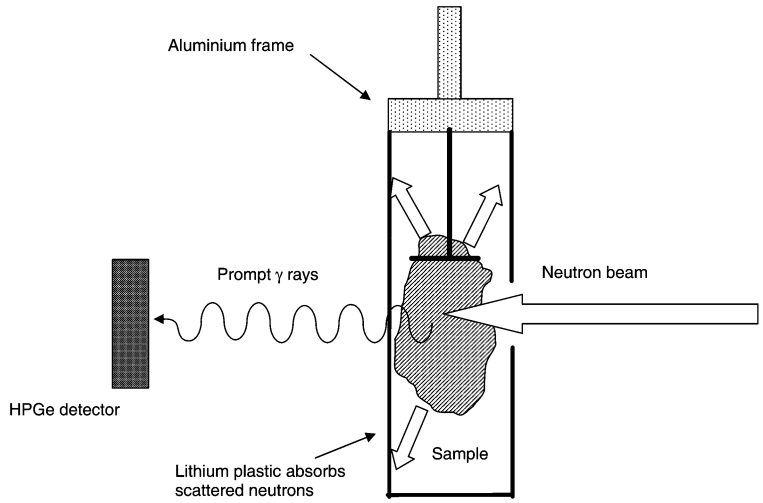

Fig. 4. – Sketch of the shielding arrangement used for PGAA measurements on the ROTAX beamline. The shielding is intended to hold back the neutrons scattered from the sample, while allowing the transmission of the prompt γ-rays. The gamma detector is actually positioned at 90° with respect to the neutron beam.

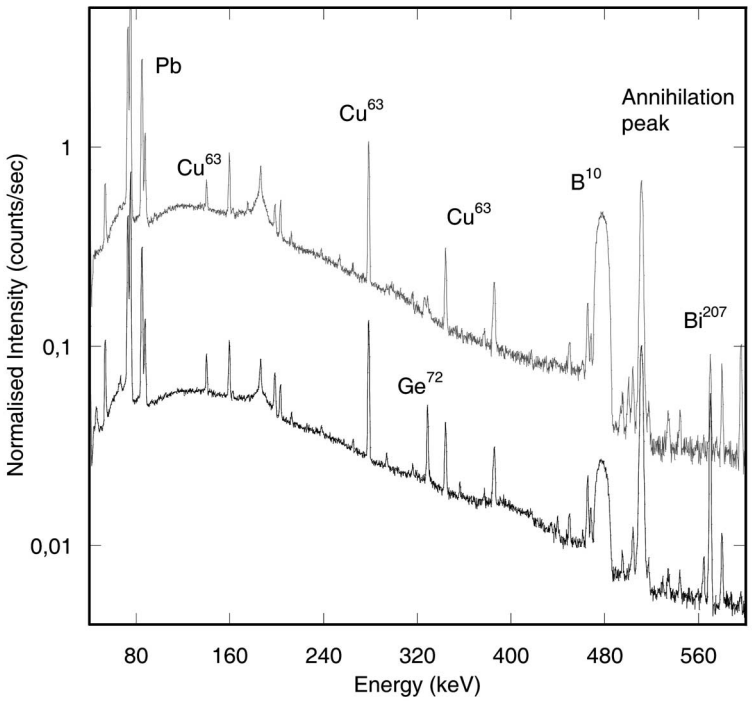

Fig. 5. – PGAA spectrum obtained from the bronze fibula, with the lithium-plastic shielding (lower black curve) and without it (upper grey curve). The reduction of the overall gamma background due to the shielding is about six-fold, and the improvement of the S/B is almost of a factor 2 for most peaks. Some identified peaks are shown as an indication.

Compton suppression and without vacuum chamber. In both cases, the energy ranges of the collected spectra are between 30 keV and 11 MeV. The detector efficiency and system non-linearity calibrations have been previously done with the help of a radioactive source set and (n,γ) measurements.

The spectrum evaluation is performed with the "HYPERMET PC" gamma spectrum evaluation software, developed at the Institute of Isotopes [12]. Following the exact determination of energy positions and intensities of the individual peaks in the spectra, the quantitative analysis is done on the basis of a data library, using the k_0-method [13].

4. – Results

Initial identification of the gamma lines in the HPGe spectra was achieved by consulting tables of gamma-ray energies, such as in ref. [14]. The peaks labelled in figs. 3 and 6 have been identified in this way. The data on the fibula from the PGAA station in Budapest are reported in table I for comparison. As we noticed, not all the identified lines actually come from the sample itself. For instance, the Pb K_α doublet at about 72 keV–75 keV is due to the lead shielding, and it is also present in spectra taken during no-sample runs (fig. 3). Other peaks in this spectrum can be ascribed to neutron capture in the germanium crystal itself. Such peaks can be considered as an intrinsic component of the background, requiring careful subtraction from sample spectra. The presence of

TABLE I. – *Elemental analysis of the limestone fragment as from PGAA measurements at Budapest PGAA station. The oxygen contents, not visible in PGAA, are calculated according to stoichiometry. Error bars are given in terms of relative uncertainty.*

	wt%	Error (%)
H	0.092	1.4
B	0.000499	1.3
C	13.8	4.9
Na	0.138	5.8
Mg	6.33	5.2
Al	0.10	9.4
Si	0.41	4.6
S	0.043	7.0
Cl	0.097	5.1
Ca	26.1	3.0
Ti	0.0037	8.2
Fe	0.033	9.2
Sm	5.0×10^{-6}	15.0
O (calc)	52.8	

environmental peaks is potentially disturbing, because it is cause of the so-called spectral interferences. As argued by Neff [15], use of high-resolution detectors (such as HPGe) reduces the problem of such interferences, but even with the highest-resolution detectors some lines cannot be resolved, but result in a distorted peak. A more sophisticated procedure for peak identification, reducing the risk of overestimating peak intensities, is to examine the simultaneous presence and relative intensities of the most intense peaks that belong to a particular element. This is actually the procedure implemented in the concentration calculation code [12].

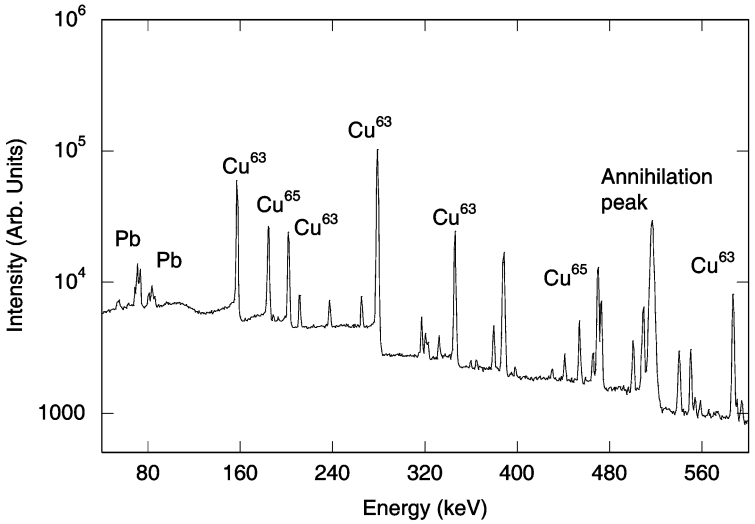

Fig. 6. – PGAA spectrum recorded from the copper axe at the Budapest PGAA facility (run time ~ 2950 s). Some identified peaks are shown as an indication.

Despite the efforts to reduce the gamma background, the spectral lines in fig. 3 are superimposed to a background continuum of variable intensity, as high as 3×10^4 counts at its maximum, corresponding to about 0.7 cps per channel. The background integrated over the entire energy range is of the order of 200 cps. Such a background is negligible for the most intense line in the spectrum, but it strongly reduces the possibility of obtaining accurate gamma line intensities for minor elements. For instance, the line at 278.25 keV identified as ^{63}Cu has an area intensity of about 4.89×10^5 counts. Since the variance in the determination of the peak area is usually calculated as $S + 2B$ (where S is the peak area and B the corresponding background), the percent standard deviation is

$$\sigma(\%) = \frac{100\sqrt{S + 2B}}{S} . \tag{7}$$

In the case of the line at 278.25 keV, this results in a good value of $\sigma(\%)$, being about 0.2%. We have to note that the line considered is one of the most intensive prompt gamma lines of copper. The analysis carried out with the HYPERMET code was concentrated on the minor lines as well, which are present in a great number, but with poorer S/B ratio. A typical uncertainty for such lines is of order 1% to 20%.

The ISIS/ROTAX measurements on the chalcolithic axe indicated that the object is composed of pure copper. For comparison, the same object was measured in air at the Budapest PGAA facility. The beam was collimated to 23 mm^2 in order to reduce dead-time effects. Three different acquisitions with collection times of 675 s, 1200 s and 2950 s were performed in order to find the most detectable trace elements. The spectrum detected with the longest acquisition time is presented in fig. 6. Due to the above-mentioned Compton suppression and to the available shielding, the background was around 5 cps with open beam, which was negligible compared to the total count rate of 1600 cps produced by the sample. Even in the case of the longest acquisition, we were unable to quantify any additional components besides Cu. This could be the effect of large difference in the neutron capture cross-sections of the other possible components, Sn and Pb. Based on the detection limit for such elements, we can estimate the tin content to be less than 1%, and the lead content to be less than 2%. Other usual trace elements, such as Sb and As were also impossible to detect. It can be noted that a recent analysis of the copper axe based on resonant neutron capture revealed a small fraction of silver in the order of 0.05% [16] which is below the detection limits for PGAA at the Budapest facility.

The second object, the limestone fragment was measured both at ISIS and in Budapest. The spectrum recorded at ISIS is presented in fig. 7, in which some elements are identified. Apart form the obvious presence of calcium, gamma lines from Si, Mn and Mg were identified. The absence of the gamma peaks from oxygen and carbon (also obviously present) is due to low sensitivity of the PGAA technique to these elements. At the Budapest PGAA, the sample was measured in vacuum using a 2×2 cm^2 cold beam for 3600 s and 16800 s. Results obtained from the measurements are presented in table I. Further details of the PGAA analysis, in addition to time-of-flight neutron diffraction results on the same samples are also reported in ref. [7]. With increasing acquisition time, detection limits for many elements improved significantly. Unfortunately, trace component of As, which was supposed to carry crucial archaeometric information, was below the detection limit of 500 μg/g.

The roman fibula was investigated at ISIS and Budapest PGAA facility. From the ISIS/ROTAX data, the presence of the following elements was clearly identified: B, Cl, Cu, Sn.

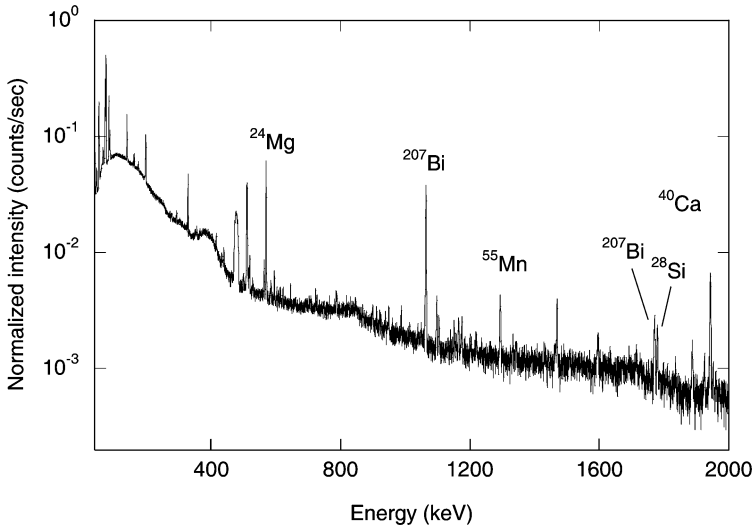

Fig. 7. – PGAA spectrum recorded from the M1 limestone at ISIS (run time $\sim$ 4 h). Some identified peaks are shown as an indication.

Moreover, some trace elements (As, Ag, In and Sb) are possibly present, but their concentration is just at the sensitivity limit with the present set-up. Pb is also present in the sample, but an estimation of its amount is difficult, due to the presence of relatively intense lines from the detector lead shielding (see fig. 3). Ge lines visible in the spectrum originate from the detector material.

The two Roman glass fragments have been measured only at ISIS. Although the exact efficiency and non-linearity parameters of the set-up used at ISIS are not well known, a qualitative element identification using the HYPERMET software was still possible. Energy calibration was done using the two most intense peaks, *i.e.* 569.6 keV and 1063.6 keV, which are likely due to the decay of ^{207}Bi produced in the lead shielding. According to the peak identification based on the software library, the following possible components were found:

H3 glass: Al, As, B, Ca, Cl, Gd, Na, Si, Sm, Sn, Sr, Cu, Mn

C1 glass: As Ba, Ca, Cl, Gd, Na, Si, Sm, Sn, V, K, Mg

5. – Conclusions

Prompt Gamma Activation Analysis (PGAA) on archaeological objects has been performed at the ISIS neutron spallation source and at the Budapest PGAA facility. PGAA is a non-destructive analytical technique, opposed to INAA which usually requires removal and grinding of the sample material in order to optimize the measurements. The flexibility of neutron sources like ISIS or the Budapest PGAA facility allows for non-destructive investigations of a wide range of samples. PGAA has been applied successfully to analyze archaeological bronze, limestone and glass. The optimized experimental condition (low background and a Compton-suppression detector system) at the Budapest PGAA facility allows for quantification of all major and some trace components of the

samples. On the other hand, the spectra measured on ROTAX at ISIS allow for a qualitative insight of the analyzed samples, offering the opportunity of cross-checking PGAA with readily available diffraction data and vice versa. At the present conditions at ISIS it is only possible to perform qualitative elemental analysis. Any further development would require a substantial reduction of the background sources which have been identified in this work, but are, to a certain extent, intrinsic to the shielding set-up at the ISIS spallation source.

The analysis of data collected on a make-shift PGAA set-up is difficult, but it can be made simpler with the use of fitting and peak-searching software like HYPERMET. However, again for a good functionality of such software a reduction of the overall γ background of the beamline is needed. Thus PGAA could be a convenient way to perform a preliminary qualitative investigation of samples which are already at ISIS for diffraction studies. As pointed out in ref. [7], the two methods of PGAA and TOF-ND can be considered as complementary. In particular, in the case of ternary alloys usually encountered among archaeological samples (like for instances bronzes with both Sn and Zn components), the indications provided by TOF-ND can be ambiguous. This is because the chemical composition can only be estimated by lattice parameter measurement via Vegard's rule. PGAA measurements performed with reasonable detection limits can remove ambiguities, giving the relative amount of the elements present in the alloy.

* * *

The provision of objects and samples for the experiments at ISIS (UK) and Budapest PGAA station (Hungary), Roman bronze fibula by A. Brown (Daresbury Laboratory, UK), the limestone sample by J. Harrell (Toledo University, USA), the copper axe by S. Shalev (Weizmann Institute, Israel), the Villa Adriana samples (A. Filabozzi, Roma-Tor Vergata University, Rome, Italy) is gratefully acknowledged. This work was performed within the CNR-CCLRC agreement. The authors acknowledge Consiglio Nazionale delle Ricerche (CNR)-Italy for financial support for the experiments performed at the ISIS pulsed neutron source.

REFERENCES

[1] Molnar G. L. (Editor), *Handbook of Prompt Gamma Activation Analysis with neutron beams* (Kluwer Academic Publisher, Dordrecht) 2004.
[2] Glascock M. D. and Neff H., *Meas. Sci. Technol.*, **14** (2003) 1516.
[3] Kockelmann W., Siano S., Bartoli L., Visser D., Hallebeek P., Traum R., Linke R., Schreiner M. and Kirfel A., *Appl. Phys. A*, **83** (2006) 175.
[4] Siano S., Bartoli L., Zoppi M., Kockelmann W., Daymond M., Dann J. A., Garagnani G. L. and Miccio M., *Proceedings of the International Conference Archaeometallurgy in Europe, Sept. 24-26, Milan, Italy*, Vol. **2** (Associazione Italiana di Metallurgia) 2003, pp. 319-329.
[5] Kockelmann W., Capon L. C., Engels R., Schelten J., Neelmeijer C., Walcha H. M., Artioli G., Shalev S., Cippo Perelli E., Tardocchi M., Gorini G. and Radaelli P. G., *J. Neutron Res.*, **14** (2006) 37.
[6] De Putter T. and Karlshausen C., *Les pierres utilisées dans la sculpture et l'architecture de l'Égypte pharaonique* (Safran, Bruxelles) 1992.
[7] Kasztovszky Zs., Visser D., Kockelmann W., Pantos E., Brown A., Blaauw M., Hallebeek P., Veerkamp J., Krook W. and Stuchfield H. M., *Nuovo Cimento C*, **30** (2006) 67.
[8] Rubinson W., *J. Chem. Phys.*, **17** (1949) 542.

[9] Pommé S. G., Hardemann F. E. M. C., Robouch P. B., Extebarria N., De Corte F. A., De Wispelaere A. H. M. J., van Sluijs R. and Simontis A. P., *Anal. Chem.*, **68** (1996) 4326.
[10] Kockelmann W., Weisser M., Heinen H., Kirfel A. and Schäfer W., *Mater. Sci. Forum*, **321-324** (2000) 332.
[11] Révay Zs., Belgya T., Kasztovszky Zs., Weil J. L. and Molnár G. L., *Nucl. Instrum. Methods B*, **213** (2004) 385.
[12] Fazekas B., Belgya T., Dabolczi L., Molnár G. L. and Simonits A., *J. Trace Microprobe Techn.*, **14** (1996) 167.
[13] De Corte F., *Czech. J. Phys.*, **53**, (Suppl. 1) (2003) A161.
[14] Database of prompt gamma rays from slow neutron capture for elemental analysis, IAEA, Wien (2006).
[15] Neff H., *Neutron activation analysis for provenance determination in archaeology*, in Ciliberto E. and Spoto G., *Modern Analytical Methods in Art and Archaeology* (Wiley, New York) 2000.
[16] Schooneveld E. M. *et al.*, *A position sensitive transmission detector for epithermal neutron imaging*, submitted to *J. Phys. D.*