ANALYSIS ACTIVITY ^{14}C OF CORAL REEF IN KAYANGAN ISLAND

Nur Faiizah Aqiilah Firman[1], Alfian Noor[2*], Muhammad Zakir[2], Maming[2], Syafyuddin Yusuf[3]

[1]Doctoral Program of Chemistry, Faculty of Mathematics and Natural Sciences, Hasanuddin University, Makassar, Indonesia, 90245
[2] Chemistry Department, Faculty of Mathematics and Natural Sciences, Hasanuddin University, Makassar, Indonesia, 90245
[3]Marine Science Department, Faculty of Marune Science and Fisheries, Hasanuddin University, Makassar, Indonesia, 90245
Corresponding author: alfiannoor744@gmail.com

ABSTRACT

The work is to determine absorption capacity, optimum time analysis, efficiency enumeration (TDCR), specific activity of ^{14}C and coral age. Steps taken are physical and chemical washing, CO_2 absorption, and analysis using liquid scintillation counter Hidex 300 SL. Due to washing, the weight loss was 4.74%. Total carbon absorbed was 1,056 grams. CO_2 absorption capacity using KOH was 47% while optimum time analysis by LSC was 30 minutes and average efficiency enumeration (TDCR) was 0.6877. It was concluded that specific activity of ^{14}C was 14.7361 DPM/gC and coral age in Kayangan Island was 310.49 years.

Keywords: Coral reef, Kayangan Island, radiocarbon dating, LSC

1. INTRODUCTION

Spermonde archipelago have a high marine biodiversity, divided into 4 zones stretching from north to south. The first zone, closest to coastline of Sulawesi Island, with average depth 10 m. Second one, about 5 km from the coastline of Sulawesi Island, with an average depth of 30 m. The third one, starting from 12.5 km from the coastline of Sulawesi with depth of 20-50 m. The fourth zone with a distance of 30 km from the mainland of Sulawesi. Kayangan Island is in inner zone with an area 2,6 ha [1][2][3][4].

Examination of ecological changes and evolution in the context of environmental variability provides an ideal framework for understanding coral reef paleoecology [5]. Age of coral reefs can be known by using radiocarbon dating. Measurement of coral age based on isotope ^{14}C activity contained in calcium carbonate of coral skeleton [6][7].

Metering activity ^{14}C use Liquid Scintillation Counter (LSC). LSC detect and measure particle β$^-$ emission released by a sample containing ^{14}C [8]. LSC Hidex 300 SL has advantage for measurement activity of ^{14}C. LSC Hidex 300 SL has automatic TDCR or efficiency enumeration without external or internal standard sources. Mensuration efficiency enumeration with TDCR (triple to double coincidences) allows determination

activities for radionuclides pure beta-emitting with high accuracy. Quench is handled directly by TDCR [9].

Preparation sample method for measuring ^{14}C activity is CO_2 absorption. This method quick, inexpensive, simple and requires less carbon [10]. The solution used as absorbent is potassium hydroxide. Potassium hydroxide absorb CO_2 that produces potassium carbonate [11]. Therefore this study was conducted to analyze ^{14}C activity and age of coral reef.

2. MATERIAL AND METHOD

Location

Coral reef was sampled in Kayangan Island waters (**Figure 1**) and kept in Radiation Chemistry Laboratory.

Figure 1. Kayangan Islands (Google^{TM} DigitalGlobe)

Coral Reef Sampling

Tools and material used in sampling are sample bag, shovel, crowbars, and cool box for sample stored. Sampling coral reef used snorkeling equipment. Coral reef sampling method used crowbar and shovel with depth 3-5 m from sea level. Type of dead coral reef is *Styllophora pistillata*.

Physics and Chemical Washing

Washing sample divided in two stages; physical washing and chemical washing. Its aim to eliminate contamination found on the surface of the coral. Sample was washed with water and brushed several times until clean. After physical washing, sample of coral was placed in container and dried [12].

Coral was immersed in a mixture of H_2O_2 30% and NaOH 1N ratio of 50:50 in a 100 mL beaker. Then, washing solution was separated from the sample with occasional sample being brushed and rinsed again with distilled water to remove the black stain on the sample's narrowest blemish. Furthermore, sample of was immersed in a mixture of H_2O_2 30% and $HClO_4$ 1% with ratio 50:50 in a 100 mL beaker for 30-120 seconds. Sample was separated from washing solution and rinsed ± 3 times with distilled water. The last process in chemical washing was that sample of coral reef was soaked in 10 mL of HCl 6N solution for 15-60 seconds and rinsed ± 3 times with distilled water. Then, sample was dried in oven at 60 °C until dry and weighed to find out weight percentage sample lost during chemical washing process [12]. Then, sample was cooled and crushed using mortar to become powder [13].

CO_2 Absorption [13]

Sample of coral reef was weighed 5 gram and put into a round bottom flask. N_2 High Purity Gas (HP) was flowed to CO_2 absorption devices. Sample was added HCl 10 % until calcium carbonate reacted. The CO_2 gas produced was flowed through acid absorber and water absorber to CO_2 absorption column. In this reaction CO_2 would be produced through the following reactions:

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$$
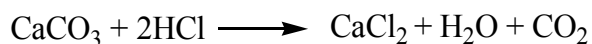
After the absorption process was complete, solution formed put into the reservoir flask for the next stage. The CO_2 absorption tool scheme can be seen in **Figure 2**.
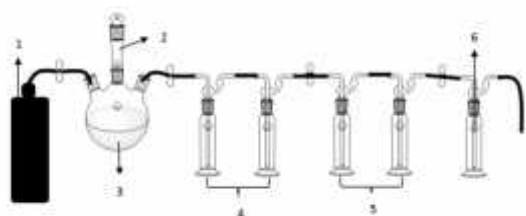

Figure 2. Design CO_2 Absorption Tool of Coral Reef Sample

Where 1). N_2 gas, 2). Sample, 3). HCl 10%, 4). Acid Absorber, 5). Water Absorber, and 6). CO_2 Absorber

Determination of Total Carbon

Carbonate solution was pipetted 5 mL and put into a 50 mL Erlenmeyer. Then, it was titrated with HCl and uses the MO indicator. The second carbonate solution was added with $BaCl_2$ 10% and filtered. Filtrate was pipetted 5 mL and a few drops of PP indicator, then titrated with HCl 5M. The difference between volume of first titration and second titration was used to determine total carbon contained in the sample

Sample and Marble (Background) Analysis Using Liquid Scintillation Counter (14)

Activity ^{14}C in the sample is expressed in units of activity, which is the decay every minute (DPM) of ^{14}C. The results of the sample enumeration with LSC Hidex 300 SL enumerators produce data in units of CPM (counts per minute) and TDCR (Triple to Double Coincidence Ratio) or known as enumeration efficiency (E), Equation 1:

$$E = \frac{Cpm}{Dpm} \times 100\% \qquad (1)$$

The statistical calculation of the radioactive sample enumeration using LSC is a very natural decay calculation in radioactive elements which emit pure β particles at random (random decay).

Determination of ^{14}C activity in coral reef samples can be known through sample enumeration with LSC Hidex 300 SL. Mixture sample solution 8 mL and scintillator 12 mL into a 20 mL glass vial. Homogeneous sample mixture and scintillator were analysis with LSC Hidex 300 SL device with a counting time of 1-240 minutes. The same was done for background counting by filling 8 mL of background solution and 12 mL of scintillator into a 20 mL vial and chopped with LSC Hidex 300 SL.

Calculate Age of Coral Reef

The age of coral reef samples can be calculated based on the comparison of modern carbon-specific activities (15.3 $\pm$ 0.1 DPM/g C) to the specific activity of the samples obtained from the result analysis using the radiocarbon decay rate equation 2:

$$t = \frac{t_{1/2}}{\ln 2} \ln \frac{A_o}{A_t} \qquad (2)$$

Where:

t   = Sample age

$t_{1/2}$ = half-life isotope ^{14}C (5730 $\pm$ 40 years)

A_t = isotope ^{14}C activity of sample

A_o = isotope ^{14}C activity on same material when plant/ animal lives

Ln2 = 0,693

3. RESULT AND DISCUSSION

Phsycal and Chemical Washing

Physical washing, sample of coral reef is brushed and washed to dissolve sediment attached to coral reef. Chemical washing with mixture H_2O_2 30% and NaOH 1N in sonication aims to remove black crust/ strains attached to the narrow gap or between septa of the coral reef. Washing wit mixture H_2O_2 30% and $HClO_4$ 1% which effectively removes the remaining stains that are still attached to the sample. The last stage, washing with HCl 6N for 15-60 minutes, separating it with solution and rinsing it several times with distilled water [12]. This process remove about 4,74 % total coral weight (**Table 1**).

Table 1. Percentage of Remove of total Coral Weight

Sample	Before Washing (g)	After Washing (g)	% Remove of total Coral Weight
Coral reef	947,444	900,312	4,74 %

Determination of Total Carbon and Absorption Capacity

Sample of coral reef was crushed until smooth. Then, solution of HCl 10% is added. The reaction of calcium carbonate with HCl produces CO_2 gas. CO_2 gas passes through the absorbent acid which contains $AgNO_3$ which functions to absorb acid; absorbent water containing silica gel. Then, it passes through the KOH solution which functions as a CO_2 absorber. The reaction of CO_2 gas with KOH can be seen in reaction:

$$CO_2(g) + 2\ KOH(aq) \longrightarrow K_2CO_3(aq) + H_2O(aq)$$
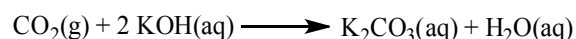
The process of CO_2 absorption by KOH, not all of them can be absorbed, which is marked by producing bubbles. To find out the amount of CO_2 absorbed using acidimetric titration. In Table 2, based on the weight of CO_2, KOH absorption capacity or percentage of KOH's ability to absorb CO_2 gas produced from coral reef samples can be known.

Table 2. CO_2 Weight and Absorption Capacity of KOH

Absorbent	Amount of CO_2	
	Weight of CO_2 (g)	Absorption Capacity (%)
KOH	1,0560	47

Measurement of samples containing ^{14}C uses CO_2 direct absorption method. This method converts the sample to CO_2 which can be analyzed using Liquid Scintillation Counter Hidex 300 SL. Beta activity in the sample associated with decay ^{14}C and compared with background [15]. Sample enumeration is carried out in

2 stages: the first determine optimum time of enumeration (**Figure 3**) and the second determine average enumeration in optimum time (**Table 3**).
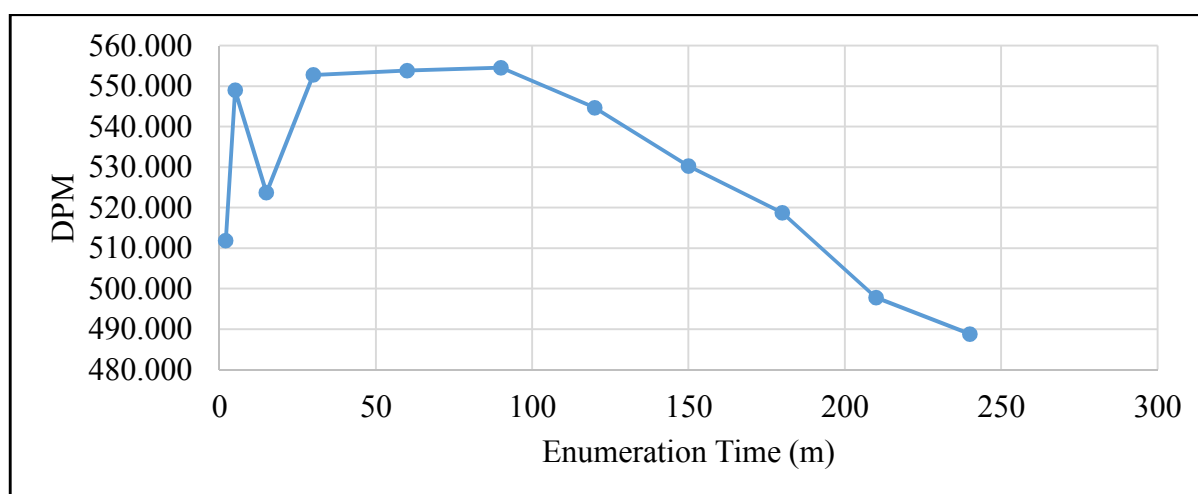

Figure 3.. Optimum Time of Enumeration

.**Table 3**. Average Enumeration in Optimum Time

No	Enumeration Time (m)	CPM	DPM	TDCR
1	30	318,030	427,080	0,744
2	30	317,460	454,950	0,697
3	30	301,660	442,490	0,681
4	30	301,720	444,840	0,678
5	30	304,560	450,450	0,676
6	30	293,250	437.690	0,670
7	30	300,520	449,290	0,668
	Average	305,3142	443,8271	0,6877

Based on the data in graph 1, DPM (disintegration per minute) in the 5th minute increased and in the 15th minute it decreased. Enumeration began to stabilize at 30 minutes. Instability enumeration value can be caused by 3 phenomena are chemical quenching, ionization quenching, and color quenching. Chemical quenching can be caused by chemical substances contained in the sample, which can reduce transfer energy process. Ionization quenching related to density excited solvent molecules. Color quenching,

phenomenon that occurs when visible sample is analyzed, which will absorb photons in the form of light before being detected by PMT [11].

Age of Coral Reef in Kayangan Island

Specific activity of sample is obtained from the difference in sample DPM and the background DPM divided by the total carbon sample, where marble as background (**Tabel 4**).

The age of a coral reef sample can be determined by comparison between

specific activity of modern carbon and the specific activity of sample obtained from equation (3). In **Table 5**, there is an average enumeration efficiency, specific

Table 4. Specific Activities ^{14}C of Sample and Background

No	DPMs	DPMb	DPMk	DPM/gC
1	427,080	419,650	7,43	7,0359
2	454,950	423,930	31,02	29,375
3	442,490	426,900	15,59	14,7632
4	444,840	431,580	13,26	12,5568
5	450,450	431,970	13,64	12,9166
6	437.690	429,070	8,62	8,1628
7	449,290	429,920	19,37	18,3428
		Average		14,7361

Table 5. Age of Coral Reef

No	Analysis	TDCR	^{14}C Activity	Age
1	Coral reef	0,6877	14,7361	310,4995

4. CONCLUSIONS

Based on the research, it can be concluded that the absorption capacity KOH was 47 %. Specific activity coral reef was 14,7361. Age of coral reef species *Styllophora pistillata* in Kayangan Island was 310,4995 years.

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REFERENCES

activities and estimated age of coral reef samples.

[1] Nurdin, A., Komatsu, T., Rani, C., Supriadi, Fakhriyyah, S., Agus, 2016, Coral Reef Destruction of Small Island in 44 Years and Destructive Fishing in Spermonde Archipelago, Indonesia, *Earth Environ. Sci.,* doi:10.1088/1755-1315/47/1/012011.

[2] Melawaty, L., Noor. A., Harlim, T., Voogd, N. D., 2014, Essential Metal Zn in Sponge *Callyspongia aerizusa* from Spermonde Archipelago, *Advances in Biological Chemistry*, **4**:86-90.

[3] Muller, E. M., Raymundo, L. J., Willis, B. L., *et al*., 2012, Coral Health and Disease in the Spermonde Archipelago and Wakatobi, Sulawesi, . *J. Indonesia Coral Reef*, **1**(3): 147-159.

[4] Kench, P. S. dan Mann, T., 2017, Reef Island Evolution and Dynamic: Insights from the Indian and Pacific Oceans and Perspectives for the Spermonde Archipelago, *Frontiers in Marine Science*, 4(145), doi: 10.3389/fmars.2017.00145.

[5] Pandofili, J. M., 2011, Coral Reef: An Ecosystem in Transition, *Springer Science*, doi: 10.1007/978-94-007-0114-4_2

[6] Chiu, T., Fairbanks, R. G., Mortlock, R. A., Cao, L., Fairbanks, T. W., Bloom, A. L., 2006, Redundant ^{230}Th/^{234}U/^{238}U, ^{231}Pa/^{235}U and ^{14}C Dating of Fossil Corals for Accurate

Radiocarbon Age Calibration, *Quatenary Science Review*, **25**, 2431-2440.

[7] Mass, T., Giuffre, A. J., Sun, C., *et al.*, 2017, Amorphous Calcium Carbonate Particles from Coral Skeletons, PNAS. doi: 10.1073/pnas.1707890114.

[8] Polach, H. A., 1987, Evaluation and Status of Liquid Scintillation Counting for Radiocarbon Dating, *Radiocarbon*, **29**(1): 1-11.

[9] Owner's Handbook Hidex 300 SL, 2010, Automatic Liquid Scintillation Counter, Hidex, Finland.

[10] Horvatincic, N., Baresic, J., Bronic, I. K., Obelic, B., 2004, Measurement of Low ^{14}C Activities in a Liquid scintillation Counter in The Zagreb Radiocarbon Laboratory, *Radiocarbon*, **46**(1): 105-116.

[11] L'Annunziata, M. F., 2012, Handbook of Radioactivity Analysis, Elsavier Inc., http://dx.doi.org/10.1016/B978-0-12-384873-4.00001-3.

[12] Adkins, J. F., Griffin, S., Kashgarian, M., *et. al.*, 2002, Radiocarbon Dating of Deep-Sea Corals, *radiocarbon*, **44**(2): 567-580.

[13] Hartoko, D. A., Noor, A., Zakir, M., and Maming, Utilization of Hydroxide Compound As CO_2 Absorbent for Measurement of Carbon-14 in Coral Reef Sample From Spermonde Archipelago, *Marina Chemica Acta,* 17(2), ISSN 1411-2132.

[14] Jauhari, and Maming, 2014, Determination of The Coral Age in Spermonde Archipelago Measurement ^{14}C Activity Using LSC (*Liquid Scintillation Counting*)

Method, *Marina Chemica Acta*, **15**(1): 13-20.

[15] Varlam, C., Stefanescu, I., Varlam, M., Popescu, I., Faurescu, I., 2007, Applying The Direct Absorption Method And LSC for ^{14}C Concentration Measurement in Aqueous Samples, *Radiocarbon*, **49**(2): 281-289.