*Marina Chimica Acta, April 2015*
*Jurusan Kimia, FMIPA UNHAS*

*Vol. 16 No.1*
*ISSN 1441-2132*

# UTILIZATION OF SODIUM HYDROXIDE AS ABSORBER FOR $^{14}C$ ANALYSIS OF CORAL AGES ESTIMATION IN LANGKAI ISLAND USING LSC (LIQUID SCINTILLATION COUNTING) METHOD

**Febby Kurniaty*, Maming, Muhammad Zakir and Alfian Noor**

Radiation Chemistry Laboratory, MIPA, Hasanuddin University
Kampus UNHAS Tamalanrea, Makassar, 90245
*contact : febby.kurniaty@yahoo.co.id, Phone: 089654345073

## ABSTRACT

Research on utilization of sodium hydroxide as absorber for $^{14}C$ analysis of coral ages estimation in Langkai Island using LSC (Liquid Scintillation Counting) method has been done. Samples analyzed comes from Langkai Island, which is relatively low disturbing by human activities. Samples were cleaned according to physical and chemical treatment using mixture of acid-base solution: NaOH , $H_2O_2$ , $HClO_4$ and HCl. This step remove about 8,62% mass of the sample and it leaves white. Carbonated of sample were remove as $CO_2$ by reaction with HCl 10% and trapped by 5M NaOH as $Na_2CO_3$. Total carbon in the sample can be determined by titration method with the total weight of carbon sample are 0,2688 g / 8 mL. Specific activity of carbon-14 in the sample that were counted by Hidex 300 SL liquid Scintillation Counter were 14.72 ± 7.92 DPM/gC related to their age. By applying specific activity of the samples and specific activity carbon-14 in the modern carbon (15.3 ± 0.1 DPM/gC) to radioisotop desintegration equation, the age were 316,90±170,506 years.

Keywords : Carbon Dating, Liquid Scintillation Counting, Coral, Spermonde Archiphelago.

## INTRODUCTION

The center of the world's marine biodiversity, especially coral reefs located in the world's coral triangle which have wide approximately 75,000 $km^2$ of coral reefs. Which Indonesia accounted for 65% with an area of about 51.000 $km^2$ of coral reefs compared with Philippines, Malaysia, Timor Leste, Papua New Guinea, and the Solomon Islands (Burke, et al., 2012 and Ron, 2010).

Coral reef ecosystem is one of the oldest ecosystem found on earth, that ups and downs in a continuous development since more than 5000 years ago (Tamrin, 2007). Biota has a life time or a very long lifespan, with a suspicion supported by some geologists as Shepard (1971), Kuenen (1960), Bird (1976), Mater and Bennett (1984), who agrees to say that 75% of all reefs reefs formed during the Pleistocene (Rositasari, 1996).

According to Neudecker (1987), Jokiel and Coles (1990) coral reef is a marine biota that life survival is largely determined by changes in ambient temperature. Coral reefs are formed from limestone $CaCO_3$, which has many functions, especially as a place to live and growing of marine biota (Nybakken, 1988). Also according to Lenterak (2013), coral reefs are able to record all the activities, habits or behaviors of earthquakes in the past by determining the age.

According to Yuliati and Akhadi (2005), the determination of the age of the coral reefs in waters have enormous benefits in studying the geographic origin

of coral samples. No exception in Spermonde Islands which is the center of the coral triangle which also has a diversity of ecosystems and species diversity of marine life that very high (Rony, 2010) which consists of 78 genera and sub-genera, with total of 262 species (Moll, 1983). So it needs to determin the age of coral reefs of the origin area.

Age determination of coral reefs can be done by using the method of radiocarbon dating. This method is based on the calculation of the $^{14}C$ activity contained in a sample of carbon (Faisal, 2009). The calendar may occur because of the carbon isotopes (carbon-14) contained in a living organism that will decay when these organisms die with a half-life of 5730 years Faure (1986).

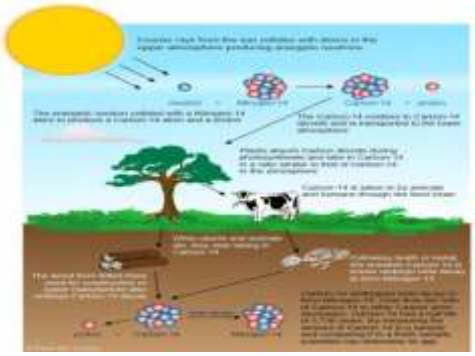

Figure 1. The natural process of carbon dating

Radiocarbon dating methods often used and aring the last two decades for age determination is the absorption method. Absorption method intended is the $CO_2$ absorption in the $^{14}C$ content of $CO_2$ which directly counted by liquid scintillation counter. The use of NaOH solvent in the absorption process resulted a chemical reaction, due to $CO_2$ with NaOH solution can directly react. Process or separation of $CO_2$ absorption by NaOH can be seen in the following reaction:

$$CO_2 + 2\ NaOH \rightarrow Na_2CO_3 + H_2O$$

Carbon-14 ($^{14}C$) has a very low specific activity even though the sample is still fresh. Therefore, for the purposes of counting requires special tools to count with low radiation (LBC, Low Background Low). Counter instruments that qualified for the radiation measurement standards are (Liquid scintillation Counting), which can reach a measurement geometries counting efficiency of about 99.99%.

Application of the LSC method (liquid scintillation Counting) by measuring the activity of carbon-14 in determining the age of a lot of the material has given some important roles, not only in the discovery of the age of ancient objects in archeology, but also thrive in the age determination of sediments, corals, shells, water , soil and other Siregar (2008). As studies by Jauhari (2013), using KOH as the absorber specific activity of $^{14}C$ in samples of coral reefs in Spermonde Island reaches 14.11 ± 0.5 dpm / GRC 669.484 ± 20 years old. However, in this study the efficiency of sample counting has not reached 100%, because the value of the activity (dpm) fluctuated. It is caused by β particles emissions of $^{14}CO_2$ by the scintillator solution is imperfectly occurred because the sample solution and the scintillator is not very homogeneous so the condition causing the generated photons is reduced and causes small count values.

The explanation of the $^{14}C$ measurement methods above, showed a less maximum result, so that further research needs to be done using different methods and absorber in order to achieve better results. Therefore, the research will be conducted on the using of sodium hydroxide for $^{14}C$ analysis on the age determination of coral reefs in the Spermonde island with LSC method (liquid scintillation counting)

## MATERIAL AND METHODS

### Materials

The materials of this study was 30% $H_2O_2$, $HClO_4$ 1 N, 1 N NaOH, ethanolamine, $N_2$ gas HP (High Purity),

10% HCl, $AgNO_3$, silica gel, marble, scintillator aqualight LLT, filter paper, distilled water and coral reefs .

**Apparatus**

Preparation tool in the form of round-bottom flask, impinger, funnel, absorption column, glass cup, mortar, gloves, oven, hammer and tools glasses commonly used in laboratories as well as β radiation count tool of carbon-14 sample is LSC Hidex 300 SL.

**Sampling**

Sampling was carried out in the island Langkai Spermonde Islands, South Sulawesi, with a depth of 4-5 meters above sea level. Sampling of coral reefs by SCUBA divers aided by tools such as drill and hammer.

**Analysis of $CO_2$**

Each limestone samples that has been dried and finely crushed to 50 grams were taken for analysis of $^{14}C$ or carbon content of the total. 20 gram samples that have been smoothed placed in a round bottom flask, then rinsed thoroughly with a solution of 10 % HCl were placed in a separating funnel until all the powder samples completely reacted with HCl. Then, the resulting $CO_2$ gas is passed into a solution of 5 M sodium hidroxide, as shown in Figure 2.

**Determination of Total Carbon**

Total carbon in the sample was calculated from the concentration of carbonate obtained by titration with HCl 5 M. Measurement of the activity of $^{14}C$ in the sample solution used liquid scintillation counter Hidex 300 SL with methyl orange indicator for the determination of total alkali and and indicators in the determination of alkaline OH phenolptalin after carbonate precipitated with 10% $BaCl_2$.

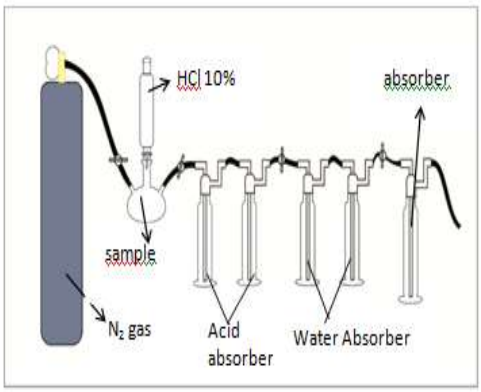


Figure 2. Design tools as $CO_2$ separation carbonate limestone sample.

**Enumeration Coral Reef Samples**

Enumeration of the samples was done by 8 mL of sample solution is pipetted into a glass vial of 20 mL, then added 12 mL of scintillator and shaken until homogeneous. Furthermore, the sample with the LSC chopped Hidex 300 SL made with interval time 1-180 minutes.

**Calculation of Absolute Age**

Age calculation is done using the formula:

$$t = \frac{t_{1\ nb\ b/2}}{ln\,2} ln \frac{A_0}{A}$$

A = Radioactivity of $^{14}C$ isotopes in the sample

$A_o$ = Radioactivity isotope $^{14}C$ during the life of plants or animals 15,3 DPM/g C (Libby, 1960)

$t_{1/2}$ = Half-life of $^{14}C$ 5730 years

Ln2 = 0,693

## RESULT AND DISCUSSION

**Sampling reef**

The sample of coral reef was taken in Langkai Island because Langkai Island is one of the outer islands within 40 km from the city of Makassar. Supported also by the condition of the island relatively quiet and relatively remote from human activity so that the condition of coral reefs around the island is generally very good. The following picture is the coral reef samples from the island.

Figure 2. The coral reef sample from Langkai Island Spermonde

**Washing Result of Coral Reef Sample**

Washing process of the samples were occurred two stages, physically and chemically leaching to eliminate all natural contamination found in samples of coral reefs, so the it results white coral due to the loss of impurities and carbon source on the sample surface. It is known by way of weighing the dry samples of coral reefs to keep the weight gained by the sample weight value of 252.653 grams with a distance of 4 meters above sea level and a loss of 8.62% impurities where the missing part of the sample was the natural contamination accumulated over the reef in surface waters and matrix rock dissolved.

**Result of Total Carbon Determination in 8 mL Sample Solution**

The determination of total carbon can be done by titration using HCl 5M. The total corbon resulted in the sample is 0,2688 g/8 mL. The total carbon that was resulted from 8 mL sample solution was used in the measurement of specific activity carbon-14 in disintegration per minute per mass unit of carbon (DPM/grC) that would be the base in age determination.

**Enumeration of samples.**

Sample enumeration is done in two stages, the stage of determining the optimum counting time and the step of determining the average value of the optimum sample chopped. The following data is the result of the determination of the optimum time of enumeration of the activity of carbon-14 contained in the sample can be seen in Table 1.

Table 1. Sample Results Optimum Time Enumeration Langkai Islands Coral Island Spermonde the LSC device Hidex 300 SL in a span of chopped 1-180 minutes.

| | **Sample** | | | |
|---|---|---|---|---|
| **Counting Time (second)** | CPM | DPM | TDCR | Beta Spectrum |
| 5 | 588,280 | 11090,750 | 0,053 | 0,00 |
| 10 | 503,860 | 7051,310 | 0,071 | 0,00 |
| 20 | 308,720 | 2782,580 | 0,110 | 0,00 |
| 30 | 122,570 | 424,780 | 0,288 | 0,00 |
| 40 | 111,170 | 358,410 | 0,313 | 1,00 |
| 60 | 92,630 | 249,930 | 0,370 | 0,00 |
| 80 | 71,530 | 133,920 | 0,534 | 1,00 |
| 100 | 67,150 | 127,090 | 0,528 | 0,00 |
| 120 | 67,710 | 129,199 | 0,524 | 0,00 |
| 140 | 69,060 | 137,060 | 0,503 | 0,00 |
| 180 | 75,900 | 160,440 | 0,473 | 1,00 |

.

To know and to determine the optimum time of enumeration in the sample can based on the cpm, dpm and tdcr which decreased then suddenly increased. This is due to the instability of the enumeration phase which causes reduced efficiency. Based on table 1, the sample obtained is the optimum counting time for 100 minutes, with DPM value of 127.09, CPM at 67.150 and TDCR value of 0.528. The optimum time is obtained, then be used to determine the average value of the sample activity of coral reefs. The average value is later used to calculate the specific activity of $^{14}C$ in samples of coral reefs. Data of optimum counting time in 100 minutes with 5 times show in Table 2.

Table 2. Data from sample enumeration Langkai Islands Coral Island Spermonde the LSC device Hidex 300 SL at the optimum time of enumeration for 100 minutes with 5 repetitions.

| | **Sample** | | | |
|---|---|---|---|---|
| **Counting Time (Second)** | CPM | DPM | TDCR | Beta Spectrum |
| 100 | 64,780 | 111,990 | 0,578 | 0,00 |
| 100 | 65,430 | 112,060 | 0,580 | 0,00 |
| 100 | 66,640 | 113,660 | 0,594 | 0,00 |
| 100 | 65,000 | 109,850 | 0,591 | 0,00 |
| 100 | 63,500 | 108,710 | 0,584 | 0,00 |
| Average | 65,07 | 111,254 | 0,5854 | 0,00 |

Based on table 2, the average values obtained at 65.07 CPM samples, the average value of DPM at 111.398 and the average value of 0.5854 TDCR. The same treatment was also carried out against the background count is 12mL scintillator inserted into the vial and added 8mL NaOH as absorber then enumerated by LSC Hidex 300SL. Data chopped optimum time background can shown in Table 3. The data is the average value of the background activity at the optimum counting time of 100 minutes can be seen in Table 4.

**Table 3**. Data Results Optimum Time Enumeration Background using scintillator aqualight the LSC device Hidex 300 SL in a span of chopped 1-180 minutes.

| | **Sample** | | | |
|---|---|---|---|---|
| **Counting time (second)** | CPM | DPM | TDCR | Beta Spectrum |
| 5 | 66,6 | 117,96 | 0,564 | 0,00 |
| 10 | 59,7 | 102,410 | 0,582 | 0,00 |
| 20 | 60,850 | 103,570 | 0,587 | 0,00 |
| 30 | 61,400 | 107,400 | 0,571 | 0,00 |
| 40 | 62,500 | 107,830 | 0,579 | 1,00 |
| 60 | 59,560 | 101,470 | 0,587 | 0,00 |
| 80 | 60,330 | 102,690 | 0,587 | 1,00 |
| 100 | 59,080 | 100,210 | 0,589 | 0,00 |
| 120 | 63,000 | 110,430 | 0,570 | 0,00 |
| 140 | 61,510 | 106,520 | 0,579 | 0,00 |
| 180 | 62,600 | 107,850 | 0,580 | 1,00 |

Table 4. The average value of data background activity by LSC device Hidex 300 SL at the optimum time of enumeration for 100 minutes.

| | **Sample** | | | |
|---|---|---|---|---|
| **Couting Time (second)** | CPM | DPM | TDCR | Beta Spectrum |
| 100 | 62,550 | 107,690 | 0,580 | 1,00 |
| 100 | 62,590 | 107,180 | 0,583 | 0,00 |
| 100 | 62,270 | 106,910 | 0,582 | 0,00 |
| 100 | 62,860 | 108,670 | 0,578 | 0,00 |
| 100 | 61,250 | 106,030 | 0,577 | 0,00 |
| Average | 62,304 | 107,296 | 0,58 | 0,00 |

**Determination of Specific Activity Sample Reef**

The specific activity of the sample will be the basis for the calculation of age. Where specific activity obtained from the disintegrations per minute (DPM) divided by the total carbon contentin 8mL of sample was mixed with12 ml of scintillator. Average specific activity (As) samples from the calculation of disintegrations per minute (DPM) per unit carbon future samples can be seen in Table 5.

**Tabel 5**. Specific activity data average carbon-14 sample Coral Island Origin Langkai Spermonde Islands

| Coral Reef | DPM | C-total (gr) | As (DPM/gr C) |
|---|---|---|---|
| Sample | 3,958 | 0,2688 | 14,72 ±7,92 |

The advantage of LSC Hidex 300SL when compared with other tools is a device Micro win system will generate the corrected absolute chopped sample quenching effect. Thus data from chopped samples in Table 8 with the specific activity of carbon-14 (14,72 ±7,92) dpm/grC shows the actual number of atoms of carbon-14 decays per minute (DPM) in anyone gram of the element carbon.

Value of the specific activity of the sample reef 14,72 ±7,92 dpm/gr C shows the value of the specific activity of the carbon that is slightly lower than the specific activity of the carbon value of 15.3±0.1 bpm modern/gr C, this shows that there has been a decay of the atomic nucleus carbon-14, which starts from samples of coral reefs die, so that the activity of carbon-14 contained in the sample is reduced and smaller than the specific activity of 15.3±0.1modern carbon dpm/gr C(Libby, 1960).

Calculation Age of Sample Reefs

Determination of the age can be calculated based on a comparison of the value of the specific activity of modern carbon (15.3 ±0.1dpm/grC) and the specific activity of the samples were obtained using radiocarbon decay rate equation:

$$t = \frac{t_{1/2}}{ln\,2} ln \frac{A_0}{A}$$

Remarks:

A = radioactivity of the isotope 14C in the sample

Ao = radioactivity of the isotope 14C when the plant or animal life (15.3 ± 0.1) DPM (Libby. 1960)

t1/2 = half-life = 5730 ± 40 years

ln 2 = 0.693

Based on the above equation, the age of the sample coral reef from Langkai island can be seen in Table 6.

Table 6. Calculation Result Data Age Reefs Based On Activity of carbon-14 in the sample.

| Sample | Age (year) |
|---|---|
| Coral reef | 316,90±170,50 |

Based on calculations performed age, the age of the sample was obtained reef is 316,90±170,50 years, age is obtained by calculating the decay rate equation radiocarbon. Age acquired are included in the category of carbon young age, this indicates that the coral reef is not a long-established on the Langkai island.

## CONCLUSION

Age of coral reefs from the Langkai island in Spermonde Islands calculated based on data from the specific activity of carbon-14 is 316,90 ± 170,50 years old.

## REFERENCES

Bird, E.C.F., 1976, *Coast; An Introduction to Systematic Geomorphology*, Australian National University Press: 219 -*243.*

Burke, L., Reytar, K., Spalding, M., dan Perry, A., 2012, *Reefs at Risk Resivited in the Coral Triangle*, World Resource Institute.

Faure, G., 1986, *Principle of Isotope Geology*: 386-404.

Jokiel, P.L., & S.L., Coles, 1977, *Effects of temperature in the mortality and growth of Hawaiian reef corals.* Mar. Biol., **43**: 201–208.

Neudecker, S., 1987, *Environment Effects of Power Plants on Coral Reefs and Ways to Minimize Them*, Pp. 103-118 *in* Human Impcats on Coral Reefs: Facts and Recommendations (B Salvant, ed.), Antenne de Tahiti Museum EPHE, Papetoai, Moorea, Polynesia Francaise.

Nybakken, I.W., 1988, *Marine Biology An Ecological Approach*, PT. Gramedia Jakarta, Jakarta.

Yuliati, H., Akhadi, M., 2005, *Radionuclides Kosmogenik For Dates, Biomedical Research Center for Radiation and Nuclear Safety*, Radiation Center BATAN

.