



Radiocarbon Dating

*Consistent Accuracy
Delivered On-Time*

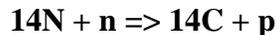
Introduction to Radiocarbon Determination by the Benzene Method

Liquid Scintillation Counting (LSC)

*Note References below that are in **red** italics indicate published methodology works by M.A. Tamers Ph.D., D.Sc. and J.J. Stipp Ph.D., owners of BETA Analytic Inc., who were among the originators of the Benzene Method of Radiocarbon Dating. Between the two of them they have published well over 100 articles on geochronology and research related to the Benzene Method of Radiocarbon dating. An additional publication proving the complete removal of Radon is referenced by D. Hood, R. Hatfield and C. Patrick (et. al) who are the current directors of BETA Analytic Inc and developers of many of the commercial radiocarbon dating procedures in use at BETA Analytic Inc.*

The 14C Method;

There are three principal isotopes of carbon which occur naturally - C12, C13 (both stable) and C14 (unstable or radioactive). These isotopes are present in the following amounts C12 - 98.89%, C13 - 1.11% and C14 - 0.0000000010%. Thus, one carbon 14 atom exists in nature for every 1,000,000,000,000 or (1 in a trillion) C12 atoms in living material. The radiocarbon method is based on the rate of decay of the radioactive or unstable carbon isotope 14 (14C), which is formed in the upper atmosphere through the effect of cosmic ray neutrons upon nitrogen 14. The reaction is;



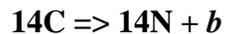
(Where n is a neutron and p is a proton).

The 14C formed is rapidly oxidized to 14CO₂ and enters the earth's plant and animal life ways through photosynthesis and the food chain. The rapidity of the dispersal of C14 into the atmosphere has been demonstrated by measurements of radioactive carbon produced from thermonuclear bomb testing. 14C also enters the Earth's oceans in an atmospheric

exchange and as dissolved carbonate (the entire ^{14}C inventory is termed the **carbon exchange reservoir** (Aitken, 1990)). Plants and animals which utilize carbon in biological food chains take up ^{14}C during their lifetimes. They exist in equilibrium with the ^{14}C concentration of the atmosphere, that is, the numbers of ^{14}C atoms and non-radioactive carbon atoms stays approximately the same over time. As soon as a plant or animal dies, they cease the metabolic function of carbon uptake; there is no replenishment of radioactive carbon, only decay.

Libby, Anderson and Arnold (1949) were the first to measure the rate of this decay. They found that after 5568 years, half the ^{14}C in the original sample will have decayed and after another 5568 years, half of that remaining material will have decayed, and so on (see figure 1 below). 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**. After 10 half-lives, there is a very small amount of radioactive carbon present in a sample. At about 50 - 60 000 years, then, the limit of the technique is reached (beyond this time, other radiometric techniques must be used for dating). By measuring the ^{14}C concentration or residual radioactivity of a sample whose age is not known, it is possible to obtain the count rate or number of decay events per gram of Carbon. By comparing this with modern levels of activity (1890 wood corrected for decay to 1950 AD) and using the measured half-life it becomes possible to calculate a date for the death of the sample.

As ^{14}C decays it emits a weak beta particle (β^-), or electron, which possesses an average energy of 160keV. The decay can be shown:



Thus, the ^{14}C decays back to ^{14}N . There is a quantitative relationship between the decay of ^{14}C and the production of a beta particle. The decay is constant but spontaneous. That is, the probability of decay for an atom of ^{14}C in a discrete sample is constant, thereby requiring the application of statistical methods for the analysis of counting data.

It follows from this that any material which is composed of carbon may be dated. Herein lies the true advantage of the radiocarbon method, it is able to be uniformly applied throughout the world on any material that contains residual carbon.

Because of this laboratories from around the world are producing radiocarbon assays for the scientific community. The ^{14}C technique has been and continues to be applied and used in many, many different fields including hydrology, atmospheric science, oceanography, geology, palaeoclimatology, archaeology, biomedicine and materials science.

The Benzene Method of Radiocarbon Dating;

The initial method of ^{14}C counting used by Willard F. Libby and his co-workers involved measuring radioactivity using modified Geiger counters. The next development in counting technology was the conversion of sample carbon to CO_2 gas for measurement in Gas Proportional counters. In the early 1950's, the first attempts were made to detect ^{14}C by the Liquid Scintillation counting method (LSC). In the 1940's, Broser and Kallman (1947) discovered that certain organic compounds (scintillators) fluoresced when exposed to ionizing radiation. Each fluorescence event is proportional to a radioactive decay event, and the frequency of these events is directly proportional to the number of ^{14}C atoms present in the sample.

The scintillation solvent is a mixture of benzene (C_6H_6) and toluene ($\text{C}_6\text{H}_5\text{CH}_3$). Benzene has been chosen because of its excellent light transmission properties and the high chemical conversion yield of sample C to benzene. The sample is first converted to CO_2 , and then reacted with molten lithium to form lithium carbide (Li_2C_2), before being catalytically trimerized to benzene.

Benzene offers several major advantages over earlier methods of radiocarbon dating; benzene contains 92% carbon by weight and is therefore a much more efficient counting medium than CO_2 (ca 25% carbon) used in gas proportional counters, and LSC allows for the physical rotation of the sample, background and modern counting solutions so that a system of "quasi-simultaneous counting" can be implemented; Noakes, Kim and *Stipp* (1965). Additionally a large number of developments in LSC in the last decades include the optimization of spectrometers, incorporating sophisticated computer and electronic hardware which enables the user to validate counting data with ease. In addition, background count rates have been significantly reduced through the addition of active and passive forms of shielding, including advanced electronics and lead barriers. For a review of LSC see: Polach, H.A. (1992) Four Decades of LS Counting and spectrometry. in, *Radiocarbon after four Decades. An interdisciplinary Perspective.* (eds) Taylor, R.E, Long, A and Kra, R. Springer-Verlag, NY.

One of the most widely known applications of LSC of ^{14}C was for the high precision dating of the radiocarbon timescale for the purposes of calibration. However, while the Benzene Method reigned as the most reliable and widely used method of carbon dating for more than 30 years, the advent of Accelerator Mass Spectrometers able to measure very small samples (at sub-milligram levels with a high level of accuracy and precision) with counting times of minutes rather than days, has all but insured that AMS will eventually become the "preferred method" of radiocarbon dating.

Benzene synthesis procedures vary considerably in different laboratories. The details outlined below describe the procedures used in the BETA laboratory.

Conversion of Sample Carbon to Benzene;

Sample Pretreatment:

Each sample or material type must first be pretreated or the material of interest isolated to insure that only the primary carbon of interest will be analyzed. As many different types of carbon containing compounds are present, different pretreatment regimes have been developed to concentrate and isolate the particular carbon fraction of interest prior to dating. (See *Pretreatment Glossary – Standard Pretreatment Protocols at Beta Analytic*).

CO₂ Generation:

The pretreated sample carbon is first oxidized to CO₂, either by combustion in an oxygen stream (for organics) or acid hydrolysis (for carbonates).

Combustion

OR

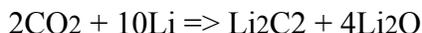
Acid Hydrolysis

Organic + CuO + ΔH => CO₂
(Sample) (900°C)

Carbonate + HCl => CO₂
(Sample)

For organics the combustion gases are bubbled through a mixture of concentrated Sulfuric Acid (H₂SO₄) and Chromium Trioxide (Chromerge) to remove tars and further oxidize or remove other compounds such as nitrogen and sulphur. For both organics and carbonates multiple Methanol/dry ice traps (~ -78°C) are employed to remove any water and non-reactable gases that remaining in the gas prior to the lithium carbide reaction.

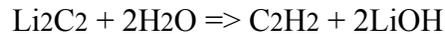
The purified CO₂ is then reacted with molten lithium in a low carbon stainless steel reaction vessel at vacuum:



This reaction was first described by Barker (1953), who developed the reaction using lithium instead of barium, and was later improved by Polach and *Stipp* (1967) and *Tamers* (1975). The CO₂ is bled slowly onto the molten Li where it is converted to Li₂C₂ through an exothermic reaction. The carbide is heated to ca. 900°C (muffle furnace temperature) and placed under active vacuum for 30 minutes to remove any unreacted gases and complete the carbide synthesis (Gupta and Polach, 1985).

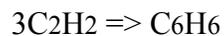
Note: Later in-house experimentation in relation to the elimination of Radon (see below) showed that the 30 minutes of active pumping following the carbide reaction did not contribute to effective Radon removal and that the removal of unreacted gases following the carbide reaction was achieved within 5 minutes.

The lithium carbide is cooled to room temperature and then hydrolyzed to acetylene gas



The acetylene is purified by passing through a series of Methanol/dry ice traps to remove water vapor and then a Phosphoric Acid (H₃PO₄) bubble trap to remove ammonia compounds.

Finally the acetylene is trimerized to benzene using a chromium activated silica-alumina catalyst (type PKN-1) which is commercially available.



Benzene is then driven off the catalyst at ca. 120°C and collected under vacuum with active pumping at dry ice temperatures ~ -78°C *Tamers* (1975). The benzene is then stored in sealed glass vial at freezing temperatures to await counting.

This sequence of reactions requires a high degree of operator skill because of the complexity of the equipment and the nature of the reactions. It is important that a standardized routine is followed carefully and consistently, so that yields remain high and there is no cross-contamination between samples.

Radon contamination

²²²Rn emits alpha and beta particles, the latter with decay energy of 5.587 meV. This decay interferes with the ¹⁴C spectrum, resulting in higher count rates and radiocarbon ages that are too young, and is more significant in older samples because of their lower count rates.

Because Radon has a short half-life of 3.82 days, many labs have adopted a technique of delaying the counting for a period of about 10 half-lives (4-5 weeks) to allow any radon that may be present to decay. In a commercial application this would create problems with regards to the availability of dating services with delivery times of months instead of days to weeks.

As such BETA employs a two stage method of Radon removal employing active pumping which has been shown to effectively eliminate any radon, *Hood, Hatfield, Patrick, Stipp, Tamers*, Leidl, Lyons, Polasch, Robertson and Zhou (1989); a 5 minute period of active pumping when the Li₂C₂ is molten at 900°C and a 30 minute period of active pumping while the benzene is being driven off into a dry-ice cooled trap.

Liquid Scintillation Spectrometry (LSC Counting);

The essential electronic components of the Liquid Scintillation (LS) Spectrometer according to Gupta and Polach (1985) are photo multiplier tubes (PMTs), high voltage supply, signal preamplifiers, pulse and summing amplifiers, coincidence logic, timer and scaler (Gupta and Polach, 1985:50). The LS spectrometer measures electronically the pulses of light generated from photon emissions emitted by a scintillator in response to a radioactive decay event. The PMTs register an electronic pulse proportional to the energy of particular beta decay when a photon or light particle is emitted within the benzene cocktail. The anode current generated from a PMT, then, is a function of the level of radioactivity (Horrocks, 1974).

The synthesized benzene is thawed and transferred into commercially available special low background 9 ml teflon and brass scintillation counting vials (produced by LKB). The counting vials contain a cocktail mixture of the sample benzene generated during the synthesis (0.3 ml to 4.0 ml) and varying amounts of radiocarbon free or “radiocarbon dead” commercially available benzene (0 ml to 3.7ml) as it is necessary to maintain a constant counting volume for LSC. In addition to the sample benzene, a solution of 0.5 ml of toluene is added which contains 0.0671 grams of the organic scintillator butyl-PBD.

The counting vial is then transferred into specially modified Packard TR1000-BA (Time Resolve 1000– Beta Analytic) spectrometer and allowed to count for a period of 1 to 4 days depending on the size, age and precision requirements.

Sample Isotopic Fractionation (Stable Isotope Ratios ¹³C/¹²C)

In order to provide radiocarbon determinations that are both accurate and precise, it is necessary to measure the stable isotopes of ¹³C and ¹²C and their ratio. This is performed by extracting a small amount of the CO₂ generated during the combustion or acid hydrolysis and measuring the ¹³C/¹²C ratio relative to the PDB mass-spectrometry standard. This ratio is later used in the calculation of the radiocarbon age and error to correct for isotopic fractionation in nature.

Fractionation during the geochemical transfer of carbon in nature produces variation in the equilibrium distribution of the isotopes of carbon (¹²C, ¹³C and ¹⁴C). Craig (1953)

first identified that certain biochemical processes alter the equilibrium between the carbon isotopes. Some processes, such as photosynthesis for instance, favors one isotope over another, so after photosynthesis, the isotope ^{13}C is depleted by 1.8% in comparison to its natural ratios in the atmosphere (Harkness, 1979). Conversely the inorganic carbon dissolved in the oceans is generally 0.7% enriched in ^{13}C relative to atmospheric carbon dioxide. The extent of isotopic fractionation on the $^{14}\text{C}/^{12}\text{C}$ ratio which must be measured accurately, is approximately double that for the measured $^{13}\text{C}/^{12}\text{C}$ ratio. If isotopic fractionation occurs in natural processes, a correction can be made by measuring the ratio of the isotope ^{13}C to the isotope ^{12}C in the sample being dated. The ratio is measured using an ordinary mass spectrometer. The isotopic composition of the sample being measured is expressed as **delta ^{13}C** which represents the parts per thousand difference (per mille) between the sample carbon 13 content and the content of the international PDB standard carbonate (Keith et al., 1964; Aitken, 1990). A $\delta^{13}\text{C}$ value, then, represents the per mille (part per thousand) deviation from the PDB standard. PDB refers to the Cretaceous belemnite formation at Peedee in South Carolina, USA. This nomenclature has recently been changed to VPDB (Coplen, 1994).

In summary, then, isotopic fractionation refers to the fluctuation in the carbon isotope ratios as a result of natural biochemical processes as a function of their atomic mass (Taylor, 1987). Variations as such are unrelated to time and natural radioactive decay. It is common practice in radiocarbon laboratories to correct radiocarbon activities for sample fractionation. The resultant ages are termed "normalized", meaning the measured activity is modified with respect to -25 per mille wrt VPDB. The correction factor must be added or subtracted from the conventional radiocarbon age.

The $\delta^{13}\text{C}$ value for a sample can yield important information regarding the environment from which the sample comes, or the mixtures of materials used to produce it. Because the isotope value of the sample reflects the isotopic composition of the immediate environment. In the case of shellfish for example, marine shells typically possess a $\delta^{13}\text{C}$ value of between -1 and +4 per mille, whereas river shells possess a value of between -8 and -12 per mille, therefore, in a case where the precise environment of the shell is not known, it is possible to determine the most likely by analysis of the $\delta^{13}\text{C}$ result.

Fractionation also describes variations in the isotopic ratios of carbon brought about by non-natural causes. For example, samples may be fractionated in the laboratory through a variety of means. Usually, this is due to lack of attention to detail and incomplete conversion of the sample from one stage to another or from one part of the laboratory to another. In Liquid Scintillation Counting, for example, incomplete synthesis of acetylene during lithium carbide preparation may result in a low yield and concurrent fractionation. Similarly, the transfer of gases in a vacuum system may involve fractionation error if the

sample gas is not allowed to equilibrate throughout the total volume. Atoms of larger or smaller mass may be favored in such a situation. If, however, the entire sample is converted completely from one form to another (e.g. solid to gas, acetylene to benzene) then no fractionation will occur.

Radiocarbon Age and Error Calculation:

Much of the information presented in this section is based upon the paper Stuiver, M. and Polach, H.A. 1977. Discussion: Reporting of ^{14}C data. *Radiocarbon* 19: 355-63.

The radiocarbon age of a sample is obtained by measurement of the residual radioactivity. This is calculated through careful measurement of the residual activity (per gram C) remaining in a sample whose age is unknown, compared with the activity present in Modern and Background samples.

Modern standard;

The principal modern radiocarbon standard is N.I.S.T (National Institute of Standards and Technology; Gaithersburg, Maryland, USA) Oxalic Acid I ($\text{C}_2\text{H}_2\text{O}_4$). ***Oxalic acid I*** is N.I.S.T designation SRM 4990 B and is termed HOx1. This is the International Radiocarbon Dating Standard. Ninety-five percent of the activity of Oxalic Acid from the year 1950 is equal to the measured activity of the ***absolute radiocarbon standard which is 1890 wood***. 1890 wood was chosen as the radiocarbon standard because it was growing prior to the fossil fuel effects of the industrial revolution. The activity of 1890 wood is corrected for radioactive decay to 1950. Thus 1950, is year 0 BP by convention in radiocarbon dating and is deemed to be the 'present'. 1950 was chosen for no particular reason other than to honor the publication of the first radiocarbon dates calculated in December 1949 (Taylor, 1987:97).

The Oxalic acid standard was made from a crop of 1955 sugar beet. There were 1000 lbs made. The isotopic ratio of HOx I is -19.3 per mille with respect to (wrt) the PDB standard belemnite (Mann, 1983). The Oxalic acid standard which was developed is no longer commercially available. Another standard, ***Oxalic Acid II*** was prepared when stocks of HOx 1 began to dwindle. The Oxalic acid II standard (HOx 2; N.I.S.T designation SRM 4990 C) was made from a crop of 1977 French beet molasses. In the early 1980's, a group of 12 laboratories measured the ratios of the two standards. The ratio of the activity of Oxalic acid II to 1 is 1.2933 ± 0.001 (the weighted mean) (Mann, 1983). The isotopic ratio of HOx II is -17.8 per mille.

According to Stuiver and Polach (1977), all laboratories should report their results either directly related to NBS Oxalic acid or indirectly using a sub-standard which is related to it.

Background Detection;

It is vital for a radiocarbon laboratory to know the contribution to routine sample activity of non-sample radioactivity. Obviously, this activity is additional and must be removed from calculations. In order to make allowances for background counts and to evaluate the limits of detection, materials which radiocarbon specialists can be fairly sure contain no activity are measured under identical counting conditions as normal samples. Background samples usually consist of geological samples of infinite age such as coal, lignite, limestone, ancient carbonate, anthracite, marble or swamp wood. By measuring the activity of a background sample, the normal radioactivity present while a sample of unknown age is being measured can be accounted for and deducted.

Conventional radiocarbon ages (BP);

A radiocarbon measurement, termed a **conventional radiocarbon age** (or CRA) is obtained using a set of parameters outlined by Stuiver and Polach (1977), in the journal *Radiocarbon*. A time-independent level of C14 activity for the past is assumed in the measurement of a CRA. The activity of this hypothetical level of C14 activity is equal to the activity of the absolute international radiocarbon standard.

The Conventional Radiocarbon Age BP is calculated using the radiocarbon decay equation:

$$t = -8033 \ln(A_{sn}/A_{on})$$

Where -8033 represents the mean lifetime of ¹⁴C (Stuiver and Polach, 1977). A_{on} is the activity in counts per minute of the modern standard, A_{sn} is the equivalent cpm for the sample. 'ln' represents the natural logarithm.

A CRA embraces the following recommended conventions:

- a half-life of 5568 years;
- the use of Oxalic acid I or II as the modern radiocarbon standard;
- correction for sample isotopic fractionation (deltaC13) to a normalized or base value of -25.0 per mille relative to the ratio of C12/C13 in the carbonate standard VPDB (more on fractionation and deltaC13);
- the use of 1950 AD as 0 BP, ie all C14 ages head back in time from 1950;
- the assumption that all C14 reservoirs have remained constant through time.

Additional terms are sometimes requested to be or reported with, or in-lieu of the standard Conventional Radiocarbon Age BP result from which all others are mathematically derived. These are the “Measured Radiocarbon Age BP”, Percent Modern Carbon (pMC), Mean Biobased Result (expressed in %), Percent Mean Biogenic Carbon Content, Percent Biomass CO₂, Fraction Modern Carbon (fmdn or fMC) as well as d14C, D14C, delta 14C, Δ14C and delta 13/12C (all of which are expressed in per mille notation (‰) rather than per cent notation.)

d14C represents the per mille depletion in sample carbon 14 prior to isotopic fractionation correction and is measured by:

$$d14C = \left(\frac{A_{sn}}{A_{on}} - 1 \right) 1000 \text{ per mille}$$

D14C represents the 'normalized' value of d14C. 'Normalized' means that the activity is scaled in relation to fractionation of the sample, or its deltaC13 value. All D14C values are normalized to the base value of -25.0 per mille with respect to the standard carbonate (VPDB). D14C is calculated using:

$$D14C = d14C - 2(\delta C13 + 25) \left(1 + \frac{d14C}{1000} \right) \text{ per mille}$$

This value can then be used to calculate the CRA using the equation given above.

$$\text{Radiocarbon age} = -8033 \ln(1 + D14C/1000)$$

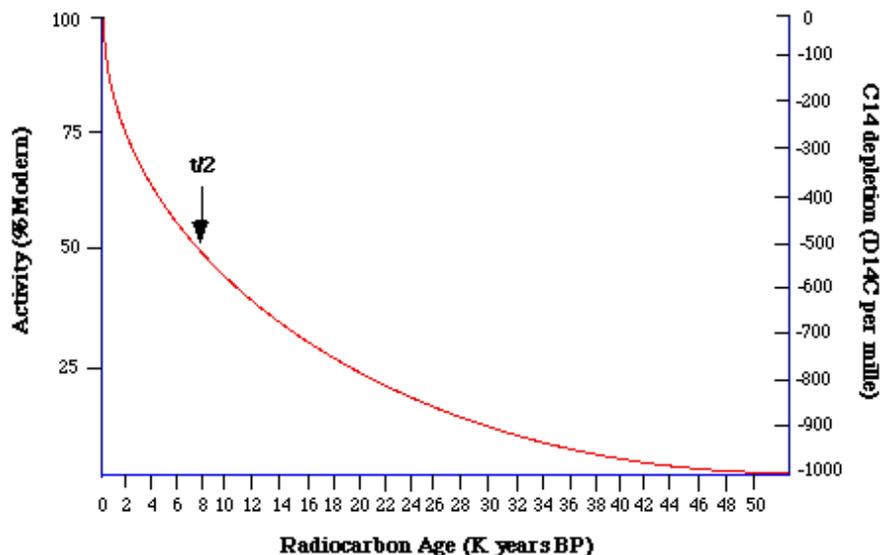


Figure 1: Decay curve for C14 showing the activity at one half-life (t/2). The terms "%Modern", or "pMC" and D14C are shown related in this diagram along with the Radiocarbon age in years BP (Before 1950 AD).

Age Reporting

If the reservoir corrected conventional radiocarbon age calculated is within the past 200 years, it should by convention be termed 'Modern' (Stuiver and Polach, 1977:362). If a sample age falls after 1950, it is termed greater than Modern, or >Modern. Absolute percent modern (%M or pMC - 'percent modern carbon') is calculated using:

$$\%M=100 \times A_{sn}/A_{abs}$$

or,

$$A_{sn}/A_{on}(1/8267^{(y-1950)}) \times 100 \text{ percent}$$

Where A_{abs} is the absolute international standard activity, $1/8267$ is the lifetime based on the new half life (5730 yr), Y = the year of measurement of the appropriate standard. This is an expression of the ratio of the net modern activity against the residual normalized activity of the sample, expressed as a percentage and it represents the proportion of radiocarbon atoms in the sample compared to that present in the year 1950 AD. Thus, %Modern becomes a useful term in describing radiocarbon measurements for the past 45 years when, due to the influx of artificial radiocarbon into the atmosphere as a result of nuclear bomb testing the 'age' calculation becomes a 'future' calculation.

If the sample approaches $D_{14}C = -1000$ per mille within 2 standard deviations, it is considered to be indistinguishable from the laboratory background, ie, not able to be separated with confidence from the laboratory count-rates which result from a sample which contains no radionuclide. In this instance, a **Greater-Than Age** is calculated. An example of a **Greater-Than Age** is >55, 000 yr or >50, 000 yr (Gupta and Polach, 1985).

Samples whose age falls between modern and background and are given finite ages. Standard errors released with each radiocarbon assay are usually rounded by convention (Stuiver and Polach, 1977). Again, not all laboratories subscribe to these conventions, some do not round up ages.

Standard Error and Sources of Error;

Statistical analysis is necessary in radiocarbon dating because the decay of C_{14} although constant, is spontaneous. It is not possible to measure all of the radioactivity in a given sample, hence the need for some kind of statistical analysis of counted data. The distribution of counted C_{14} decay events will, over time, yield a pattern. The pattern is termed a "normal distribution curve". A normal or "Gaussian" distribution describes the symmetrical bell shaped cluster of events around the average or mean of the data. In a

normal distribution, 2 out of 3, or 68% of the values or counts observed will fall within one standard deviation of the average of the data. At two standard deviations, 95% of the observed counts will fall within the range and at three standard deviations, 99% of the counts which comprise the normal distribution will fall within this region. Each radiocarbon date is released as a conventional radiocarbon age with 'standard error'. This is the '±' value and by convention is ± 1 sigma. The standard error is based principally upon counting statistics, however other sources of error are possible and their effects are listed below;

Summary: The accuracy of radiocarbon dates (modified from Polach, H.A. 1976).

Sources of Error	Effect upon Age Determination	Measures to minimize the error incurred
1. Precision of age determination	Statistical: Typically ±1%Modern or less	Big samples, longer count times, repeat sample assays
2. Inherent		
a. C14 half-life	Libby half life 3% too low	Multiply CRA's by 1.03 if necessary
b. C13/C12 fractionation	Variable, up to 450 yr for shell.	Stable isotope analyses using Mass Spec.
c. C14 Modern standard	Variable > 80 yr	International crosscheck of secondary standards.
d. Variation in past C14 production rates	0-800 yr, beyond ca12 ka not determined	Tree ring calibration; otherwise interpret results in radiometric timescale.
e. Distribution of C14 in nature	Surface ocean latitudinal dependence -400 to -750 yr. Deep ocean -1800 yr.	Interpretation of results.
f. Changes of C14 concentration in the atmosphere.	Industrial effect ca -2.5% and atom bomb effect +160% in atmosphere	Interpretation of results
3. Contamination.	Nil to 300 yr up to 15 ka; >20 ka possible beyond 25 ka.	Interpretation of results, analysis and dating of extracted pretreated fractions.
4. Biological age of material	<10 yr to>1000 yr	Identification of species of material in the case of wood and charcoal to short lived samples only.
5. Association of sample and event	Intermediate	Interpretation of results
6. Human	Intermediate	Care in field and laboratory
7. Interpretation of results	Intermediate	Care in interpretation, interdisciplinary approach and collaboration

Accuracy and Precision in Radiocarbon Dating;

It is important to note the meaning of "accuracy" and "precision" in radiocarbon dating. Accuracy refers to the date being a 'true' estimate of the age of a sample within the range of the statistical limits or \pm value of the date. Thus, for the sake of argument, if we were radiocarbon dating a sample of human bones from an individual who we knew died in 1066 AD, and obtained a date of 1040 ± 40 AD, we would have dated the event of his death accurately. If however the date obtained were 1000 ± 15 AD, we would be inaccurate. In terms of precision, however, the former is imprecise in comparison to the latter because of the larger stated error value. As such it can be seen that the date of 1000 ± 15 AD while being highly precise is, in this instance, inaccurate.

Reservoir Effects;

A Conventional Radiocarbon Age or CRA, does not take into account specific differences between the activity of different carbon reservoirs. A CRA is derived using an age calculation based upon the decay corrected activity of the absolute radiocarbon standard (1890 AD wood) which is in equilibrium with atmospheric radiocarbon levels (as mentioned previously, 1890 wood is no longer used as the primary radiocarbon standard, instead Oxalic Acid standards I and II were correlated with the activity of the original standard). In order to ascertain the ages of samples which were formed in equilibrium with different reservoirs to these materials, it is necessary to provide an age correction. Implicit in the Conventional Radiocarbon Age BP is the fact that it is not adjusted for this correction.

Radiocarbon samples which obtain their carbon from a different source (or reservoir) than atmospheric carbon may yield what is termed **apparent ages**. A shellfish alive today in a lake within a limestone catchment, for instance, will yield a radiocarbon date which is excessively old. The reason for this anomaly is that the limestone, which is weathered and dissolved into bicarbonate, has no radioactive carbon. Thus, it dilutes the activity of the lake meaning that the radioactivity is depleted in comparison to ^{14}C activity elsewhere. The lake, in this case, has a different **radiocarbon reservoir** than that of the majority of the radiocarbon in the biosphere and therefore an accurate radiocarbon age requires that a correction be made to account for it.

One of the most commonly referenced reservoir effects concerns the ocean. The average difference between a radiocarbon date of a terrestrial sample such as a tree, and a shell from the marine environment is about 400 radiocarbon years (see Stuiver and Braziunas, 1993). This apparent age of oceanic water is caused both by the delay in exchange rates between atmospheric CO_2 and ocean bicarbonate, and the dilution effect caused by the mixing of surface waters with upwelled deep waters which are very old (Mangerud 1972). A reservoir correction must therefore be made to any conventional shell dates to account for this difference. Human bone may be a problematic medium for dating in some instances due to human consumption of fish, whose C^{14} label will reflect the ocean

reservoir. In such a case, it is very difficult to ascertain the precise reservoir difference and hence apply a correction to the measured radiocarbon age.

Spurious radiocarbon dates caused by volcanic emanations of radiocarbon-depleted CO₂ probably also come under the category of reservoir corrections. Plants which grow in the vicinity of active volcanic fumaroles will yield a radiocarbon age which is too old. Bruns *et al.* (1980) measured the radioactivity of modern plants growing near hot springs heated by volcanic rocks in western Germany and demonstrated a deficiency in radiocarbon of up to 1500 years through comparison with modern atmospheric radiocarbon levels. Similarly, this effect has been noted for plants in the bay of Palaea Kameni near the prehistoric site of Akrotiri, which was buried by the eruption of the Thera volcano over 3500 years ago (see Weninger, 1989). The effect has been suggested as providing dates in error for the eruption of Thera which has been linked to the demise of the Minoan civilization in the Aegean. One modern plant growing near the emanations had an apparent age of 1390 yr. The volcanic effect has a limited distance however. Bruns *et al.* (1980) found that at 200 m away from the source, plants yielded an age in agreement with that expected. They suggested that the influence of depleted CO₂ declined rapidly with increasing distance from the source. Radiocarbon discrepancies due to volcanic CO₂ emissions are a popular source of ammunition for fundamentalist viewpoints keen to present evidence to show that the radiocarbon method is somehow fundamentally flawed.

Suess or Industrial Effect;

Since about 1890, the use of industrial and fossil fuels has resulted in large amounts of CO₂ being emitted into the atmosphere. Because the source of the industrial fuels has been predominantly material of infinite geological age (*e.g.* coal, petroleum), whose radiocarbon content is nil, the radiocarbon activity of the atmosphere has been lowered in the early part of the 20th century up until the 1950's. The atmospheric radiocarbon signal has, in effect, been diluted by about 2%. Hans Suess (1955) discovered the **industrial effect** (also called after him) in the 1950's. A number of researchers found that the activity they expected from material growing since 1890 AD was lower. The logical conclusion from this was that in order to obtain a modern radiocarbon reference standard, representing the radiocarbon activity of the 'present day', one could not very well use wood which grew in the 1900's since it was affected by this industrial effect. Thus it was that 1890 wood was used as the modern radiocarbon standard, extrapolated for decay to 1950 AD

Atom Bomb Effect;

Since about 1955, thermonuclear tests have added considerably to the C¹⁴ atmospheric reservoir. This C¹⁴ is 'artificial' or 'bomb' C¹⁴, produced because nuclear bombs produce a huge thermal neutron flux. The effect of this has been to almost double the amount of C¹⁴ activity in terrestrial carbon bearing materials (Taylor, 1987).

De Vries (1958) was the first person to identify this 'Atom Bomb' effect. In the northern hemisphere the amount of artificial carbon in the atmosphere reached a peak in 1963 (in the southern hemisphere around 1965) at about 100% above normal levels. Since that time the amount has declined owing to exchange and dispersal of C14 into the Earth's carbon cycle system. The presence of bomb carbon in the earth's biosphere has enabled it to be used as a tracer to investigate the mechanics of carbon mixing and exchange processes.
