**Introduction**

Image

The idea of doing this project did not come quickly. I was originally flipping through books that only had projects which were already done to death. As I looked through these books consisting mainly of medicinal plants, my good friend suggested that I do something that I planned on doing later as a career. I, of course, have always dreamed of getting into Archaeology. I know there are aspects of archaeology which include Biology so I did not have to think hard to come up with a subject. Carbon dating immediately sprang to mind. This is a rather complex procedure to determine the date of a sample obtained by archaeological digs.

And so the search for information began. The first stop made was the Pleasanton Library. There was limited information at this library due to the complexity of the subject. I found a total of two chapters that included any information about 14C dating. So more drastic measures were needed. We gathered a small group who all needed to get information about research projects and headed out to the libraries at the UC Berkeley campus. This was a great success as there were separate libraries for each particular subject. One library was for Anthropology alone. Anthropology encompasses the subject of Archaeology and the library held an abundance of information on Carbon Dating. Here I found many different books containing every thing I wanted to know. It included a book with procedures both before and during the tests. There were several other books that included explanations of the procedures and a way to interpret results to find accurate dates.

There are many basic concepts in understanding how Carbon dating works. As described in Archaeological Techniques for Amateurs, " Carbon 14 or "heavy carbon" is a radioactive isotope of ordinary Carbon formed in the atmosphere through the bombardment of Nitrogen by cosmic rays.". 14C is absorbed by plant life and all animal forms in a stable rate and ratio. This means that all living things contain a certain amount of 14C. The diagram below was based on a diagram found in The Fabulous Isotopes

and shows how the radioactive Carbon 14 is formed.

diagram

"At the time of death the absorption of 14C ceases and the residual 14C within starts to disintegrate at a fixed rate". Archaeological Techniques for Amateurs. This is known as the half life of Carbon. The Carbon within the sample will last for about 50,000 years. It is logical to suppose that by determining the percentage of 14C present in sample one can then come up with an estimated date. About 0.1% of 14C decays a year.

photo1

Willard F. Libby developed the Carbon 14 dating technique after WW2 and consequently won a Noble Prize for his work in 1960. According to the very useful Waikato radiocarbon website which I will refer to many times throughout this report, c14.sci.waikato.ac.nz, Libby along with the help of Anderson and Arnold discovered that 14C decayed at a constant rate. "They found that after 5568 years, half of the C14 in the original sample will have decayed and after another 5568 years, half of the remaining material will have decayed, and so on (see figure 1 from web site)"

chart

" The half life (*t*1/2) is the name given to this value which Libby measured at 5568+/-30 years. This became known as the Libby Half Life." Waikato University Radiocarbon Lab Website

Libby used modified Geiger counters to measure radioactivity. "These are devices to detect and measure ionizing radiation, as emitted from radioactive sources." www.mathematik.uni-marburg.de .

Diagram

But after the discovery the development of the dating method lead to two other techniques for dating. The conversion of carbon in the sample into CO2 gas which can then be measured was the next step in the development of Carbon dating. This method developed after Libby's findings is called Liquid Scintillation Counting. Broser and Kallman were the scientists who discovered the technique in the 1940s. They found that organic compounds or scintillators become florescent when exposed to ionizing radiation. The Waikato website again explains this process. " Each fluorescence event is proportional to a radioactive decay event, and the frequency of these events is directly proportional to the number of 14C atoms present in the sample." In this method Benzene is used as the scintillation solvent. In the website of the Radiocarbon Laboratory of the University of Zurich, Switzerland , www.geo.unizh.ch/c14/, the process is also summed up well.

"The benzene is produced as follows: Carbon dioxide, obtained by burning the sample, reacts with metallic lithium to form lithium carbide. The lithium carbide is hydrolyzed to acetylene which is subsequently converted to benzene by catalytic trimerisation. A small amount of Carbon dioxide is taken during the above process to enable the measurement of the stable isotope ratio 13C/12C. Scintillation counting results are statistically analyzed and reported as conventional radiocarbon ages corrected with 13C values."

The picture below is the synthesis line used for converting carbon dioxide into benzene which is located at the University of Zurich.

photo3

The second technique developed after LSC is more widely used. This is called Accelerator Mass Spectrometry. This involves directly measuring the radioactivity of a sample. The Zurich University website again gives a good description.

" The radiocarbon age is calculated from the measured ratio of carbon isotopes. Samples are chemically pre-treated and burned in sealed quartz glass ampoules. The resulting carbon dioxide gas from the ampoule is converted to graphite by one of the machines shown below."

"Mark II" Prototype"

photo4

The next step is explained in this quote from the Waikato website:

"The Graphite is ionized by bombarding it with caesium ions and then focused into fast-moving beam (energy typically 25keV). The ions produced are negative which prevents the confusion of 14C with 14N since nitrogen does not form a negative ion. The ions enter the accelerator. As they travel to the terminal (which is at about 2MV), they are accelerated so much that when they collide with the gas molecules in the central "stripper canal", all of the molecular ions (such as 12CH2 and 13CH) are broken up and most of the carbon ions have four electrons removed making them into C3+ ions. These are then accelerated down the second half of the tandem accelerator reaching energies of about 8MeV. The second magnet selects ions with the momentum expected of 14C ions and a Wien filter checks their velocity is also correct. Finally the filtered 14C ions enter the detector where their velocity and energy are checked so that the number of 14C ions in the sample can be counted."

This next image from the Waikato website shows the structure and process of Accelerator Mass Spectrometry involving the counting of the radioactive atoms in a sample.

image5

Very important, however, are the pre-treatments which the samples must undergo to remove contaminants before testing can take place. The relevance of these tests are what I decided to base my research around. It is important to take into account the fact that many of the samples you work with will have been exposed to the elements which can alter the amount of 14C they contain. In the Pedological Perspectives in Archaeological Research it is said one must take into account the biological influences when trying to date a sample. Some of these biological influences are O2, moisture, temperature, C concentration and soil reactivity. Some of these variables can be measured by soil texture and depth below the soil surface at which the sample was found. Also the specific mean annual temperature and rainfall at the site and soil pH should be taken into account when determining what kind of contaminates to look for. For example: "rainfall and temperature affect soil development. Soil pH decreases with increased rainfall. Low pH directly affects extent of leaching and the rate of organic decomposition."

There are several different treatments that can be used to remove different contaminants or can be used depending on different types of samples. For example some samples are more sensitive than others and require a much more gentle treatment. Wood is a sample that is fairly durable and can stand up to harsher pre-treatments. Treatments range from chemical washes to careful work with tweezers and a microscope.

At the Beta Analytic, INC website, a Professional radiocarbon dating service, they offer numerous pre-treatments and explain what kind of samples the treatment is used on.

An "acid/ alkali/ acid" wash is used to remove carbonates and secondary organic acids. This is a method typically applied to charcoal, wood, some peats, some sediments and textiles. An "acid wash" is used to again get rid of carbonates. The alkali wash is not used due to the fact that the primary carbon is soluble in the alkali. This is applied to organic sediments, some peats, small wood or charcoal, and special cases. In "collagen extraction", used primarily for bone, acid washes are used to eliminate the mineral. A alkali wash is used to again get rid of organic acids in the sample. An "acid etch" is applied to shell, calcite and calcareous nodules. This involves the removal of secondary carbonate components. Some samples can be "neutralized" using de-ionized water. Usually this is applied to carbonate that have precipitated from ground water ( strontium carbonate and barium carbonate) and have had hardly any exposure to the atmosphere. An "acid/ alkali/ acid/ cellulose extraction" is used in treating wood that is highly contaminated or very old. All is extracted save the wood cellulose.

All of these pre-treatments are Chemical pre-treatments. There are also physical pre-treatments. These involve anything that does not include a chemical treatment. This is mainly work done by hand in removing obvious contamination of rootlets etc. Samples can be scraped clean with a scalpel, dentist drill or carborundum paper.

Now comes the part of the introduction that you have patiently waited for. I will explain how I have used all of the above information to formulate a question for research. I mentioned earlier that I would be using the pretreatment methods in my research. My aim in this Research project is to find out how much of a difference the pretreatment methods made in the final estimation of a sample's age.

" Is there a significant difference between the results of a pretreated sample and the results of the same sample with no pretreatment?"

In carrying out this idea I first had to find a way to test or collect data. I looked up a number of labs to see which ones did radiocarbon dating. Lawrence Livermore Lab was close by and it was a thought to find someone who could advise me. But I later found out that testing is a rather long and fairly expensive operation. The equipment used in testing cost around $2-3 billion a year in upkeep. So I thought of another way to attack my question. I would send out letters to different scientists around the globe and ask for results of tests that had already taken place. I inquired for possible results from a sample of wood and also asked for the method of pretreatment it was subjected to. I also asked if it was tested as a control without the pretreatment and also with the pretreatment.

These letters I sent to professors at Waikato University in New Zealand, to Professors at the University of Zurich, Switzerland, and to Professors at Purdue University where the PRIME Lab operates. I got wonderful replies back from all three areas giving information and web addresses at which there is a great deal of information.

The following report will thank all three and give the results of the information I collected.

Image of artifact

**Hypothesis**

If the contaminants in raw samples contain a great amount of radiocarbon 14 and contaminants are removed in a pretreatment before testing then the results after testing will differ *greatly* and produce a more accurate date estimation.

**Experiment / Survey**

I wrote letters to several different professors though-out the globe asking them for experiment results on their previous radiocarbon dating tests. The actual carbon dating procedure was so complex, as I found out, that it would have been impossible for me to even attempt to set up an experiment. Here is a basic outline of the letter I distributed to different places.

"Hello there,

I am a student from Amador Valley High School in Pleasanton, California doing a research project for my advanced placement Biology class. I am looking for help in gathering data for my assignment. It is a fairly exciting Assignment and I hope that I will be able to get enough replies.

My assignment is based around the field of Carbon dating as it is a topic that interests me and I will to enter the field of Archaeology in the future.

I understand there are several preparation tasks that must be completed before each test, including acid washes and some manual work picking out contamination.

The data I need is simply this.......I wish to know the results after testing if the preparation is carried out, and the results after testing when there is no preparation. I am trying to determine how great the margin of error is between the two and how much of an influence the preparation had on testing.

I was wondering if the raw sample was included as a control?? I think that wood or bone samples are good sample examples. ........

Thank you for you help, Best Regards,

Hillary Reid "

In response to my letter I received three wonderful replies from professors and scientists from different parts of the globe. I received a letter from Fiona Petchey who is the Deputy Director for the Radiocarbon Dating Laboratory of the University of Waikato in New Zealand. She sent me a letter giving me a web address containing information I could use about contaminants and the pretreatments involved in cleaning samples. She did however inform me that there were no tests she knew of that tested the effectiveness of pretreatments. The web address proved to be full of information and helped me aquaint myself more with the carbon dating process.

Another letter I received was from David Elmore who is a Professor of Physics and Director of the Prime Lab at Purdue University. He agreed that it was a good idea to measure both prepared samples and raw ones but the reason it is probably not done is the extra cost of running the tests. His opinion was that in many cases the result would not be too different and that modern contamination is removed through processing and that will make a raw sample look younger.

The last letter I received was from Ivan Woodhatch who works at the University of Zurich in the Department of Geography. He also gave me some good replies. He told me no testing that is done does not include the standard cleaning process. At their laboratory they use the Acid/ Alkali/ Acid cleaning method to remove carbonates that generally make the sample appear older and human acids which make the sample appear younger. Other cleaning methods are carried out if the sample requires special treatment e.g. the sample is covered in preservatives, lacquer or paint. He gave me a good website address on which I found information and test results needed for this research.

I found tables of data relating to the carbon dating of the Dead Sea Scrolls on the internet source given to me by Ivan Woodhatch. (www.radiocarbon.org). It told the types of pretreatments used on the samples taken depending on types of know contaminants. It also contained the processes of the testing and the final results. There are two different types of pretreatments carried out, and since that all samples were treated I decided to do a comparison between the two.

I will explain the method involved in the pretreatment and in the experiment.

Also I have chosen two samples to compare. One has been treated due to modern contamination and one has just been treated with the standard procedures due to a reasonably clean appearance.

The first was a sample of parchment from the document that was 23.35mg in weight. Seeing as it had been contaminated with Perspex glue due to the fact it had been strengthened with a backing of rice paper. This sample was also difficult to clean as it had been attached to a backing of silk. Sample 2 was a sample of parchment that was 4.90mg was relatively clean and required no special treatment. I will be comparing the difference of the final results and try and determine if there is a great difference possibly due to the difference of pretreatments.

**Preparation method for sample 1-modern contamination**

For 30 minutes wash the sample in an ultrasonic bath of acetone. Then the sample is washed in ~1N HCL for 10 minutes then rinsed in distilled water and washed in 0.1% NaOH for another 10 minutes then again washed in distilled water. The sample is finally dried in a vacuum oven.

**Preparation method for sample 2- no apparent contamination**

The sample is washed in ~1N HCL for 10 minutes then rinsed in distilled water and washed then in 0.1% NaOH for another 10 minutes and again rinsed in distilled water. The sample is dried in a vacuum oven.

**Testing -AMS method**

The accelerator mass spectrometry testing method was used in processing the 14C amounts. The samples were combusted with CuO to make CO2. 0.2 ml of this sample was taken to analyze the ratio of 13C. This analysis will be used to make accurate corrections to the 14C age. The rest of the CO2 is converted to graphite using the equipment. The graphite was loaded into an accelerator target holder. The AMS machinery is then used to analyze the quantity of 14C by measuring the velocity of the radioactive ions. The 14C ages were all corrected to a ratio 13C value of -25%.

**Results**

|  |  |  |  |
| --- | --- | --- | --- |
|  | 14C ages (yr. BP) | Calibrated ages | Paleographic ages |
| Sample 1 | 1954+/-38 | 45 BC - AD 120 | 100-50 BC |
| Sample 2 | 1984+/-33 | 93 BC - AD 80 | 100-80 BC |

Graph of Calibrated ages v Paleographic ages.

**Conclusion**

The data collected shows a small amount of age difference between the samples. Although one sample went through a special cleaning process it did not appear overly different, indicating the cleaning process was probably very thorough. Calibrated age is estimated by taking into consideration the fact that the ratio of 14C in the atmosphere has fluctuated during different time periods. Although there is always a constant ratio of 14C to 13C one needs to determine how the amount of 14C has changed. The standard way of doing this is found by looking at tree rings. There are trees such as Bristlecone pines that have existed for several thousands of years. The tree rings are able to show how the climate has fluctuated over the years. A tree ring can either be tested for 14C or growth can be analyzed to find the changing weather patterns. Using these standard calibration methods one can adjust dating to a more accurate estimation. The paleographic ages are the time periods in which the artifacts supposedly originated.

In determining a difference between the samples, I looked at how much of a result difference there is. In sample 1 the calibrated dates show it is slightly younger that sample 2. Sample 1 is estimated to have originated in 45 BC to AD 120. This is a younger date in comparison to sample 2 which is 93 BC - AD 80. Seeing as sample 1 was the sample that required the extra cleaning due to modern contamination of Perspex glue ( which is said to make a sample appear younger ) it is possible that there might have been some residual contamination. The cleaning that was done probably made rather a lot of difference. Without the cleaning that was done Sample 1 would have appeared much younger that it did, giving false results. I can therefore conclude, with the information I was able to collect, that the pretreatment of samples is somewhat necessary in coming up with a more accurate date. Even thought the difference may be minimal the big picture is that accuracy is always a goal that one strives to meet.

I admit that I did find a few hiccups with this project, the main one being that no Laboratory actually did a control where no pretreatment was used. But I was able to work through this slightly. I learned that pretreatments are more of a standard practice and are necessary to promote accuracy. The difference they make is hard to tell as there is no control done. But evidence would suggest that they do make some bit of difference. In answering my original question I would say that if there were a control test available I think it would show a great difference of results.

Bibliography

1) Hammond, Philip c.; Archaeological Techniques for Amateurs

Princeton, New Jersey

D. Van Nostrand Company, Inc. 1963

2) Mckown, Robin; The Fabulous Isotopes

New York,

Holiday House , 1962

3) SSSA, Pedological Perspectives in Archaeological Research

SSSA Special Publications Number 44

Wisconsin, USA

Soil Science Society of America, Inc , 1995

4) Gillespie, Richard; Radiocarbon User's Handbook

Oxford

Oxford University Committee for Archaeology, 1984

5) Radiocarbon WEB- info

http://www.c14dating.com

6) PRIME Lab web page

http://primelab.physics.purdue.edu

7) Radiocarbon - An International Journal of Cosmogenic Isotope Research

www.radiocarbon.org

8) Beta Analytic - Radiocarbon Dating Service

www.radiocarbon.com

9) University of Zurich, Switzerland

www.geo.unizh.ch/c14/