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# Methodological aspects about the use of the radiocarbon dating in historical time sites

## Aspectos metodológicos a cerca del uso de la datación radiocarbónica en los yacimientos del periodo histórico

**KEY WORDS:** Mass Spectrometry, Isotopes, Dating

**PALABRAS CLAVES:** Espectrometría de masas, isótopos, datación

**GAKO-HITZAK:** Masen Espektrometría, isotopoak, Datazioa.

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### ABSTRACT

In this paper basic concepts concerning radiocarbon dating and Accelerator Mass Spectrometry (AMS) technique, and specifically the Centre for Isotopic Research on Cultural and Environmental heritage (CIRCE Laboratory) AMS facility, will be given. Problem of contaminations in radiocarbon AMS measurements will be introduced, and the sample preparation laboratory and the graphitisation lines that are used at the CIRCE Laboratory will be presented.

Moreover problems of sampling and interpretation of the archaeological radiocarbon dates will be treated in consideration of the nature of interdisciplinary research and of the impact of radiocarbon dating on archaeology.

### RESUMEN

En este documento se proporcionarán conceptos básicos sobre la datación por radiocarbono y la técnica de espectrometría de masa de aceleradores (AMS), y específicamente, sobre las instalaciones de AMS del Laboratorio CIRCE (*Centre for Isotopic Research on Cultural and Environmental heritage*, Ondare Kultural eta Ingurumen-ondarearen Ikerketa Isotopikorako Zentroa) AMS instalazioei buruzko kontzeptuak. AMS teknikan bitartez egindako neurketen ondoriozko erradiokarbono bidezko kutsadura izango dugu aztergai artikulu honetan. Horrez gain, laginak prestatzeko laborategia eta CIRCE Laborategian erabiltzen diren grafitizazio-lerroak ere aipatuko ditugu.

Además, se abordarán problemas de muestreo e interpretación de las dataciones arqueológicas obtenidas por radiocarbono, en consideración a la naturaleza de investigación interdisciplinar y al impacto que la datación por radiocarbono tiene en la arqueología.

### LABURPENA

Testu honetan, erradiokarbono bidezko datazioari buruzko oinarriko kontzeptuak eta masen azeleratzaileen bidezko espektrometría-teknikari (AMS) buruzkoak irakurri ahal izango ditu irakurleak; zehatzago esateko, CIRCE Laborategiko (*Centre for Isotopic Research on Cultural and Environmental heritage*, Ondare Kultural eta Ingurumen-ondarearen Ikerketa Isotopikorako Zentroa) AMS instalazioei buruzko kontzeptuak. AMS teknikan bitartez egindako neurketen ondoriozko erradiokarbono bidezko kutsadura izango dugu aztergai artikulu honetan. Horrez gain, laginak prestatzeko laborategia eta CIRCE Laborategian erabiltzen diren grafitizazio-lerroak ere aipatuko ditugu.

Gainera, erradiokarbono bidez lortzen diren datazioen laginketari eta interpretazioari dagozkion arazoak ere landuko ditugu, diziplinarteko ikerketetan eta erradiokarbono bidezko datazioetan duten eragina kontuan hartuz.

## 1- INTRODUCTION

In the last few years the isotopic methodologies plaid a role more and more important both in interdisciplinary and applied researches, and in a growing number of analysis and control procedures in industrial, environmental, biomedical, archaeometry and agricultural domains. These measurement methods, in general, have been developed in the framework of fundamental researches in physics, and then, once recognized the potentialities, the procedures and the precisions

that can be obtained, have been routinely applied in several domains as highly sensitive indicators of natural and anthropogenic phenomena.

The isotopic ratios of all elements present in nature undergo, during the chemical and physical processes which characterize the terrestrial ecosystem evolution, fractionation effects that can be detected with the modern measurement techniques. The conventional or stable isotope mass spectrometry (IRMS) of most abundant natural elements represents then a powerful search tool

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widely used in the field of sciences applied to the diagnostics of cultural and environmental heritage and the agricultural field. The measurement of the isotopic composition of elements such as Carbon, Oxygen and Nitrogen, in the different environmental compartments, such as atmosphere, soil, vegetation, water bodies, etc., turned out to be a powerful tool to quantify small variations of fluxes of such elements, often due to anthropogenic activities, and then get information on still unclear mechanisms.

Moreover the presence in the environmental matrices of cosmogony elements with long half-life allows to significantly enlarge the diagnostic possibilities, provided that the sensitivity of the isotopic ratio measurements would be pushed to level not accessible by the conventional mass spectrometry. A very sophisticated methodology which allows the needed ultrasensitive measurement is the Accelerator Mass Spectrometry (AMS), used to measure the rare isotope concentrations (normally radioactive cosmogenic isotopes with long half-lives), which are a very sensitive indicators of natural processes, that have characterized in the past the terrestrial ecosystem evolution and the human activity.

Strength points of IRMS and AMS isotopic methodologies are their high precision and sensitivity (of the order of  $1/10^5$  and  $1/10^{15}$  respectively), that allow, on one side, to detect tiny isotopic discrimination effects (fractionation) that elements present in nature undergo during the chemical and physical processes that characterize the terrestrial ecosystem evolution and, on the other side, to access processes that involve species existing in nature at "ultratrace" levels. In detail, in the following table we show quantitative parameter for precision and sensibility of IRMS and AMS technique, respectively.

	IRMS	AMS
Precision: R / R	$10^{-2}$	2-3 $10^{-1}$
Sensibility: R	$10^{45}$	$10^{12/15}$

Tabla I. IRMS and AMS: precision and sensibility.

## 2- RADIOCARBON DATING

Several dating techniques have been developed during the past decades, based on natural radionuclides acting as chronometers. The  $^{14}\text{C}$

isotope, the so-called "radiocarbon", is the most employed and reliable of these chronometers. The main principles of this dating method were formulated by W. Libby and his colleagues in the late 1940's (Libby, 1949). All those finds that were once part of the biosphere can be dated by radiocarbon measurements: wood, charcoal, bones among others, but, for example, not pottery (even though one can try to date some organic residues that can be found in). In order to understand the use of radiocarbon as a dating method, it is important to understand where radiocarbon is produced and how it gets into different part of the environment. Moreover radiocarbon is a short half-life radioactive isotopes ( $^{14}\text{C}$  - half life = 5730y), and it is present in different quantities in different reservoir due to a dynamic equilibrium between its production and its loss through radioactive decay. Therefore  $^{14}\text{C}$  is useful for the dating of organic material only because it becomes fixed into organisms during their life. Indeed carbon enters in the biosphere from the main atmospheric and aquatic carbon reservoirs through the process of photosynthesis in green plants, including algae. Carbon dioxide, with its ambient proportion of radiocarbon, is incorporated into the plant. The uptake process does involve some fractionation or preferential take-up of the lighter isotopes, but this can be accounted for by measurements of the stable isotopes  $^{12}\text{C}$  and  $^{13}\text{C}$ . Once photosynthesis has locked carbon from the environment into the organism, the proportion of radiocarbon will then fall off exponentially at a rate that is quite independent of any chemical or physical conditions (such as temperature, pH, atomic bindings etc.). Further details concerning the basic principle of the radiocarbon dating method can be found in literature (Ramsey,2008).

## 3- ACCELERATOR MASS SPECTROMETRY

### 3.1 Sample preparation

Every sample dated by radiocarbon - using AMS in particular - has to undergo a preliminary physical and chemical treatment to remove contaminations (external carbon might alter the real content of  $^{14}\text{C}$  in the sample) and to convert it into the most suitable form for the measurement. In the case of AMS, the samples to be measured are inserted in the source of the accelerator itself as elemental carbon, in the form of graphite. The treatment protocol for the  $^{14}\text{C}$  AMS analysis of solid samples usually comprises 3 main steps:

1. Chemical separation and purification according to sample type, with the aim of external carbon contamination suppression and/or isolation of the fraction of carbon of interest (Green 1963; Longin 1971; Mook and Streurman 1983; Fowler et al. 1986; Hoefs 1987; Six et al. 2002);

2. Oxidation of the sample carbon to CO<sub>2</sub> (via combustion for the organic materials or acidification for the carbonaceous materials) and its purification by other gases, potential poisons for the reduction step;

3. Reduction of CO<sub>2</sub> to graphite.

Each step of this procedure, however, might introduce its own contaminations. Treatment procedures constitute, at present, the limiting factor for AMS analyses in terms of sample throughput, background contamination (bkg), and measurement reproducibility. The background for the entire procedure is checked and corrected by running the entire pretreatment procedure on several kinds of <sup>14</sup>C blanks (processed blanks). Improvements on the treatment phases, thus decreasing the background introduced by these procedures, allow the measurement of samples with low <sup>14</sup>C values. High degrees of reproducibility for the graphite production ensure the feasibility of high-precision AMS (Steier et al. 2004) while stabilizing current yields and isotopic fractionation of the targets. A systematic study of contamination sources and isotopic fractionation phenomena and their relationships with the imposed treatment conditions can lead to an improvement of the AMS technique precision and sensitivity (Hua et al. 2001). Usually, most of the contamination during sample treatment is due to the CO<sub>2</sub> gas production, handling (Step 2), and reduction (Step 3) (Aerts-Bijma et al. 1997). While combustion processes are well characterized in terms of controlling parameters (i.e. amounts of reagents, temperature, and reaction times), graphitization processes are less securely linked with reaction conditions because of their composite nature.

Graphitization is achievable via two kinds of reducers:

1. Hydrogen (H<sub>2</sub>) using Fe or CO as catalysts at 600–700 °C with a cold finger for water trapping (Vogel, 1984);

2. Zinc (Zn) using Fe or CO as catalysts (Jull. 1986; Slota 1987) and TiH<sub>2</sub> (Vogel 1992).

The CIRCE AMS laboratory deals with a variety of sample types such as charcoal, bone, wood,

tree rings, peat, shell, foraminifera, soil (paleosols, bulk or fractions of soils), and atmospheric and respired CO<sub>2</sub>, treated using the standard chemical protocols and graphitized according to 2 different reduction protocols.

In order to meet the AMS system potential and to respond to the increasing demand of <sup>14</sup>C dating by AMS, have been developed new sample preparation lines and their characterization in terms of background, fractionation, and contamination has been realized. In particular, multireactor preparation lines based on sealed quartz tubes, muffle combustion, and Bosch reaction graphite production have been set, tested, and routinely used for samples with masses >1 mg (CO<sub>2</sub>/H<sub>2</sub> process). In order to increase the sample preparation throughput, a second line based on the zinc reduction process has been implemented.

### 3.2 AMS facility

At the Department of Environmental Sciences (DSA) of the Second University of Naples, <sup>14</sup>C AMS research has been performed over the last decade both for archaeological and environmental applications (Lubritto et al. 2004; Marzaioli et al. 2005). In early 2005, a new accelerator mass spectrometry (AMS) system was installed at the Centre for Isotopic Research for Cultural and Environmental Heritage (CIRCE) laboratory in Caserta, Italy, and acceptance tests were completed by the end of February (Terrasi, 2007). The system is based on a tandem accelerator 9SDH-2 (built by National Electrostatics Corporation, USA) with a maximum terminal voltage of 3 MV. The goal of the facility is to reach a throughput for radiocarbon measurements of more than 1000 samples/yr, and, in the near future, to extend AMS measurements to other isotopes (<sup>10</sup>Be, <sup>26</sup>Al, <sup>127</sup>I, <sup>236</sup>U). Layout of the CIRCE AMS system is showed in the following figure.

The achievable precision and accuracy were determined through the measurement of blank samples (Aesar graphite) with respect to a reference standard (IAEA C3, cellulose). In order to perform high-precision AMS (<0.3% that means an error on the radiocarbon dating of +/- 25-30 years), it is necessary to introduce a stable (and as low as possible) contamination in the prepared samples and to reach a stable value in the fractionation induced by the preparation lines.

# Circe Accelerator

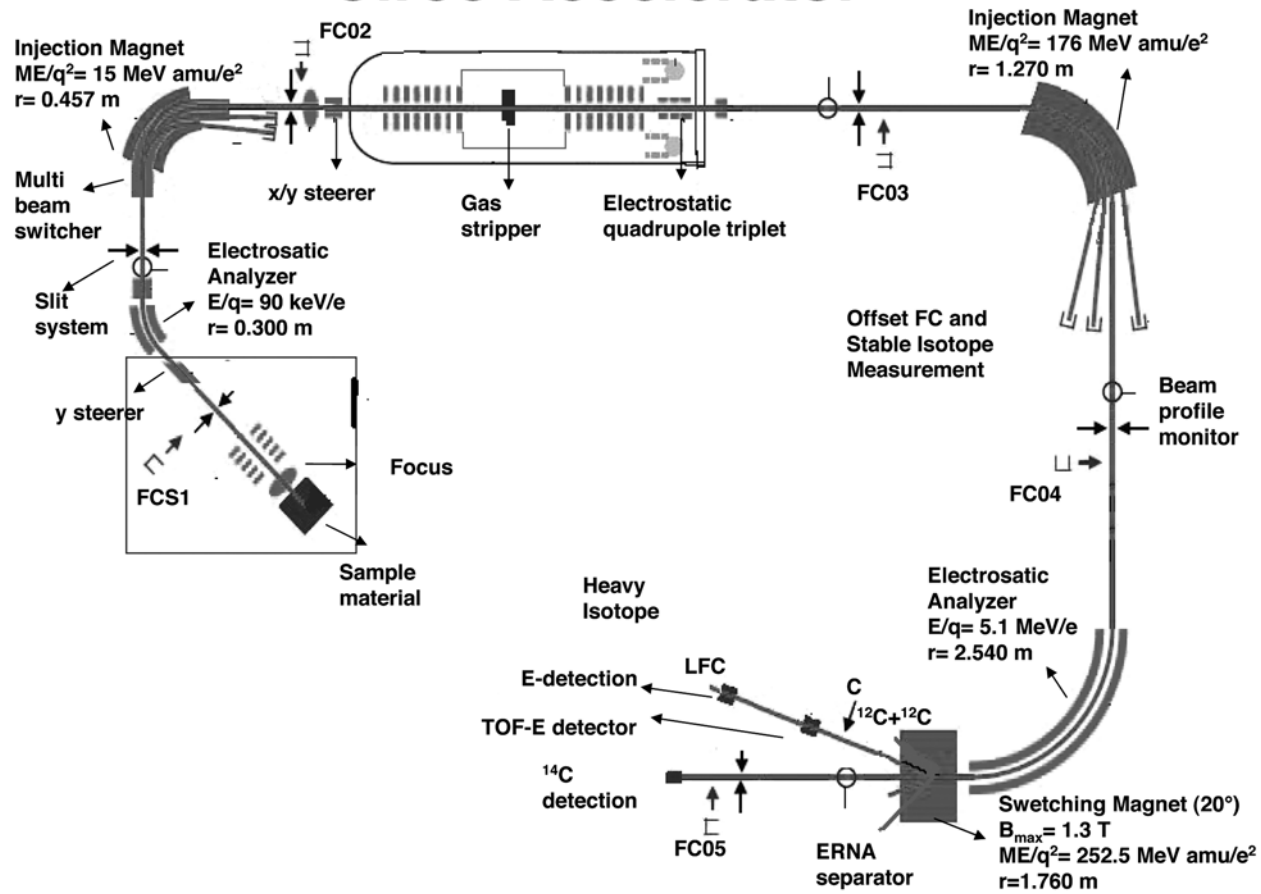


Fig. 1. Layout of the CIRCE AMS system.

The sample preparation lines developed at CIRCE produced samples of mass  $>1$  mg characterized by negligible fractionation effects and an apparent age for blank samples corresponding to 53,300 yr with a standard deviation of 2500 yr. For the mass range  $>1$  mg, the line is utilized for routine measurements of unknown samples; systematic checks on secondary standards included in each measurement batch indicate that an accuracy  $<0.3\%$  (±30 years) is achieved for modern samples in normal operation (Terrasi, 2007).

## 4- SOME GENERAL COMMENTS AND CONCLUSION

Radiocarbon dating is a method that has had the most important influence on the study of archaeology. In particular in this latter context it is very important to identify some general "rule of use of the method". In the following we do some general comment to the application of radiocarbon dating method to the archaeology.

a) *The radiocarbon dating process starts well before the measurements take place.* In other words the "radiocarbon dating is not a black box". As suggested in literature (Ramsey, 2008) we should consider radiocarbon dating process as composed by three different phases:

- *History of samples* which includes everything related to the sample prior the investigation, as for example information about reservoir of carbon, organism lifecycle and diagenesis;
- *Investigation* which include sampling of find, sample preparation and AMS measurements, following the protocol discussed above;
- *Interpretation* which include the calibration procedure and statistical analysis of results.

b) The selection of samples from an archaeological context requires considerable archaeological expertise, principally because it is important that the sample taken relates directly to some event or process on archaeological interest. The first stages

of the radiocarbon dating methodology are essentially an extension, on a finer scale, of archaeological excavation. Sampling procedure needs to get information that can be related back to the original organism(s) and, in doing so, one must try to gather as much information as possible about the sample, which might be useful in interpreting any radiocarbon measurements made.

c) Every radiocarbon sample is different in terms of the degree of preservation and the range of contaminants present.

d) The precision of the measurements depends on the number of  $^{14}\text{C}$  present in the sample: it is important to retain as much of the original material as possible

e) Radiocarbon measurement is essentially only an isotope ratio measurement. To use it for chronological purposes it needs to be interpreted in the light of our knowledge of the past environment. Once has been identified the reservoir(s) from which the carbon originates, we must then make use of the record of past radiocarbon concentration embodied in the calibration curve. In this context it is important to remind that precision on radiocarbon age is high (RC age error at CIRCE AMS Lab is 25 y), but because of the need of the calibration process it is not possible to get very high calendrical age precision for some of the radiocarbon timescale, because of the sort of variability in radiocarbon concentrations over time. Moreover for single samples, increasing measurement precision to much less than 0.3%, or 25/30  $^{14}\text{C}$  years, does not result in appreciably better precision in establishing age.

f) It is important to think carefully about how the radiocarbon-dated events relate to the archaeological processes. For each sample, it is important to consider the age at time of deposition and the certainty of association with the date of archaeological interest. On the other hand the much easier access to radiocarbon dates now can tempt people not to think in detail about each date and simply treat large numbers of dates as data to be summarized. In some cases this may be fine, but there are some dangers of systematic biases creeping in (Ramsey, 2008).

g) Sometimes radiocarbon process give dates that do not make sense archaeologically: these can be due to some measurement problem but much more often they are due to misinterpretation of the

sample context. Moreover if we are dealing with more complicated situations in which we wish to analyse groups of dates (rather than groups of radiocarbon measurements), we need ways of dealing with the probability density functions that come from the calibration (bayesian statistics).

h) As future perspective in the radiocarbon science, will be important understanding more of past environment (i.e. calibration curve), to improve measurement methodology (i.e. treatment of samples, AMS precision, half-life of radiocarbon) and interpretation methods (i.e. Bayesian statistics), but will be indispensable to increment the dialogue between laboratories and user of radiocarbon.

#### 4. BIBLIOGRAFÍA

- AERTS-BIJMA AT, MEIJER HAJ, VAN DER PLICHT J.  
1997 AMS sample handling in Groningen. *Nuclear Instruments and Methods in Physics Research B* 123(1-4):221-5.
- FOWLER AJ, GILLESPIE R, HEDGES REM.  
1986 Radiocarbon dating of sediments. *Radiocarbon* 28(2A):441-50.
- GREEN JW.  
1963 Wood cellulose. In: Whistler RL, editor. *Methods in Carbohydrate Chemistry*. New York: Academic, Press. p 9-21.
- HOEFS J.  
1987 *Stable Isotope Geochemistry*. 3rd edition. Berlin: Springer-Verlag. 241.
- HUA Q, JACOBSEN GE, ZOPPI U, LAWSON EM, WILLIAMS AA, SMITH AM, MCGANN MJ.  
2001 Progress in radiocarbon target preparation at the ANTARES AMS Centre. *Radiocarbon* 43(2A):275-82.
- JULL AJT, DONAHUE DJ, HATHEWAY AL, LINICK TW, TOOLIN LJ.  
1986 Production of graphite targets by deposition from CO/H<sub>2</sub> for precision accelerator  $^{14}\text{C}$  measurements. *Radiocarbon* 28(2A):191-7.
- LIBBY, W. F.  
1949 Age determination by radiocarbon content: world-wide assay of natural radiocarbon, *Science*, 109(2827), 227-8.
- LONGIN R.  
1971 New method of collagen extraction for radiocarbon dating. *Nature* 230(5291):241-2.
- LUBRITTO C, ROGALLA D, RUBINO M, MARZAIOLI F, PASSARIELLO I, ROMANO M, SPADACCINI G, CASA G, DI LEVA A, DE CESARE N, D'ONOFRIO A, GIALANELLA L, IMBRIANI G, PAL-



- MIERI A, ROCA V, ROLFS C, SABBARESE C, STRIEDER F, SCHUERMANN D, TERRASI F.
- 2004 Accelerator mass spectrometry at the 4MV Dynamitron Tandem in Bochum. *Nuclear Instruments and Methods in Physics Research B* 222(1-2):255-60.
- MARZAIOLI F, LUBRITTO C, BATTIPAGLIA G, PASSARIELLO I, RUBINO M, DETLEF R, STRUMIA S, MIGLIETTA F, D'ONOFRIO A, COTRUFO MF, TERRASI F.
- 2005 Reconstruction of past CO<sub>2</sub> concentration at a natural CO<sub>2</sub> vent site using radiocarbon dating of tree rings. *Radiocarbon* 47(2): 257-63.
- MOOK WG, STREURMAN HJ.
- 1983 Physical and chemical aspects of radiocarbon dating. In: Mook WG, Waterbolk HAT, editors. *Proceedings of the First International Symposium "14C and Archaeology."* Groningen 1981. *PACT* 8:31-55.
- PASSARIELLO I, MARZAIOLI F, LUBRITTO C, RUBINO M, D'ONOFRIOA, DE CESARE N, BORRIELLO G, CASA G, PALMIERI A, ROGALLA D, SABBARESE C, TERRASI F.
- 2006 Radiocarbon sample preparation at the CIRCE AMS laboratory in Caserta, Italy. *Radiocarbon* 49(2):225-32.
- SIX J, CALLEWAERT P, LENDERS S, DE GRYZE S, MORRIS SJ, GREGORICH EG, PAUL EA, PAUSTIAN K.
- 2002 Measuring and understanding carbon storage in afforested soils by physical fractionation. *Soil Science Society of America Journal* 66(6):1981-7.
- SLOTA JR PJ, JULL AJT, LINICK TW, TOOLIN LJ.
- 1987 Preparation of small samples for <sup>14</sup>C accelerator targets by catalytic reduction of CO. *Radiocarbon* 29(2):303-6.
- SOUTHON J.
- 2007 Graphite reactor memory – Where is it from and how to minimize it? *Nuclear Instruments and Methods in Physics Research B* 259(1):288-92.
- STEIER P, DELLINGER F, KUTSCHERA W, PRILLER A, ROM W, WILD EM.
- 2004 Pushing the precision limit of 14C AMS. *Radiocarbon* 46(1):5-16.
- TERRASI F, ROGALLA D, DE CESARE N, D'ONOFRIO A, LUBRITTO C, MARZAIOLI F, PASSARIELLO I, RUBINO M, SABBARESE C, CASA G, PALMIERI A, GIALANELLA L, IMBRIANI G, ROCA V, ROMANO M, SUNDQUIST M, LOGER R.
- 2007 A new AMS facility in Caserta/Italy. *Nuclear Instruments and Methods in Physics Research B* 259(1):14-7.
- VOGEL JS.
- 1992 Rapid production of graphite without contamination for biomedical AMS. *Radiocarbon* 34(3):344-50.
- VOGEL JS, SOUTHON JR, NELSON DE, BROWN TA.
- 1984 Performance of catalytically condensed carbon for use in accelerator mass spectrometry. *Nuclear Instruments and Methods in Physics Research B* 5(2):289-93.