Analysis activity $^{14}$C of coral in Barrang Caddi Island, Spermonde Archipelago

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Abstract. This study aims to determine carbon-14 activity on coral from Barrang Caddi. Several stages of research were physical and chemical cleaning to eliminate contamination on coral. CO$_2$ absorption pre-treatment method, titration to determine total carbon absorbed in the process of absorption CO$_2$ and enumeration with LSC Hidex 300 SL to determine the optimum time of enumeration, the average value of activity $^{14}$C and specific activities $^{14}$C. In this study, marble from marble karst, Maros, was used as a background. The results show that the absorption capacity was 0.2188 mol CO$_2$/mol OH, the absorption efficiency of 21.87%, total carbon mass was 0.168 gram, optimum counting time was 15 minutes, average activity $^{14}$C was 433,597 DPM, enumeration efficiency was 0.567 and specific activity was 15.262 DPM/gC. It was concluded that coral in Barrang Caddi relatively new.

1. Introduction

Spermonde archipelago have high coral diversity, which are 78 genera and subgenera with a total of 262 species [1]. Coral reef is one of the oldest ecosystems that have wealth biodiversity and variation history more than a million years. This is because many coral organisms form skeleton (CaCO$_3$) at isotopes equilibrium with seawater [2].

Carbon have three isotopes which found in nature, $^{12}$C, $^{13}$C, and $^{14}$C. Abundance $^{12}$C is ~99.8 % of the total carbon on the earth, $^{13}$C is 1 %, while $^{14}$C is found one in every 1 million carbon atoms. $^{14}$C is radioactive and produces beta emissions with half-life 5730 years. $^{14}$C decays to $^{14}$N with low energy emissions of beta radiation with an average energy 49.5 keV and maximum energy 156 keV [3,4].

$^{14}$C is produced in the upper atmosphere, where neutrons from sunlight hit $^{14}$N and form $^{14}$C. Chemically, $^{14}$C cannot be distinguished from $^{12}$C and $^{13}$C, then joins carbon cycle on the earth through photosynthesis and exchange CO$_2$ air-sea. $^{14}$C solved in the sea, lake, and river enter shells, corals and other marine organisms. When living, organisms form equilibrium between radiocarbon decay and their environment; which is $^{14}$C decays replaced by $^{14}$C from environment. After death, equilibrium between radiocarbon decay and $^{14}$C from environment will stop, so that $^{14}$C activity begins to decrease. $^{14}$C loss by decay can be determined time death organisms [5,3,6].

One of the methods can be used to measure radiocarbon activity is LSC. LSC is the main technique for measuring beta emission radionuclides, alpha emission, and radionuclide decay with electron capture. Although including conventional radiometric techniques, LSC remains competitive for the measurement of various radionuclides. Advantages of using LSC are simple preparation procedures and high enumeration efficiency that can reach 100%. New generation, LSC Hidex 300 SL is
equipped with the TDCR system, a system capable of simultaneously correcting quench [7,8,9]. Therefore, this research was conducted to analysis activity $^{14}$C of coral in Barrang Caddi Island.

2. Experimental

2.1. Material and Methods

2.1.1. Sampling method
Coral sample was obtained from marine near Barrang Caddi Island at coordinates S: 05.07735°, E: 119.31938° with a depth of 4-5 m above sea level. Sample was taken dead coral.

2.1.2. Material and equipment
Materials was used in this research were H$_2$O$_2$ 30%, HCl 10 %, HCl 6 N, KOH 1N, AgNO$_3$, HClO$_4$ 1 %, N$_2$ gas *(High Purity)*, filter paper, silica gel, MO indicator, PP indicator, distilled water, aquaLight LLT scintillator *(Hidex)*,marble originated from marble karst, Maros Regency as background, and coral.

Equipment was used in this research include sampling device SCUBA *(Self Contained Underwater Breathing Apparatus)*, shovel, crowbar, and cold box. Preparation equipment were series of absorption devices, oven, gloves, mortar, balance, hammer, and glass tools commonly used in laboratories. $\beta$ radiation counting devices *(LSC Hidex 300 SL)*.

2.1.3. Physical and chemical cleaning
Physical cleaning, coral was cleaned, brushed several times, rinsed with distilled water and dried. Then, determine the initial weight of coral. Chemical cleaning, sampled was immersed with mixture H$_2$O$_2$ 30 % and KOH 1N with ratio 50:50 and ultrasonic for ± 15 minutes. Coral separated from cleaning solution and rinsed several times with distilled water. Then, immersed with H$_2$O$_2$ 30% and HClO$_4$ 1% for 30-120 seconds. Then, immersed with HCl 6 N for 15-60 seconds and rinsed with distilled water. The sample was dried in oven at 60 °C. Coral was reweighed to obtain percentage reduction weight during chemical cleaning process [10].

2.1.4. CO$_2$ absorption
Coral sample was weighed with variation mass from 5 to 50 grams and put into round bottom flask. Sample was added HCl 10% and released CO$_2$ gas. CO$_2$ gas passed through acid absorber *(AgNO$_3$)*, water absorber and CO$_2$ Absorber *(KOH)*. The reaction occurs [11,12]:

\[
\text{CaCO}_3(s) + \text{HCl}(l) \rightarrow \text{CaCl}_2(s) + \text{CO}_2(g) + \text{H}_2\text{O(aq)}
\]

\[
\text{CO}_2(g) + 2 \text{KOH(aq)} \rightarrow \text{K}_2\text{CO}_3(aq) + \text{H}_2\text{O(aq)}
\]

After process completed, N$_2$ gas *(high purity)* was flowed absorption device with CO$_2$ gas produced.

2.1.5. Determine total carbon
Total carbon was calculated based on the difference between the first and second stages of titration. The first stage, sample was added MO indicator and titrated with HCl 5 M. The second stage, sample was added BaCl$_2$ until saturation, then precipitate was filtered. Solution was added PP indicator and titrated with HCl 5 M [11].

2.1.6. Measurement of $^{14}$C activity in coral samples
Sample 8 mL was mixed with Scintillator AquaLight LLT 12 mL and put in vial 20 mL. Then, analyzed with LSC Hidex 300 SL for 2-240 minutes. Marble as background [13,14].
3. Result and discussion

3.1. Physical and chemical cleaning

Corals are cleaned physically and chemically. This was done to eliminate modern carbon contamination originating from surface coral (endolytic activity), which could influence $^{14}$C activity value [10].

3.2. CO$_2$ absorption

The amount of gas absorbed by the KOH can be determined by determining total carbon through the titration process to obtain the following Table 1:

**Table 1.** The values of absorption capacity, absorption efficiency and total carbon mass

| Absorption Capacity | Absorption Efficiency | Total carbon mass   |
|---------------------|-----------------------|---------------------|
| $0.2187 \text{ mol CO}_2/\text{mol OH}$ | $21.87\%$             | $0.168 \text{ gram}$ |

3.3. Measurement of $^{14}$C activity

Enumerator Liquid scintillation has the role of detecting particle emissions of $\beta$ from $^{14}$C contained in sample. LSC output from analysis process were DPM for estimating nuclear disintegrations per minute, total count or total count per minute (CPM) and TDCR for measuring quench or efficiency of enumeration [15].

Sample was added with cocktail containing scintillator and scintillator solvent. Function adding cocktails is to convert decay energy from radionuclide samples becoming photons of light, then forwarded to PMT [16,17]. Measurement $^{14}$C activity in coral was carried out in two stages. The first stage, determined optimum time of counts. The second stage, determined the average value of counts at optimum time.

![Figure 1. Optimum Time of Counts](image_url)

Based on Figure 1, the value of enumeration at the beginning of time instability. Enumeration began to stabilize in the 15th minute (optimum time), with DPM value 504.510 and TDCR value 0.669. There are several factors that can affect enumeration instability, a). Instability between carbonate solution and scintillator, b). Quench effect (chemical quench and color quench). Chemical quench occurs during transfer energy from solvent to scintillator. Chemical species can capture or take $\pi$ aromatic solvent thus reducing availability $\pi$ for efficiency transfer energy [16]. The second stage,
sample was counted repeatedly during optimum time, it was found that the average CPM, DPM, and TDCR were 285.271; 433.597 and 0.657.

3.4. Determine specific activity of $^{14}$C
Specific activity of $^{14}$C was used for determining coral age. Specific activity was obtained from difference DPM sample and DPM background divided by total carbon. Marble used as background standard [18,19]. The specific activity was obtained 15.262 DPM/gC. Compared to specific activities between sample and modern carbon [20], it was found that the coral analysed was still relatively modern.

4. Conclusions
In this research concluded that specific activity of $^{14}$C in coral sample (15.262 DPM/gC). So, the coral age was obtained relatively modern.

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