RADIOCARBON DATING USING LSC

Yustina Tri Handayani[1], Widodo Soemadi[1], K. Isogai[2]

1.Center for Education and Training, National Nuclear Energy Agency
2. Japan Chemical Analysis Center (JCAC)

ABSTRAK

RADIOCARBON DATING MENGGUNAKAN LSC. *Radiocarbon Dating* merupakan salah satu aplikasi teknik nuklir yang digunakan untuk menentukan umur suatu obyek. Penentuan umur dengan metode tersebut terhadap sampel kayu (dari kuil Horyuji) dan kulit kerang (dari hasil penggalian di area JCAC) dilakukan di Japan Chemical Analysis Center dalam kerangka Instructor Training Program. Dalam penentuan tersebut digunakan standar SRM 4990C, blanko kayu dan kapur. Preparasi sample, standard dan blanko dilakukan dengan metode sintesis benzene. Kedapatulangan proses preparasi sebesar 86,8%. Benzene yang dihasilkan ditambah sintilator cair dan dilakukan pengukuran menggunakan Pencacah Sintilasi Cair Wallac 1220 Quantulus selama minimum 10 jam. Didapatkan umur dari kayu (1204 ± 37) tahun dan umur dari kulit kerang (7160 ± 45) tahun, dengan tingkat kepercayaan 68%.

ABSTRACT

RADIOCARBON DATING USING LSC. Radiocarbon dating is a method of nuclear technique for obtaining age estimates on organic materials. Determination of wood (from Horyuji Shrine) and coral sample (from JCAC area) is due in Japan Chemical Analysis Center in the frame of Instructor Training Program. It uses SRM 4990C, wood and marble blanks. Preparation of samples, standard, and blanks is due by benzene synthesis method. Chemical Yield of preparation was 86,8%. Liquid scintillator is added and counted using Liquid Scintillation Counter (LSC) Wallac 1220 Quantulus at least 10 hours. The result of wood age is (1204 ± 37) years (BP) and coral age is (7160 ± 45) years (BP) in term of confidence level 68%.

Key word: Carbon Dating, Benzene Synthesis Method, Liquid Scintillation Counting, Isotopic Tractionation or IJCPC, SRM 4990C, ABA method, ADA method.

INTRODUCTION

One of the most interesting application of nuclear techniques is dating of ancient object of either natural origin, such as ancient rock, or of human origin, such as object made by prehistoric people. Radiocarbon dating is a method of obtaining age estimates on organic materials. It has been used to date samples as old as 50,000 years. The method was developed immediately following World War II by Willard F.Libby and co-worker, and has provided age determination in archeology, geology, geophysics, and other branches of science.

There are three natural isotopes, 12C, 13C, 14C. Carbon- 14 (^{14}C) is radioactive and is constantly being produced in the upper atmosphere by the bombardment of cosmic neutron upon 14N, which is present there in large amounts. The equation of this reaction is

$$^{14}N + {}^{1}n \longrightarrow {}^{14}C + {}^{1}p$$

The carbon- 14 thus produce immediately begins to decay.

$$14C \longrightarrow 14N + e^-$$

$$T_{1/2} = 5730\ y$$

Because 14e is being both formed in the atmosphere and removed by its decay, a constant concentration is maintained, a steady-state concentration is achieved. This 14e becomes Incorporate d in carbon dioxide in the atmosphere where it can be taken in by plant through the process of photosynthesis. The intake of 14e into animal is by consumption of such plants or by the consumption of plant-eating animals. While they are alive, plants and animals consume and excrete carbon so that they also maintain a steady-state concentration of 14e and are thus equilibrium with their surroundings. Once they die however , the 14e that they possess is not replaced as the organism decay, so the 14e concentration begins to decrease. The half-life ($T_{1/2}$) is 5730 y; therefore, if we find that the 14e concentration in an object that had once been living has dropped to half its initial value, we could conclude that the object is 5730 years old. After about 50,000 years, the amount of l"e remaining will be so small that the fossil cannot be dated reliably.

The natural l"e concentration in the geologically recent contemporary "pre-bomb" biosphere was approximately 13.5 disintegrations p~~minute (dpm) per gram of carbon. Modem e emits about 15 dpm per gram of material.

METHOD

A measurement of 14e content of an organic sample will provide an accurate determination of sample's age if it is assumed that:

1. the production of 14e by cosmic rays has remained essentially constant long enough to establish a steady-state in the 14e/12e ratio In the atmosphere;
2. there has been a complete and rapid mixing of 14e throughout the various carbon reservoirs;
3. the carbon isotope ratio in the sample has not been altered except by decay;
4. the total amount of carbon in any reservoir has not been altered.

In addition, the half-life of 14e must be known with sufficient accuracy, and it must be possible to measure natural levels of 14e to appropriate levels of accuracy and precision.

Modern Standard

. Ninety five percent of activity of oxalic acid from the year 1950 is equal to measured activity of the absolute radiocarbon standard which is 1890 wood. 1890 wood was chose~ as the radiocarbon standard because it was prior to the fossil fuel effects of the industrial revolution. The activity of 1890 wood is corrected for radioactivity decay to 1950. Thus 1950, is year 0 BP (Before Present) 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.

Calculation of Age

According to international agreement (convention), conventional 14e ages must fulfill certain requirements as follow (Stuiver and Polach, 1977), so that they can be compared worldwide.

1. The reference year for conventional ages is AD 1950. This is indicated with the letters bp or BP (for "before present);
2. NBS (National Bureau of Standards Washington, D.C.) oxalic acid is used as standard for time zero.
3. The half-life of 5568 year introduced by Libby is used for calculating conventional 14e ages. The physical half-life of (5730 ± 40) year is used for date relevant to geophysics. These dates are about 3% larger than the corresponding conventional 14e ages.
4. The measured 14e activities is corrected to -25 per mil(δ^{13}e correction) before conversion to 14e ages. The fractionation occurs because of the mass difference of the Carbon isotopes.

Isotopic fractionation of $^{13}C/^{12}C$

$$\delta^{13}C = \frac{R - R_{PDB}}{R_{PDB}} \times 1000\ (‰)$$

where

R : Ratio of mass of ^{13}C to ^{12}C ($^{13}C/^{12}C$) in the investigated sample

R_{PDB} : Ratio of mass of ^{13}C to ^{12}C ($^{13}C/^{12}C$) in the standard sample (PDB)

Note: The fractionation of ^{14}C is about double that of ^{13}C

Thus the correction of the ^{14}C activity is follow.

$$A_{corr} = \{\ 1 - 2(\delta^{13}C + 25)/1000\ \}$$

where

Acorr: Corrected activity of 14C

Conventional Radiocarbon age (BP) calculation

sample and the standard deviation uses the following equation.

$$A = A_0 \cdot e^{-\lambda t}$$

$$t = \frac{T_{1/2}}{\ln 2} \cdot \ln\frac{A_0}{A} = 8033 \cdot \ln\left(\frac{A_0}{A}\right) = -8033 \cdot \ln\left(\frac{A}{A_0}\right)$$

$$t = -8033 \cdot \ln \left[\frac{\ldots \left(1 - \frac{2(25 + \delta^{13}C)}{1000}\right)}{0.7459 \cdot \ldots \, t_{STD} \ldots} \right]$$

T : Conventional radiocarbon age (BP)

$T_{1/2}$: Libby ^{14}C half-life 5568 years

A_0 : Initial specific activity of 14C (Bq/gC)

A : Present specific activity of 14C (Bq/gC)

n_{SA} : Total number of the unknown sample counts

t_{SA} : Total counting time of the unknown sample

n_{STD} : Total number of the modern carbon standard counts

t_{STD} : Total counting time of the modern carbon standard

n_B : Total number of the background counts

t_B : Total counting time of the background

W_{STD} : Carbon weight of the modern standard benzene

W_{SA} : Carbon weight of the unknown sample benzene

$\delta^{13}C$: Isotopic ratio of $^{13}C/^{12}C$ of the modern carbon standard

$\delta^{13}C$: Isotopic ratio of $^{13}C/^{12}C$ of the unknown sample

Pretreatment Technique

Many samples from terrestrial environments, such as wood, charcoal, and peat, will often contain small amounts of absorbed carbonates from percolating groundwater. The most common method of treating samples thought to be contaminated with these substances is the acid-base-acid (ABA), sometimes called the acid-alkali-acid (AAA) method. After being physically pretreated and reduced size, the sample is washed in hot diluted (10%) HCl in a beaker for approximately an hour, or until the reaction appears to have ceased. Then it is rinsed in a buchner funnel with distilled water to reduce the pH levels toward neutral. Following this, the sample is immersed in a 5% diluted, boiling NaOH solution for approximately an hour, after which it is rinsed or centrifuged again. The NaOH pre-treatment produces two fractions, base soluble and insoluble. The former may kept for dating purposes by being acidified, rinsed and dried in an oven. The latter too, must be acidified because the NaOH pretreatment sometimes involves an exchange between the NaOH and atmospheric CO_2. The NaOH absorb CO_2 from the surrounding air. The final acid wash ensures that any such contamination is removed.

Conversion of purified samples for dating by Liquid Scintillation Counting

In the majority of LSC facilities, the scintillation solvent is benzene (C6H6) or a mixture of benzene and toluene (C6~CH3). Benzene has been chosen because of its excellent light transmission properties and high chemical conversion yield of sample C to benzene. The sample is first converted to CO_2. then reacted with molten lithium to form lithium carbide (Li_2C_2), before being catalytically trimerised to benzene.

The method involves:

1. Carbon dioxide preparation
   The combustion of organic matter in an oxygen stream or combustion bomb (for organic materials), or hydrolysis of carbonates by acids, and the subsequent wet chemistry purification and recovery of CO_2 are carried out in a glass vacuum system;
2. Lithium carbide (LhC_2) formation
   The purified CO_2 is then reacted with molten lithium in a stainless steel reaction vessel at 700°C.
3. Acetylene synthesis
   Lithium carbide is cooled, then acetylene (C_2H_2) gas is produced by reacting with water at room temperature;
4. Benzene synthesis
   The purified acetylene is trimerised to benzene using suitable catalyst.. There is a variety of vanadium or chromium activated catalyst available.

Principle of Liquid Scintillation Counting (LSC)

Primary application of LSC is the counting of weak beta emitters such as tritium and 14C . In liquid scintillation measurement, the sample of radioactive material is dissolved into liquid scintillator consisting of solvent and solute. Since each of radioactive source is surrounded by the scintillator molecules, all of the radiation are change into photon, so that the efficiency is very high.

Scintillator is an energy transducer to transform radiation energy into light energy or fluorescence or photon. Radiation excites liquid scintillator molecules to higher energy states and cause this scintillator emit photons. The photons hit the photocathode surface of a photomultiplier tube and transformed to electric pulses which are finally fed into the multichannel pulse height analyzer.

MATERIALS AND EQUIPMENTS

Materials :

Wood sample
Shell sample
Distilled Water
Ice
Liquid Nitrogen
Oxalic Acid Standard
Molten lithium
Hydrochloric Acid(HCI) 1 N
Hydrochloric Acid (HCI) 6 N
Sodium Hydroxide (NaOH) 1 N

Equipments :

Glassware
Cutter and cutting plate
Mortar
Hot plate
Oven
Furnace
Combustion vessel
Apparatus for the benzene synthesis
LSC (Wallac 1220 Quantulus)

The chemical yield of sample preparation is 86.8%. It does not affect the results, because the preparations of the standard, the unknown sample and the background sample are same procedural..

Ifno correction for the fractionation, the difference of age is about 1.5% for wood and 3.7% for shell/coral.

If the calculation of the age used Tin of 14C of 5730, the ages are 1204 years and 7368 years for wood and coral respectively. The differences are 2.9% for both.

SUMMARY

1. The chemical yield of sample preparation is 86.8%
2. The age of wood = (1204 ±37) years BP and the age of coral = (7160 ± 145) years BP in term of confidence level of 68%.

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RESULT AND DISCUSSION

Result of $CaCO_3$ preparation is as follow

Process	Parameter	Value
	Weight of $CaCO_3$	20.28 g
	Weight of C atom in $CaCO_3$	2.4346 gC
$CaCO_3 \longrightarrow CO_2$	Pressure (P)	73.61 kPa
	Temperature (T)	24.0°C
	Volume (V)	6.62 L
	R	8.29388
	C = n x 24 C = PV/RT C = 73.61 x 6.62/8.29388/(273+24.0)x12	2.3739 gC
	Chemical yield = 2.3739/2.4346 x 100%	97.5%
$CO_2 \longrightarrow C_2H_2$	Pressure (P)	34.70 kPa
	Temperature (T)	24.5°C
	Volume (V)	6.62 L
	R	8.29388
	C = n x 24 C = PV/RT C = 34.70 x 6.62/ 8.29388/(273+24.5)x24	2.2344 gC
	Chemical yield = 2.2344/2.3739 x 100%	94.1%
$C_2H_2 \longrightarrow C_6H_6$	Total weight	92.69 gr
	Weight of vial	90.40 gr
	Weight of benzene	2.29 gr
	C = 2.29 gr x 72/78	2.1138 gr
	Chemical yield = 2.1138/2.2344 x 100%	94.6%
$CaCO_3 \longrightarrow C_6H_6$	Chemical yield = 0.975 x 0.941 x 0.946	0.868 (86.8 %)

Table 1. Result of 14Cactivity measurement by Wallac 1220 Quantulus

Sample	Benzene content [illegible]	Carbon content [illegible]	Counting time (min)	Count	Count rate [illegible]	Standard deviation [illegible]
SRM4990C	1.7498	1.6152	6419.92	146520	22.823	0.0596
Marble blank	1.7901	1.6524	6419.92	1910	0.298	0.0068
Wood	1.4644	1.3518	6419.95	78505	12.228	0.0436

[illegible]	[illegible]	[illegible]
SRM 4990C-blank	22.525	0.0600
Wood - blank	11,931	0.0442

Sample	$\delta^{13}C$ (per mil)	$(25+\delta^{13}C)$ (per mil)
SRM 4990C	-17.8	7.2
Wood	-25	0

Calculation	Age of sample (year)	standard deviation of age (year)
	1204	37

Table 2. Result of 14Cactivity measurement by Wallac 1220 Quantulus

Sample	Benzene content [illegible]	Carbon content [illegible]	Counting time [illegible]	Count	Count rate [illegible]	Standard deviation [illegible]
SRM4990C	1.7498	1.6152	987.63	22751	23.036	0.1527
Marble blank	1.7901	1.6524	987.65	271	0.274	0.0167
Coral	0.9864	0.9105	987.64	4293	4.347	0.0663

Sample	Count rate (cpm)	Standard deviation (cpm)
SRM4990C- blank	22.762	0.1536
Marble - blank	4.072	0.0684

Sample	$\delta^{13}C$ (per mil)	$(25+\delta^{13}C)$ (per mil)
SRM 4990C	**-17.8**	**7.2**
Coral	**0**	**25**

Calculation	Age of sample (year)	standard deviation of age (year)
	7160	145

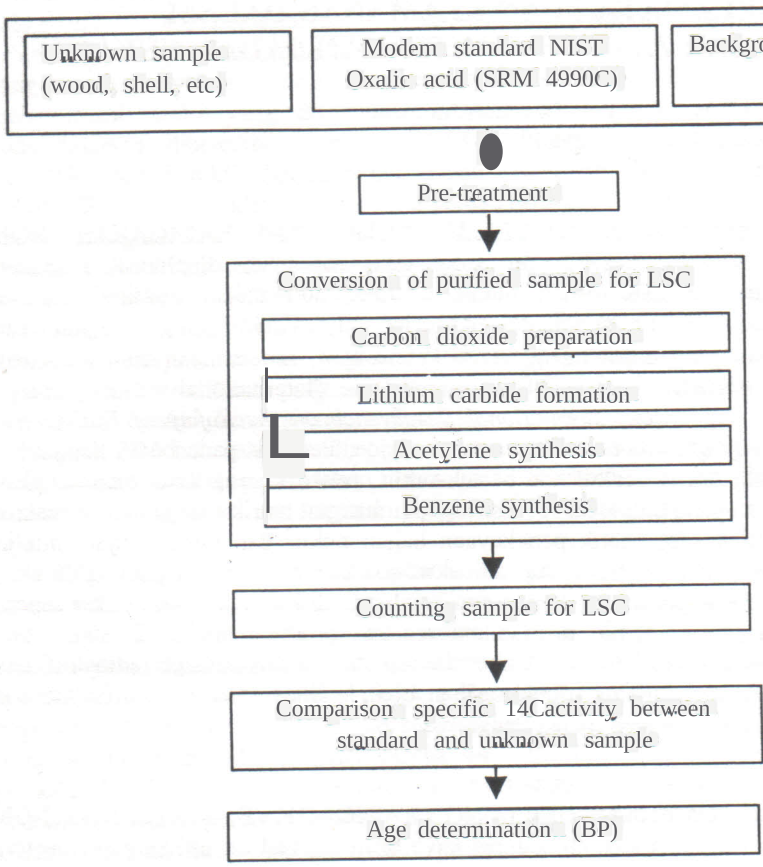
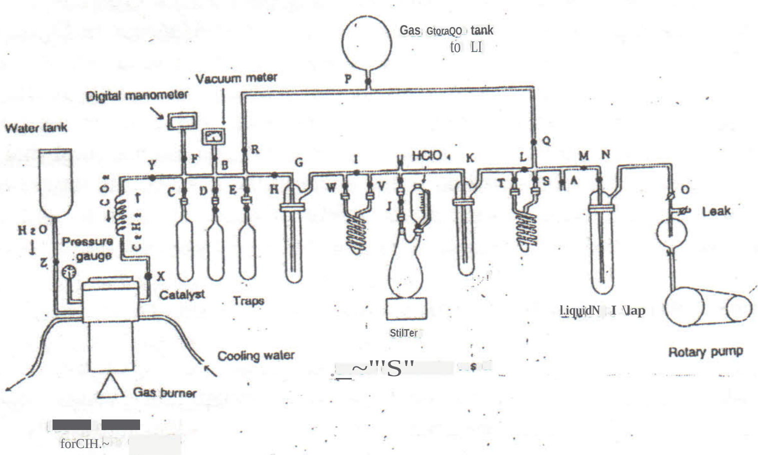


Figure 1. Outline of 14CDating



Apparatus for the Benzene Syntyhesis method at Jr.At