PRL-TN-2021-113 Technical Note



# SPADE : Software for PRL AURiS Data Exploration

by

Pratheeksha Nayak & M.G.Yadava (Geosciences Division)



भौतिक अनुसंधान प्रयोगशाला, अहमदाबाद Physical Research Laboratory, Ahmedabad

https://www.prl.res.in/

**Disclaimer:** This technical report is based on the work carried out by the authors at PRL. It is assumed that due credit/references are provided by the authors. PRL assures no liability whatsoever for any acts of omissions and any of the issues arising due to the use of results.

# **SPADE : Software for PRL AURIS Data Exploration**

# Pratheeksha Nayak\* & M.G.Yadava

Received 01 November 2020; revised 08 March 2021; accepted 25 March 2021; published 30 March 2021.

# Abstract

SPADE is a web application developed in-house for processing raw data obtained during analysis in 1MV AMS (PRL-AURiS) installed in Physical Research Laboratory, Thaltej. It is an interactive web application developed using Python for Windows, Linux and Mac operating systems. It can be used to estimate isotopic ratios of  $\frac{^{14}C}{^{13}C}$ ,  $\frac{^{14}C}{^{12}C}$  and  $\frac{^{13}C}{^{12}C}$  and radiocarbon ages of samples analysed in PRL-AURiS. This report presents a detailed account of the software development aspects, user interface, user inputs, outputs obtained, advantages and future scope of SPADE.

Geosciences Division, Physical Research Laboratory, Ahmedabad \*Corresponding author: pratheeksha@prl.res.in

#### Contents

1	Introduction	1
1.1	SPADE, A Web Application for Radiocarbon Age Estimation	l-
1.2	Radiocarbon dating and AMS	1
2	Structure of Raw AMS Data	2
3	Software Development Aspects of SPADE	2
3.1	Packages	2
3.2	Production	2
3.3	Advantages of In-house Software Development	2
4	About SPADE	3
4.1	Getting Started	3
4.2	Isotopic Ratios	3
4.3	Radiocarbon Ages	5
5	Summary and Future Scope	5
6	Acknowledgments	6
	References	6
	Appendices	7
А	Graphitisation	7
В	PRL-AURIS	7
С	Obtaining isotopic ratios and associated errors	7
D	Estimating radiocarbon age of samples	7

#### 1. Introduction

# 1.1 SPADE, A Web Application for Radiocarbon Age Estimation

Web applications are programs stored on a remote server and accessed via browsers. Such applications can be designed for a wide variety of purposes and need not be installed prior to usage. They can be accessed through multiple browsers available in various platforms like desktop, laptops or mobile phones. The applications can be made highly interactive and easy to use.

SPADE is a web application developed in-house using Python to use the raw data obtained from Accelerator Mass Spectrometry and obtain radiocarbon age estimates for samples. It is available as a stand-alone executable for Windows, Linux and Mac operating systems. It has an interactive interface that facilitates user experience and can be deployed anywhere and used without requiring the user to install Python or any of its packages.

#### 1.2 Radiocarbon dating and AMS

Natural carbon comprises of three isotopes  ${}^{12}C$ ,  ${}^{13}C$  and  ${}^{14}C$ , out of these  ${}^{12}C$  and  ${}^{13}C$  are stable whereas  ${}^{14}C$  is radioactive having half-life of 5730 years. Interaction of cosmic rays with the upper atmosphere results in continuous production of radiocarbon ( ${}^{14}C$ ). It rapidly combines with oxygen forming carbon dioxide ( ${}^{14}CO_2$ ) which mixes very well in the atmosphere and enters the biosphere. Since the rate of formation of  ${}^{14}C$  is fairly constant, there exists a dynamic equilibrium between its formation and decay. This results in a constant  ${}^{14}C$  level in living organisms.

Once an organism dies or a system is isolated from dynamic carbon cycle, fresh intake of <sup>14</sup>C stops and <sup>14</sup>C already accumulated undergoes exponential decay with time as

$$A = A_0 e^{-\lambda t}$$
(1)

where, A represents the remaining or residual activity (the number of decays per unit time) at time t, A<sub>0</sub> represents the initial activity and  $\lambda$  represents the decay constant [Bowman, 1990]. Radiocarbon measurements are done by two methods. First by conventional method (beta decay detection based) and second by more recent method, Accelerator Mass Spectrometry (AMS, counting of <sup>14</sup>C isotopes).

AMS was developed to overcome the limitations of the conventional beta counting technique. The conventional method relies on the beta radiation produced by <sup>14</sup>C atoms that happen to decay during the measurement. Whereas, the AMS measures the <sup>14</sup>C atoms directly. This makes the AMS method more sensitive. Smaller samples can be measured and the measurement is quicker than the conventional method. Longlived radio isotopes like <sup>10</sup>Be, <sup>26</sup>Al, <sup>36</sup>Cl, <sup>41</sup>Ca and <sup>129</sup>I can also be measured in AMS [Budzikiewicz and Grigsby, 2006, Jull, 2014].

# 2. Structure of Raw AMS Data

PRL-Accelerator Unit for Radioisotope Studies (PRL-AURIS) is a mass spectrometer installed at Physical Research Laboratory, Thaltej and is attached with a 1 Million Volt Tandem Accelerator. The samples to be analysed are converted into graphite form (see Appendix A) and pressed into targets which are placed in the AMS. The isotopes are separated and measured. Refer to Appendix B for a detailed description and schematic of PRL-AURIS.

The carousel of AMS can accommodate upto 50 graphite samples at a time. For any given sample, each measurement (run) is defined either by the number of counts or the duration of counting. For instance, the stop condition for a run could be 10,000 counts or 10 'blocks' (1 block = 30 seconds). The samples along with standards, blanks and check standards constitute a 'batch' (run cycle) which specifies the order in which the samples are processed in the AMS. The batches are repeated multiple times in order to improve the precision of the results. For each sample in each batch, a '.fsires' file is generated which gives information about the input conditions, internal parameters and output related to the particular sample such as sample ID, position in the sample carousel, measurement times etc. along with isotopic ratios  $(\frac{14C}{13C}, \frac{14C}{12C} \text{ and } \frac{13C}{12C})$  of the samples and the number of  $^{14}C$  counts in each block.

# 3. Software Development Aspects of SPADE

SPADE is a browser based web application available for major operating systems like Windows, Linux and Mac in the form of an executable file. The application is developed using Python which is a modern high level language that supports both object oriented and functional way of programming. The extensive support for various packages for data visualisation and analysis makes it a great choice of language for development of such applications. The initial design of the software was a command line interface (CLI) which was later evolved to a browser based mode to make the application platform independent.

#### 3.1 Packages

SPADE is developed using a number of Python packages which facilitate the framework of data loading, filtering, visualisation, interactive interface, analysis, displaying and downloading final results. Some of the important packages used are

- bfDash : A web framework which is ideal for building data visualisation applications. It has highly custom interfaces like drop-down menus, buttons, file selection etc., which help in building highly interactive user applications.
- **Plotly** : An open source library for plotting which helps create interactive plots that are of publication quality.
- **Pandas** : A powerful package that facilitates working with structured data such as dataframes. It facilitates fast and efficient data manipulation, indexing, transforming, reading and writing data in different formats.

Along with these, other packages used are **numpy** for numerical computations, **scipy** modules for statistical computations and **uncertainties** module for evaluating errors etc.

#### 3.2 Production

SPADE is available in the form of stand-alone executable for Windows, Linux and Mac operating systems which are developed using **PyInstaller**. This package packs any application along with its dependencies and provides multi-platform, stand-alone executable. The advantage of such a stand-alone application is that it can be run without having to install Python, interpreter or any of the packages used.

#### 3.3 Advantages of In-house Software Development

In-house software development using open source packages can be a great way to develop software that are easy to maintain, customize and ensure continued good performance. Open source packages are well written codes developed specifically by the community for a particular task and they are well tested and regularly updated. Using these make sure that developing desired software consumes minimal time and effort. SPADE can be modified to include additional features that help in our understanding of samples used for radiocarbon dating. The application can be used by anyone from anywhere in the world and is cost effective as compared to its proprietary counterparts.

# 4. About SPADE

SPADE is developed using Python and processes the raw output data given by PRL-AURiS and converts it into radiocarbon ages. This is achieved in two steps. The first step uses the output data files of AMS which are in '.fsires' format and extracts isotopic ratios of the samples  $\left(\frac{{}^{14}C}{{}^{13}C}, \frac{{}^{14}C}{{}^{12}C}\right)$  and  $\frac{{}^{13}C}{{}^{12}C}$  for further calculations. In the next step, the isotopic ratios of samples, standard and blank are used to estimate radiocarbon ages of samples. Figure 1 shows a workflow of SPADE along with the user inputs required.



Figure 1. Workflow of SPADE

#### 4.1 Getting Started

The application is made available in the form of a standalone executable named 'SPADE.exe' for Windows, Linux and Mac operating systems. Since all dependencies are packed along with the executable, there are no prerequisites for using SPADE. Upon executing 'SPADE.exe', a web application gets hosted locally in the address 'http://127.0.0.1:8050/' and can be accessed via any browser. It has three stages of user inputs namely, 'Input Files', 'Isotopic Ratios' and 'Radiocarbon Ages' (see Figure 2).



**Figure 2.** SPADE : User interface of interactive web application for estimation of radiocarbon ages.

**Input Files** The output of the AMS is available in the form of '.fsires' files, which give a summary of input conditions,

internal parameters and output related to the particular sample such as sample ID, position in the sample carousel, measurement times, detector counts etc. Each run cycle of the AMS produces an output file corresponding to every sample. These files act as the input files for our application. The *Select File(s)* button can be used to navigate to the folder containing the '.fsires' files and select the files corresponding to the samples to be analysed. Based on sample IDs, the number of unique samples loaded is displayed. The *RESET* button can be used to reset the application at any time.

**Plots** Plots of isotopic ratios of  $\frac{{}^{14}C}{{}^{13}C}$ ,  $\frac{{}^{14}C}{{}^{12}C}$  and  $\frac{{}^{13}C}{{}^{12}C}$  are generated once the input files are loaded. Plotly provides interactive legend for batches which gives the user the freedom to dynamically select or deselect batches for any particular sample. Figure 3 shows an instance of SPADE where samples are loaded and plots are generated. The default state considers all batches for all samples. Particular batches that need to be omitted from further analysis can be deselected for all samples using the "Reject batches" menu or for desired samples through the interactive legend. The isotopic ratios are calculated for the selected batches which is considered the present state of each sample. Plotly also offers other interactive options at the top right corner of each plot such as zoom, pan, download as png etc (see Figure 4).

#### 4.2 Isotopic Ratios

The <sup>14</sup>C measurements are prone to random errors at different stages of measurement. To improve the precision of our estimates, the samples are processed in the AMS for multiple batches. Averaging the results over multiple batches reduces the random errors and hence provides better estimates of the true values. Conventionally, the mean is used as an estimate of the true value and the associated error is given by the standard error of mean (SEM). However, the SEM is representative of the precision of the estimate but it does not capture the spread in the measurements. Hence, standard deviation can be used. In addition, a weighted average approach is used where the weights are derived from the observed standard deviation. Provision has been made in our application, to estimate the isotopic ratios using mean or weighted mean and to estimate the associated error using standard deviation, standard error of mean or error in weighted mean [Bevington and Robinson, 2003, Scott et al., 2007]. Appendix C outlines the procedure followed to obtain these estimates.

The section titled 'Isotopic Ratios' takes the user inputs required to estimate the isotopic ratios of the samples and the associated errors. The two required inputs are *Method* which is a drop-down menu from where the user can select one of the three methods outlined in Appendix C and *Reject batches* which is a drop-down menu of batch numbers. The batches selected here are omitted from further analysis for all the samples. The deselection is also reflected in the plots of all samples. Particular batches for specific samples can



Figure 3. Interactive plots for all samples in the dataset are loaded. Users can dynamically select or deselect batches for any/all samples.



Figure 4. Batch 7 has been deselected for all samples and is dynamically reflected in the plots as seen for the sample 'PRL\_1'. Other interactive options provided by Plotly can be seen at the top right corner of the plot.

Description	counts	err_13_12	Mean_13_12	err_14_12	Mean_14_12	err_14_13	Mean_14_13	Sample_ID
51	6866	1.2425E-04	1.2486E-02	2.6912E-15	1.6261E-13	1.4235E-13	1.3019E-11	PRL_1
S2	9465	1.1169E-04	1.2571E-02	3.8375E-15	2.3103E-13	1.6457E-13	1.8362E-11	PRL_2
\$3	9677	1.5238E-04	1.2048E-02	4.0587E-15	2.3879E-13	1.1293E-13	1.9811E-11	PRL_3
S4	10706	9.7128E-05	1.2421E-02	6.0840E-15	5.3651E-13	1.8484E-13	4.3185E-11	PRL_4
\$5	10575	9.3076E-05	1.2139E-02	5.3147E-15	4.7704E-13	1.6850E-13	3.9292E-11	PRL_5
56	10650	2.4411E-05	1.1812E-02	3.6868E-15	7.2439E-13	2.3002E-13	6.1319E-11	PRL_6
ANTHRACITE BLANK	85	1.5392E-04	1.2140E-02	1.2613E-16	2.7162E-15	1.1628E-14	2.2408E-13	PRL_7
NBS 0X-1	11276	1.2917E-04	1.2432E-02	1.9015E-14	1.2929E-12	5.2162E-13	1.0397E-10	PRL_8
NBS 0X-2	11689	5.5008E-05	1.3085E-02	1.5775E-14	1.8438E-12	6.6778E-13	1.4090E-10	PRL_9

# **Isotopic Ratios**

Figure 5. Representative image of the results generated by the 'Isotopic Ratios' section. The isotopic ratios of  $\frac{{}^{14}C}{{}^{13}C}$ ,  $\frac{{}^{14}C}{{}^{12}C}$  and  $\frac{{}^{13}C}{{}^{12}C}$  and  $\frac{{}^{13}C}{{}^{12}C}$ 

also be omitted from further analysis at the users' discretion using the interactive legend of the plot for that sample. The *Results* consist of a table listing the sample IDs, mean isotopic ratios and associated errors, the number of  $^{14}$ C counts and description of each sample (See Figure 5).

#### 4.3 Radiocarbon Ages

Blank (or background) values are an estimate of the extra counts measured in the detectors which have origin other than the actual <sup>14</sup>C from the sample. For example, for the <sup>14</sup>C count, this could come in the form of scattered beams of <sup>12</sup>C, <sup>13</sup>C and carbon hydrides with equivalent charge [McNichol et al., 2001]. Also reagents used in carbon dioxide and graphite preparations, if contaminated by modern carbon may contribute to such undesired <sup>14</sup>C counts. To estimate background level, graphite prepared from a <sup>14</sup>C free material (geologically old material, such as anthracite or marble, labelled as process blank) is used to estimate small amounts of <sup>14</sup>C that is introduced consistently during the processing of samples. Target from such a material is introduced in the AMS along with the samples and is labeled as 'background' or 'blank'.

Absolute radiocarbon standard corresponds to atmospheric equilibrium activity ( $A_0$  in equation 1) in the year 1950 (normalised to  $\delta^{13}$ C = -25‰). But since the actual value was lower due to industrial revolution, wood from the year 1890 was chosen to correspond to primary standard for radiocarbon measurements. This value can also be obtained using two secondary standards prepared by NIST (National Institute of Standards) which are oxalic acids I and II (HoxI and HOxII). Oxalic acid I was made from sugar beet crop of 1955 and oxalic acid II from French beet molasses of 1977. To account for the increase in specific activity of <sup>14</sup>C due to human perturbations, 95% of the specific activity, in 1950 AD, of oxalic acid I (normalised to  $\delta^{13}$ C = -19‰) and 75% of the specific activity of oxalic acid II (normalised to  $\delta^{13}$ C = -25‰) are used as

standard values [Stuiver and Polach, 1977, Stenström et al., 2011].

Radiocarbon age of each sample is estimated according to equation 1 after taking into account background contribution, isotopic fractionation and standard values and errors are propagated appropriately. A detailed account of the procedure followed to estimate the radiocarbon ages of samples is presented in Appendix D. The section titled 'Radiocarbon Ages' takes the user inputs required to estimate the radiocarbon ages of samples. The two required inputs are *Standard* and *Background* which are drop-down menus of sample IDs from which the ID(s) of standard (along with appropriate radio button depending on whether the standard used is Oxalic Acid I or Oxalic Acid II) and background sample(s) needs to be selected. If multiple standards or backgrounds are selected, average values of isotopic ratios and <sup>14</sup>C counts of the selected samples are used for further analysis.

The *Results* consist of a table listing the sample IDs, ages estimated using both  $\frac{^{14}C}{^{13}C}$  and  $\frac{^{14}C}{^{12}C}$  along with the errors in estimation of ages and description of each sample (See Figure 5). The last two rows correspond to background and standard used for the analysis. The description column for these rows lists the sample(s) selected in each case. The results of the analysis can be saved using the *Download Results* button which downloads a zipped folder consisting of the plots of isotopic ratios (in the present state) and an excel file containing a compilation of the final results as shown by the *RESULTS* of both steps. The inputs given for the analysis are included as part of the header. The last two rows correspond to the background and standard used for the analysis.

# 5. Summary and Future Scope

A cross-platform web application is developed that can process raw data in form of '.fsires' files resulting from AMS analysis. A detailed discussion on the application to estimate radiocarbon ages of samples is presented. Provisions are made to estimate the isotopic ratios of  $\frac{^{14}C}{^{13}C}$ ,  $\frac{^{14}C}{^{12}C}$  and  $\frac{^{13}C}{^{12}C}$  using mean or weighted mean and the error associated with these as standard deviation, standard error of mean or error associated with weighted mean, based on the users' discretion. Undesired batches can be interactively deselected and omitted from further analysis. Multiple standards or backgrounds can be used where necessary and results containing plots, user inputs and tables can be downloaded.

In future, this application can be hosted from PRL server so that it can be accessed from LAN/internet as per the configuration. Since it is a web application, it can be accessed cross-platform from various browsers. SPADE can also be extended to accommodate other dating techniques supported by PRL AURIS. Advantage of this application is that it can be modified depending upon the needs and requirements of the users of AMS and deployed anywhere free of cost, unlike the commercial counterparts where access is limited and modifications and feature additions are not possible.

# 6. Acknowledgments

We thank N B Vaghela, Shivam A, Harsh Raj and Ankur Kumar J Dabhi for their cooperation and inputs at various stages. Special thanks to AJT Jull of University of Arizona who provided valuable inputs through the course of an interaction held at PRL.

The editor, D. Pallamraju, thanks the reviewers S. V. S. Murty, and D. V. Subhedar for their assistance in evaluating this Technical Note.

# References

- P. Bevington and D. K. Robinson. *Data Reduction and Error Analysis for the Physical Sciences*. McGraw-Hill Education, 2003.
- R. Bhushan, M. G. Yadava, M. S. Shah, and H. Raj. Performance of a new 1mv AMS facility (AURiS) at PRL, Ahmedabad, India. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 439:76–79, Jan. 2019.
- S. Bowman. *Radiocarbon Dating*. University of California Press, 1990.
- H. Budzikiewicz and R. D. Grigsby. Mass spectrometry and isotopes: A century of research and discussion. *Mass Spectrometry Reviews*, 25(1):146–157, Jan. 2006.
- D. J. Donahue, T. W. Linick, and A. J. T. Jull. Isotope-Ratio and Background Corrections for Accelerator Mass Spectrometry Radiocarbon Measurements. *Radiocarbon*, 32(2):135–142, 1990.
- A. J. T. Jull. The AMS Method of Radiocarbon Dating. In *Reference Module in Earth Systems and Environmental Sciences*. Elsevier, Jan. 2014.

- A. P. McNichol, A. J. T. Jull, and G. S. Burr. Converting AMS Data to Radiocarbon Values: Considerations and Conventions. *Radiocarbon*, 43(2A):313–320, 2001.
- R. J. Schneider, G. A. Jones, A. P. McNichol, K. F. von Reden, K. L. Elder, K. Huang, and E. D. Kessel. Methods for data screening, flagging and error analysis at the National Ocean Sciences AMS Facility. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 92:172–175, June 1994.
- E. M. Scott, G. T. Cook, and P. Naysmith. Error and Uncertainty in Radiocarbon Measurements. *Radiocarbon*, 49(2):427– 440, 2007.
- K. E. Stenström, G. Skog, E. Georgiadou, J. Genberg, and A. Johansson. A guide to radiocarbon units and calculations. page 18, 2011.
- M. Stuiver and H. A. Polach. Discussion Reporting of 14c Data. *Radiocarbon*, 19(3):355–363, 1977.

# Appendices

# A. Graphitisation

A sample whose age is to be estimated is processed in radiochemical lines and its carbon is converted into  $CO_2$  and later into graphite. A method that can be used to convert  $CO_2$  into graphite is Fe-Zn method, where iron (Fe) is heated to 550° C and Zinc (Zn) is heated at 450° C, and the following reactions take place:

$$Zn + CO_2 \rightarrow ZnO + CO$$
 (2)

$$CO \rightarrow C + O_2 \tag{3}$$

$$Zn + O_2 \rightarrow ZnO$$
 (4)

In this process, iron acts as a catalyst and the graphite formed gets coated on the iron. Graphite ( $\sim$ 0.3mg) is then pressed into specially designed aluminium capsules (called target) which are loaded into AMS for isotopic ratio measurements and counting of <sup>14</sup>C.

#### **B. PRL-AURIS**

Graphite targets prepared from samples, standards and blanks are placed in a carousel that can accommodate up to 50 targets and is the initial part of the ion source. After good evacuation, targets are sputtered with a Cesium ion beam and  $C^{-}$  beam is produced. This is crucial in separating nitrogen, which although has a mass of 14, does not form a negative ion. But negative ions such as <sup>13</sup>CH<sup>-</sup>, <sup>12</sup>CH<sub>2</sub><sup>-</sup> with mass 14 are also formed. In the next stage, the ions are injected into an accelerator at 1 MV and passed through a stripper gas (Ar). Here, the negative ions are stripped of electrons, resulting in formation of positive ions. At this stage, the molecules such as <sup>13</sup>CH<sup>-</sup>, <sup>12</sup>CH<sub>2</sub><sup>-</sup> having mass of 14 dissociate and hence are prevented from interfering with the measurements in further stages. The positive carbon ions  $(C^+)$  are further accelerated and passed through a magnet that can separate different isotopes. Since heavier ions curve less in comparison to the lighter ones, different isotopes form separate beams. <sup>12</sup>C and <sup>13</sup>C are measured as currents in Faraday cups and the number of <sup>14</sup>C atoms is detected using a particle detector [McNichol et al., 2001, Jull, 2014]. A schematic of AURiS is shown in Figure 6.

# C. Obtaining isotopic ratios and associated errors

Suppose a sample is run in the AMS for '*n*' batches, for any given batch '*i*', the isotopic ratios  $(\frac{{}^{14}C}{{}^{13}C}, \frac{{}^{14}C}{{}^{12}C} \text{ and } \frac{{}^{13}C}{{}^{12}C})$  each have mean  $\mu_i$  and standard deviation  $\sigma_i$ .

**Method 1** Mean isotopic ratio( $\mu$ ) is calculated as,

$$\mu = \frac{\Sigma \mu_i}{n} \tag{5}$$

and associated error is the standard deviation given by,

$$\sigma = \sqrt{\frac{\Sigma(\mu_i - \mu)^2}{n - 1}} \tag{6}$$

where *n* is the number of batches and  $\mu_i$  and  $\sigma_i$  and are the mean and standard deviation of the *i*<sup>th</sup> batch.

**Method 2** Mean isotopic ratio  $(\mu)$  is the same as in Method 1 whereas associated error is given by the standard error of mean which is calculated as,

$$\text{SEM} = \frac{\sigma}{\sqrt{n}} \tag{7}$$

Method 3 Weighted mean is calculated as,

$$\mu = \frac{\Sigma(\frac{\mu_i}{\sigma_i^2})}{\Sigma(\frac{1}{\sigma^2})} \tag{8}$$

and the error associated with the weighted mean is calculated as,

$$\sigma_{\mu} = \sqrt{\frac{1}{\Sigma(\frac{1}{\sigma_i^2})}} \tag{9}$$

# D. Estimating radiocarbon age of samples

#### Subtracting blank values

Isotopic ratios of  $\frac{{}^{14}C}{{}^{13}C}$  or  $\frac{{}^{14}C}{{}^{12}C}$  are represented by *R* hereafter. Background ratio ( $R_{blank}$ ) is subtracted [Stenström et al., 2011] from the gross measured ratio ( $R_{measured}$ ) to get net corrected ratio (R').

$$R' = R_{measured} - R_{blank} \tag{10}$$

#### **Correction for fractionation**

Since in nature, the differential uptake of one isotope with respect to another results in isotopic fractionation, the  $\frac{^{13}C}{^{12}C}$  ratios are different for different samples. To account for this effect, measurements are normalised to a  $\delta^{13}$ C of -25% [Jull, 2014] where  $\delta^{13}$ C is the relative deviation of the  $\frac{^{13}C}{^{12}C}$  ratio of the sample w.r.t a standard.

$$\delta^{13}C = \left(\frac{\left(\frac{^{13}C}{^{12}C}\right)_{sample}}{\left(\frac{^{13}C}{^{12}C}\right)_{standard}} - 1\right) \times 1000 \tag{11}$$

where the standard used is VPDB (Vienna Pee Dee Belemnite), which has a  $\frac{{}^{13}C}{{}^{12}C}$  ratio of 0.011180.



Figure 6. Schematic of AURiS installed at Physical Research Laboratory, Ahmedabad [modified from Bhushan et al., 2019]

#### Ratio(R) for modern standard

The NIST standards namely oxalic acids I and II are represented by HoxI and HOxII respectively.

For 
$$R = \frac{{}^{14}C}{{}^{13}C}$$
,  
 $R_{HOxI,-19} = R'_{HOxI} \times \left[\frac{1 + (\frac{-19}{1000})}{1 + (\frac{\delta^{13}C_{HOxI}}{1000})}\right]$  (12)

$$R_{HOxII,-25} = R'_{HOxII} \times \left[\frac{1 + (\frac{-25}{1000})}{1 + (\frac{\delta^{13}C_{HOxII}}{1000})}\right]$$
(13)

For  $R = \frac{{}^{14}C}{{}^{12}C}$ ,

$$R_{HOxI,-19} = R'_{HOxI} \times \left[\frac{1 + \left(\frac{-19}{1000}\right)}{1 + \left(\frac{\delta^{13}C_{HOxI}}{1000}\right)}\right]^2$$
(14)

$$R_{HOxII,-25} = R'_{HOxII} \times \left[\frac{1 + \left(\frac{-25}{1000}\right)}{1 + \left(\frac{\delta^{13}C_{HOxII}}{1000}\right)}\right]^2$$
(15)

Then,

$$R_{modern} = 0.95 R_{HOxI,-19} = 0.7459 R_{HOxII,-25}$$
(16)

# Calculating fraction modern(Fm) and radiocarbon age Fraction Modern (Fm) is given by,

For  $R = \frac{{}^{14}C}{{}^{13}C}$ ,

$$Fm = \frac{R'_{sample}}{R_{modern}} \times \left[\frac{1 + (\frac{-25}{1000})}{1 + (\frac{\delta^{13}C_{sample}}{1000})}\right]$$
(17)

For 
$$R = \frac{{}^{14}C}{{}^{12}C}$$
,

$$Fm = \frac{R'_{sample}}{R_{modern}} \times \left[\frac{1 + (\frac{-25}{1000})}{1 + (\frac{\delta^{13}C_{sample}}{1000})}\right]^2$$
(18)

Percent modern carbon (pMC) is given by [Stenström et al., 2011],

$$pMC = Fm \times 100\% \tag{19}$$

Further, age of samples is calculated as,

$$age = -\tau \times \log(Fm) \tag{20}$$

where  $\tau = 8033$  years, the Libby mean life [Donahue et al., 1990].

#### **Estimation of error**

There are two types of error associated with each sample, namely internal error and external error. Internal error (interr) is estimated according to Poisson statistics and depends on the number of  $^{14}$ C counts. Internal error in *Fm* is given by [Schneider et al., 1994],

$$Fm_{interr} = Fm \times \sqrt{\left[ \left( \frac{(N_{sample} + N_{blank})}{(N_{sample} - N_{blank})^2} \right) + \left( \frac{(N_{standard} + N_{blank})}{(N_{standard} - N_{blank})^2} \right) \right]}$$
(21)

where N is the  ${}^{14}$ C counts.

The external error (exterr) accounts for the measurement error associated with the AMS. It is obtained by using the methods outlined in Appendix C and propagated appropriately. The error in estimation of age is given by the larger of internal and external errors [McNichol et al., 2001]. The estimates of radiocarbon ages are rounded off based on the conventions of Stuiver and Polach [1977].

PRL research	पीआरएल के
encompasses	अनुसंधान क्षेत्र में
the earth	समविष्ट हैं
the sun	पृथ्वी एवं
immersed in the fields	सूर्य
and radiations	जो निमीलित हैं
reaching from and to	चुंबकीय क्षेत्र एवं विकिरण में
infinity,	अनंत से अनंत तक
all that man's curiosity	जिन्हे प्रकट कर सकती है
and intellect can reveal	मानव की जिज्ञासा एवं विचारशक्ति