International Conference on Nuclear Data for Science and Technology 2007
DOI: 10.1051/ndata:07452

Nuclear reaction data for IBA applications to cultural heritage diagnostics

G. Maino and E. Menapace

ENEA and University of Bologna, 2 via Fiammelli, 40129 Bologna, Italy

Abstract. Main aspects are discussed concerning nuclear reaction cross-sections for PIXE and PIGE analyses, especially referring to cultural heritage diagnostics, within the framework of ion beam analysis (IBA) methods, also reviewing recent results from international Conferences on Nuclear Data for Science and Technology and from NEA-NSC meetings and IAEA initiatives on the matter.

1 Introduction

Nuclear data relevant to light-element analysis in archaeometry are specifically considered and their impact on the knowledge and conservation of the cultural heritage is pointed out, especially discussing most significant examples concerning the beneficial use from the evaluated nuclear data on the results obtained by the application of this nuclear analytical technique. Consistently, relevant topics are discussed concerning the evaluation of the requested nuclear reaction data, on the basis of the existing experimental values and nuclear model calculations, according to the appropriate parameterisation and the effects on the calculation results. Recent results are presented for (p,xγ) reaction data, by comparing critically selected experimental data and the relevant model calculations, with regard to significant isotopes of low- and medium-mass elements of actual interest when considering alloys and other fabrication techniques for archaeological objects.

Among these methods, many are based on the use of ionising radiation and a short review is presented of non-destructive nuclear techniques applied to the investigation of cultural heritage artefacts [1,2].

2 Ion Beam Analysis and nuclear data Needs

The *Ion Beam Analysis (IBA)* techniques have become widespread for material characterisation not only for industrial applications, but also for environmental investigations, for cultural heritage conservation purposes, etc. [3,4]. Consequently, a NEA Workshop promoted by the NSC on "Ion and Slow Positron Beam Utilisation" (Lisboa, Portugal, September 15–17, 1998) [5] particularly concerned presentations and discussions on the overall matter.

The main techniques adopted in this context are:

- NRA (Nuclear Reaction Analysis), by ion beam induced nuclear reactions on target nuclides producing a light charged particle;
- NRP (Nuclear Resonance Profiling) or R-NRA (Resonant Nuclear Reaction Analysis) utilizing narrow resonances in nuclear reactions and relevant scanning of the incident beam energy;
- PIGE (Particle Induced Gamma-ray Emission) measuring prompt gammas emitted from ion induced nuclear reactions;
- non-Rutherford ERDA by nuclear elastic recoil at forward angles.

Therefore, nuclear data of special interest concern differential cross sections for proton and alpha particle non-Rutherford elastic scattering and nuclear reaction data of p, d and He-3 interactions with $A < 40$ nuclides typically for incident energies below 5 MeV.

The *RBS (Rutherford Backscattering)* technique allows the determination, from the energy spectrum of backscattered protons, of the concentration of various elements in a surface layer and/or measurements of the thickness of the same layer. Applications to the investigation of artistic objects thus refer, for instance, to determination of elements concentration profiles in patina layers on bronze objects [6], study of the alteration processes of lead objects and control of their conservation conditions using lead reference samples [7–9].

As a first attempt, primary importance, then relevant needs have been recognized for a comprehensive and accessible collection of reliable cross section data for NRA, for non-Rutherford elastic scattering cross sections of protons and alpha particles on $A < 40$ nuclides and specifically for deuteron induced reactions on carbon, nitrogen and oxygen isotopes. Differential cross sections are especially required for IBA, rather than the total ones, as requested for application purposes.

The main characteristics of PIXE are the following [10–13]: (a) analysis is performed directly on the object, but restricted to its surface, with an open air beam facility, through a very thin window ($0,1\,\mu$ Si_3N_4), and a helium flux (no sampling); (b) $Z > 9$ to 11 elements (O to Na) can be studied; (c) practical minimum detection limit is approximately 10^{-9}, thus allowing possibilities of trace detection and analysis; (d) very thin beam spot size, approximately Ø $10\,\mu$ to 1 mm on the surface of the object, and step by step scanning device.

PIXE technique may also be quantitative, even if main difficulties of the relevant analysis depend strictly on the thickness of the considered object: when a thin layer is considered, matrix effects are negligible, namely the proton energy loss

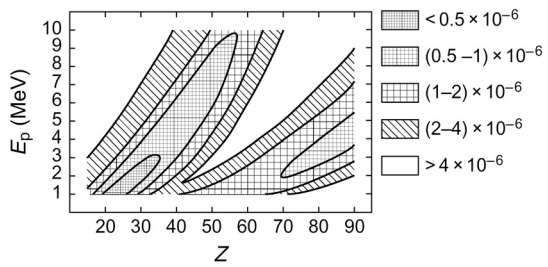

Fig. 1. MDL as a function of atomic number, Z, and incident proton energy.

within the layer and therefore the relevant variation of X-ray production cross section as well as the X-ray self-absorption within the target. In this case, the X-ray production for Z element is:

$$N_{X_j}(Z) = \sigma_{X_j}(Z, E_0) \cdot N_Z \cdot t \cdot N_p = \sigma_{X_j}(Z, E_0) \cdot \frac{N_{Av} \cdot \rho_Z t}{A} \cdot \frac{Q}{e},$$

where σ_{Xj} is the X-ray production cross section for j series of Z element, with E_0 beam energy, N_Z number of atoms of Z element in the volume unit, t target thickness, N_p number of beam particles that passed through the target, N_{Av} Avogadro number, ρ_Z mass density of (Z, A) element into the target. Finally, Q is the total beam charge and e the electron charge.

In the case of thick targets, previous results can be extended by integration over the total thickness of the considered object along the beam path. An exponential term then accounts for the X-ray self-absorption mechanism. The number of detected photons is proportional to the concentration, ρ_Z/ρ, of the considered element and the relevant quantitative results of the analysis can be very accurate both for main elements (representative of the matrix) and trace elements, up to ppm. The high sensitivity of PIXE technique is generally expressed by the *minimum detection limit* (MDL, see fig. 1), in terms in mass concentration, e.g. by the limit of detectability of a peak in the observed spectrum.

Within the framework of an IAEA initiative, an interlaboratory comparison for PIXE analysis has been carried out, resulting in a set of well-characterized test, reference and calibration spectra, including analysis software. All spectra and original files of measurements of aerosol, alloy, biological and glass samples, with extracted test and reference spectra, are available upon request from IAEA [14].

In order to achieve X-ray fluorescence analysis of lightweight elements in a matrix made of heavy-weight elements [15], a solution can be provided by a beam line equipped with an intermediate target acting as a proton induced low energy secondary X-ray source of an element with an atomic number between those of the elements to be analysed and those of the matrix. Consequently the target emits, according to the PIXE mode, X-rays which then permits the emission of characteristic X-rays of the lightweight elements to be analysed, without being blurred by the ones of the heavy-weight elements of the matrix. Therefore, a germanium target will produce X_K photons of 9,98 keV, an energy adapted to the excitation of X_K lines of copper and zinc included in a lead matrix, without interfering with the X_L lines of this

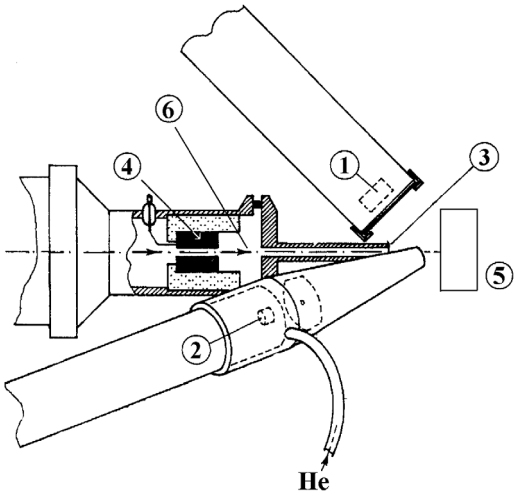

Fig. 2. PIXE experimental set-up for analyses on thick targets: 1) Big detector; 2) small detector (with helium flux); 3) exit window; 4) collimator; 5) target; 6) trajectory of proton beam.

metal (10,45 et 10,55 keV) and thus allowing detection of both copper and zinc.

Use of specific nuclear reactions, generally threshold ones, as (p,n), (p,2n), (d,n), etc., is made to determine lightweight elements concentration in metallic matrices. A typical application is non-destructive determination of oxygen content in archaeological bronze objects. Concerning the nuclear data for PIGE, the present availability has been considered reasonably well by the specialists, stating that little work needs to be done, even if the exigency has been expressed of new measurements and of compilations for thick target yields as a function of incident particle energy. Future needs are expected with regard to the covariance data availability, in order to deduce reliable confidence intervals in the analysis results.

As most of the data in the literature are given as graphs and often out of the range normally used in IBA, many of the IBA community started to measure the data of interest and to exchange their results through the Internet site SigmaBase, then the "ad hoc" experimental data base – NRABASE, shortly discussed in the following section – has been produced and is actually updated. However, main and general need has been expressed that the nuclear reaction cross sections and elastic scattering data of importance for IBA be achieved in an internationally stable data base, including evaluations.

In fact, as the above NRABASE revealed numerous discrepancies in the reported cross section measurements, which are far beyond the experimental errors, the need of appropriate evaluations has been recognized, particularly for deducing the cross section dependence on the scattering angle in all the angular interval of interest to the users, starting from the rather few measured values. The exigency of a role of the IAEA in coordinating activities on selected evaluations has been expressed, possibly through an appropriate CRP convening both evaluators and users.

For the purpose of the evaluations, even if the reaction mechanisms are known and significant examples have been reported on good results in reproducing experimental values, it has been recognized that improvements on specific models

and the related parameterisation and computing codes are still needed, particularly to allow confident interpolation and extrapolation rules and procedures with respect to the experimental datasets.

3 Basic data for profiling light elements by means of IBA

Quantitative estimate of depth profiling of light elements in RBS measurements strongly depends on the quality and availability of accurate non-Rutherford elastic scattering cross sections for proton and alpha-induced reactions on light elements as well as for light-ion projectiles, such as deuteron, ^{3}He and ^{4}He. Either absolute cross sections or differential data are needed together with experimental parameters like solid angle and beam charge. Moreover, accurate and reliable thin film reference targets are required for the isotopes of interest, thus providing valuable sources for determining the stopping power. The scanning electron microscopy can provide additional essential information about the surface morphology of samples. Data bases of physical parameters are strongly needed for analysis of specific thin films and surfaces such as compilation and critical assessment of existing data, theoretical calculations, identification of priority angles and energies for reference measurements, ERDA and RBS cross section evaluations.

IAEA Co-ordinated Research project (CRP), entitled *The use of ion beam techniques for analysis of light elements in thin films, including depth profiling,* started in the second half of 2000 year. Specific objectives of this initiative have been the assessment of ion beam techniques in the investigation of light elements in thin films and material surfaces by developing coordinated research efforts involving accelerator groups and material science groups from the IAEA member States. A first Research Coordination Meeting was held in Vienna from December 12 to 15, 2000 with presentation of reports, lectures and discussion of achievements and perspectives for future work.

Generally, IBA techniques depend on the availability of reliable experimental cross section data, which are extremely important in the planning of measurements and for computer simulation of observed spectra. The information in the literature mainly deals with particular reactions and the considered energy interval and angles at which experiments were performed are often out of ranges normally used in IBA applications. Therefore, although a large amount of valuable cross sections be available, only a few of them are suitable for IBA. Cross sections needed for IBA involve nuclei whose concentration or depth profile should be determined in a given sample. Moreover, cross sections may strongly depend on scattering angles in many interesting cases and, as far as differential cross sections rather than total ones are usually used in IBA, these data can be safely adopted only when the scattering geometry is very close to that adopted in the quoted measurements.

A data base for charged-particle nuclear reaction data has been then produced by IAEA. The above mentioned NRABASE 2.0 database presents differential cross sections for nuclear reactions induced by protons, deuterons, ^{3}He and alpha particles on thirty target isotopes ranging from hydrogen to silver. This compilation is based on evaluated experimental data from the literature [16].

4 Concluding remarks

To sum up this work, it is then worth remarking the following items: IBA techniques are powerful tools to derive unique information as for corrosion, degradation and, generally, conservation conditions of materials. Careful analyses of specific systems require accurate evaluations and establishment of complete databases, in particular for stopping powers and relevant cross sections. The physical parameters to be accurately determined are, therefore, nuclear reaction cross sections of importance for NRA analysis of light elements and stopping powers and ranges of light and heavy ions in various matrices. Light elements (H, Li, B, C, N, O, etc.) play an important role as constituents of many important organic as well inorganic materials in historical and artistic objects. To a large extent these materials occur in the near-surface area of a bulk material with altered or degraded composition.

References

1. Atti dei Convegni Lincei **11**, Rome, 1976.
2. G. Maino, in *Challenges of Nuclear Structure* (Singapore, 2002), p. 583.
3. M.B.H. Breese, D.N. Jamieson, P.J.C. King, *Materials Analysis Using a Nuclear Microprobe* (Wiley, New York, 1996).
4. G. Maino, E. Menapace, in *Radiation Physics for Preservation of the Cultural Heritage* (CLUEB, Bologna, 2005), p. 119.
5. *Ion and Slow Positron Beam Utilisation*, *Workshop Proceedings, Costa da Caparica, Portugal, Sept. 15–17, 1998* (OECD, Paris, 1999).
6. E. Ioannidou et al., Nucl. Instrum. Meth. B **161-163** (1999).
7. J.-C. Dran, M. Dubus, B. Moignard, J. Salomon, in *Proceed. Workshop on Research for Protection, Conservation and Enhancement of Cultural Heritage Opportunities for European Enterprises*, Strasbourg (2000).
8. L. Espie, M. Aucouurier, Art Surf. Eng. **17**, 205 (2001).
9. M. Dubus et al., in *Proceed. 6th Int. Conf. on Non-Destructive Testing and Micro-analysis for the Diagnostics and Conservation of the Cultural and Environmental Heritage*, Vol. **2**, Rome (1999), p. 1739.
10. S.A.E. Johansson, J.L. Campbell, *PIXE: A Novel Technique for Elemental Analysis* (John Wiley & Sons Inc., Chichester, 1988).
11. S.A.E. Johansson, J.L. Campbell, K.G. Malmqvist, *Particle-Induced X-Ray Emission Spectrometry (PIXE)* (John Wiley & Sons. Inc., Chirchester, 1995).
12. P.A. Mandò, Nucl. Instrum. Meth. B **85**, 815 (1994).
13. T. Calligaro et al., Nucl. Instrum. Meth. B **161-163**, 328 (1999).
14. Report IAEA, Vienna, Dec. 12–15, 2000, Report F1-RC-831 (2001).
15. L. Bertrand et al., in *Proceed. Congrès Rayons X et Matière 01*, Strasbourg (2001).
16. A.F. Gurbich, *NRABASE 2.0 – Charged-particle nuclear reaction data for Ion Beam Analysis*, IAEA Report NDS-201, March 1997.