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# DETERMINATION OF KOH EFFICIENCY AS CARBOSORB IN DETERMINING AGE OF CORAL REEF SAMPLES IN SELAYAR ISLANDS THROUGH LSC METHOD (LIQUID SCINTILLATION COUNTING)

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## ABSTRACT

Research using the method of LSC (Liquid Scintillation Carbon) in determining the age of coral reefs in the Selayar islands has been carried out. The samples of coral reefs were taken between the tides. Sample preparation was carried out physically and chemically using an acid-base mixture solution: NaOH, $H_2O_2$, $HClO_4$ and HCl produced coral samples that looked whiter with weight reduction of up to 1.6%. Carbonate is separated into CO2 by reaction with 10% HCl and absorption with KOH 1 M as $K_2CO_3$. Total carbon is determined by the titration method which produces 0.0542 g of total carbon sample. Specific activity of $^{14}C$ measured by enumeration with LSC is 12.0542 DPM/gC. The age of coral reef samples obtained from sample specific activity data was 1971,728 years

**Keywords**: Carbosorb, Selayar Islands, Liquid Scintillation Counting, Coral Reef

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## 1. INTRODUCTION

The story of the maritime empowerment of the kingdoms of Majapahit and Gowa or the resilience of maritime sailors with sandeq boats that can cross the ocean cannot be used as a backing in tracking and projecting the condition of Indonesia in the future. Understanding the reality of the development of contemporary science, especially in the maritime field, has become a starting point for how historical knowledge is empowered. Every reality will clash with the conditions in their respective times, nothing is truly static, the cause is eternal is only a change [1].

Indonesia has a vast sea area with an area of more than 75% reaching 5.8 million $km^2$. Indonesia have marine biodiversity, including the content of coral reefs reaching more than 400 species [2].

Coral reefs are one of the oldest ecosystems on earth. According to [3], coral reef ecosystems have experienced tide for approximately 5000 years. In fact, geological studies prove that 75% of coral species have existed since the Pleistocene era [4]. Modern / fossil massive coral reefs are composed of deposits of calcium carbonate ($CaCO_3$) which can grow from a scale of millimeters to centimeters per year.

Coral reefs contain radioactive elements which are measured by carbon element isotopes, namely carbon-14 ($^{14}C$). Element $^{14}C$ emits beta particles (β) and will decay half in 5,730 years to become

stable $^{14}N$. Carbon-14 persists in materials such as trees and corals that are tens of thousands of years old. This phenomenon is useful in radiocarbon dating [5].

The radiocarbon dating method is used to determine the age of various objects. Measurements are based on the results of the calculation of $^{14}C$ activity or the ratio of the number of radioactive isotopes 14C that exist on the object using the standard of a radioactive known number of isotopes [6]. Furthermore, [7] states that the radiocarbon dating method was chosen based on the assumption that the proportion of cosmogenic $^{14}C$ radionuclides (radioactive isotopes) in the body of living things is always constant because continuous input, expenditure or decay. After living things do not show life activity, $^{14}C$ inclusion does not occur again. However, because radioactivity $^{14}C$, the radionuclide decays so that the amount of $^{14}C$ will decrease exponentially by time. Determination of the remaining $^{14}C$ activity contained by coral reef samples will correlate with the age calculated from the example no show life activities. This age can be calculated using the decay half-life of the $^{14}C$ isotope.

Liquid Scintillation Counting (LSC) is popular in radiocarbon dating. According to [8], LSC has a very high detection efficiency. The geometry of the measurement achieves enumeration efficiency of around 99.99%. The other advantages of this method are ease of sample preparation, data processing, and the ability of spectrometers to synthesize and analyze different nuclides simultaneously [9].

There are two methods pre-treatment radiocarbon analysis with LSC, benzene synthesis and $CO_2$ absorption [10]. [11], stated that the method of $CO_2$ absorption in the last two decades has been widely used to measure $^{14}C$ in various samples such as trees, seawater, sediments and coral reefs.

This research, $CO_2$ absorption method was used because it was easier, more economical and simpler than other methods. To absorb $CO_2$, a solution that has the ability as an absorbent is used, namely KOH. Use KOH as adsorbent is based on the ability of $CO_2$ adsorption efficiency and enumeration efficiency on LSC instruments.

## 2. MATERIAL AND METHOD

### Materials

The materials used in this research were: HCl 6 N, NaOH 1 M, KOH 1 M, $H_2O_2$ 30%, $BaC_{l2}$ 10%, Methyl Orange (MO), $HClO_4$ 1%, Phenol Thalein (PP), Aqualight LLT, filter paper, aquades and coral reefs from the Selayar Islands. Preparation equipment in the form of separating funnel, hotplate, ruler, statif, mortal, gloves, oven, hammer and glass tools commonly used in the laboratory as well as β radiation counter from carbon-14 samples, namely LSC Hidex 300 SL.

### Sampling

Sampling was carried out in selayar islands, South Sulawesi. Samples of coral reefs were taken in tides.

### Phisical and Chemical Cleaning

Cleaning is initial stage in sample preparation before carbonate separation in the sample [12].

Physical cleaning, samples of coral reefs were washed with water and brushed several times until they clean. After

physical cleaning, coral reef is placed in a container and dried. Then the coral reefs are cut into small pieces and then weighed to determine the initial weight before chemical cleaning [12].

Chemical cleaning begins with immersion of coral samples into a mixture of 50/50 $H_2O_2$ 30% and 1 N NaOH in a 100 mL beaker and ultrasonic for ± 10 minutes. Then solution is separated from the sample, brushed and rinsed again with distilled water to remove black stains which are in the narrowest blemish of the sample. Furthermore, the coral reef samples were soaked back in a mixture of 50/50 $H_2O_2$ 30% and $HClO_4$ 1 N in a 100 mL beaker for 30 seconds- 2 minutes. The last process in chemical cleaning is a sample of coral reefs soaked in 10 mL of HCl 6 N solution for 15-60 seconds and rinsing again with distilled water repeatedly. Coral reef were dried in oven at 105 $^0$C to dry and weighed again to find out percentage of lost weight during the chemical cleaning process [12].

## Separation of Carbonate as $CO_2$

$CO_2$ analysis in coral reef was carried out as $CO_2$ gas by KOH. The stages in separating carbonates as $CO_2$ samples were carried out by adding HCl 10% to 10 grams of sample powder of coral reefs placed in a round bottom flask until HCl 10% was used to react with calcium carbonate in 10 grams of sample. The reactions that occur between calcium carbonate and phosphoric acid are as follows:

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + CO_2 + H_2O$$

$CO_2$ produced is flowed into the KOH 1 N absorbent solution to produce $K_2CO_3$ as in the following reaction:

$$2KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$$

The scheme of the series of $CO_2$ absorption samples of coral reefs can be seen in Figure 1.

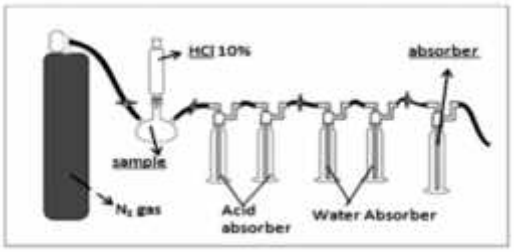


**Figure 1**. Design of a carbonate separation tool

## Determination of Total Carbon

The total carbon in sample solution (dissolved $K_2CO_3$) can be calculated from the carbonate concentration obtained from the titration of the sample solution with HCl. 10 mL of sample solution inserted into erlenmeyer 50 mL, added methyl orange indicator and titrated with HCl 5 N. Then sample solution 10 mL put into Erlenmeyer 50 mL and added with $BaCl_2$ 10% saturated. Then the solution is filtered and the filtrate obtained is put into Erlenmeyer 50 mL, added Phenol Pthalein indicator and titrated with HCl 5 M.

## Measurement $^{14}$C Activity with LSC Hidex 300 SL

The activity of $^{14}$C in sample is expressed in unit disintegration per minute (DPM) of $^{1}$4C. The results of sample enumeration with Liquid Scintillation Counter Hidex 300 SL produced data in CPM units (counts per minute) and TDCR

(Triple To Double Coincidence Ratio) or known as efficiency of enumeration (E).

$$E = \frac{Cpm}{Dpm} \times 100\%$$

Statistical calculation of radioactive sample using LSC is natural decay calculation on radioactive elements that emit pure beta particles at any time or random decay.

Determination of $^{14}C$ activity in coral reef can be determined through enumerating samples with LSC Hidex 300 SL. Mixture sample 8 mL and aqualight scintillator 12 mL in vial 20 mL. Then, analysis for 5-1440 minutes. The same procedure is done in the background as a comparison.

**Determined Age of Coral Reef**

The age of a coral reef sample can be calculated based on a comparison of specific carbon activity (15.3 ± 0.1 dpm / gr C) to sample specific activities obtained from enumeration using the radiocarbon decay equation [13]:

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

**RESULT AND DISCUSSION**

**Sampling of Coral Reef**

Sampling of coral reefs was carried out in the Selayar Islands. The selection of place for sampling coral reefs is due to its proximity to the southern part of the Spermonde Islands. Supported also by the condition of the island which is classified relatively far from human activities so that the condition of the sample of coral reefs around the island is good. The sample is a coral reef fossil which can be seen in Figure 2.

**Figure 2**. Coral Reefs from Selayar Islands

**Cleaning of Coral Reef**

Physical cleaning is done using running water and then rinsed with distilled water. This cleaning can remove mud and some stains that are attached on the surface of coral reef. Furthermore, chemical cleaning process starts from immersing the sample in a mixture (50/50) of $H_2O_2$ 30% and NaOH 1 N and is ultrasound for ± 10 minutes to remove various stains that stick. Furthermore, the samples were immersed in a mixture of acid-base (50/50) $H_2O_2$ 30% and $HClO_4$ 1% to remove the remaining brown / yellow organic stains attached to coral polyps and could not be lost in the first soaking. The use of Perklorid acid in the second immersion can dissolve 5-6% of the sample weight (Adkins, 2002). Therefore immersion is only done in about 30 seconds.

The final process in chemical cleaning is done by soaking the sample in 10 mL HCl 6 N for ± 30 seconds. This immersion is done to reduce $CO_2$ absorbents adsorbed on the surface of the sample during the washing cleaning [12].

A series of washing processes were able to eliminate impurities found on sample surface as can be found in Table 1.

**Table 1.** Difference weight of samples before and after the cleaning process.

| Before Cleaning (gram) | After Cleaning (gram) | Percentage of Sampel Reduced (%) |
|---|---|---|
| 188,433 | 185,449 | 1.6 |

## Separation of Carbonate in Samples

Coral reefs contain calcium carbonate. The carbonate separation process of coral samples was carried out by adding HCl 10% to coral samples which placed into a round bottom flask. Reaction occurs between calcium carbonate and phosphoric acid:

$$CaCO_{3(s)} + 2HCl_{(l)} \rightarrow CaCl_{2(s)} + CO_{2\,(gas)} + H_2O_{\,(l)}$$

$CO_2$ gas absorbed by the KOH solution through chemical reaction will produce dissolved $K_2CO_3$ with the following reaction:

$$2KOH_{(l)} + CO_{2(gas)} \rightarrow K_2CO_{3(l)} + H_2O_{(l)}$$

## Determination of Carbon Total in Samples

Determination of total carbon was carried out using the titration method using HCl 5 M. The titration was used to determine the carbonate concentration in 8 mL samples. The total carbon obtained from the calculation results is 0.1085 grams.

Total carbon obtained from sample solution was used in calculating $^{14}C$ specific activity expressed in units of disintegration per minute per unit of carbon mass (DPM / grC) which forms the basis for calculating the age of the sample.

## Measurement Activity $^{14}C$ Sample with LSC Hidex 300 SL

CPM decreases occur because the number of nuclei that decay during interval time decreases exponentially. Based on the results of the data in Table 5 can be observed fluctuations in the value of DPM.

Fluctuations in enumeration are caused by chemical fluorescent effects when analysis. This can be caused by the presence of oxygen or dirt in the vial container which affects the efficiency of enumeration. Increasing the count value in the 150th minute was due to the effect of phase instability between the sample solution of dissolved $K_2CO_3$ and the scintillator.

In the 90th minute the value of the $^{14}C$ activity begins to reach stability, this is indicated by the stable CPM and DPM values. Obtained CPM value 295,190, DPM 490,630 and (TDCR) 0,601 or 60,41%.

**Table 2.** Determine the optimum time for samples of the Selayar Islands using LSC HIDEX 300 SL in range 5-240 Minutes

| Time (Minute) | CPM | DPM | TDCR |
|---|---|---|---|
| 5 | 539,490 | 1200,510 | 0,449 |
| 15 | 437,060 | 757,520 | 0,576 |
| 30 | 356,500 | 675,370 | 0,527 |
| 60 | 315,390 | 550,140 | 0,573 |
| 90 | 295,190 | 490,630 | 0,601 |
| 120 | 229,170 | 449,460 | 0,511 |
| 150 | 220,710 | 493,200 | 0,547 |
| 180 | 214,910 | 384,650 | 0,558 |
| 210 | 215,080 | 380,650 | 0,565 |
| 240 | 214,480 | 381,120 | 0,564 |

Source: Data from enumeration with LSC Hidex 300 SL, February-April 2018

Phase stability also affects enumeration efficiency (TDCR). The decrease in TDCR value is caused by the effect of quenching in the sample solution, causing photons produced in emission β particles decrease. The highest $^{14}C$ of

enumeration efficiency is around 0.8 or 80% [14]. TDCR value shows the efficiency of enumeration in the 90th minute is higher than the 60 and 120 minutes so that time is used as the optimum time to sample analysis.

The optimum time obtained was used to determine the average activity value of $^{14}C$ in a coral reef sample with 10 repetition. The results of the enumeration obtained an average CPM value was 208,652, the DPM value was 373,177, and TDCR was 0,559. The average value data is used to obtain specific coral reef activities. The results of the repeat enumeration of coral reef can be seen in Table 3.

Table 3. Data from the enumeration results in determining the optimum time for samples of the Selayar Islands reefs using LSC HIDEX 300 SL devices in 10 repetitions

| Time (Minute) | CPM | DPM | TDCR |
|---|---|---|---|
| 90 | 211,590 | 378,600 | 0,558 |
| 90 | 212,760 | 379,620 | 0,561 |
| 90 | 209,930 | 368,580 | 0,569 |
| 90 | 208,750 | 373,590 | 0,558 |
| 90 | 209,020 | 376,480 | 0,555 |
| 90 | 210,170 | 380,870 | 0,551 |
| 90 | 208,490 | 372,460 | 0,559 |
| 90 | 205,660 | 367,550 | 0,559 |
| 90 | 206,260 | 371,890 | 0,554 |
| 90 | 203,890 | 362,130 | 0,563 |
| Average | 208,652 | 373,177 | 0,559 |

Source: Data from enumeration with LSC Hidex 300 SL, February-April 2018

Data the optimum background time counts range 5-240 minute are presented in Table 4.

Similar treatment is carried out on background enumeration. Scintillation solution was inserted 12 mL into the vial and added 8 mL of the solution absorbed by KOH and marble as background. Marble is chosen as background because it is considered material that not have radioactivity so that it can provide correction factor for the atmospheric cosmic rays calculated by LSC. When marble shows that there is $^{14}C$ radioactivity, it is suspected that the specific activity of $^{14}C$ from the coral reef deviates as much as $^{14}C$ specific activity on the marble. [7]. Data the optimum background time counts range 5-240 minute are presented in Table 4.

Table 4. Data from the enumeration of the determination of the optimum background time using the LSC HIDEX 300 SL device range 5-240 minutes

| Time (Minutes) | CPM | DPM | TDCR |
|---|---|---|---|
| 5 | 307,640 | 368,490 | 0,834 |
| 15 | 293,570 | 332,960 | 0,881 |
| 30 | 311,260 | 392,260 | 0,793 |
| 60 | 273,890 | 401,800 | 0,681 |
| 90 | 276,120 | 418,350 | 0,660 |
| 120 | 273,920 | 412,600 | 0,663 |
| 150 | 272,990 | 411,220 | 0,663 |
| 180 | 274,660 | 408,760 | 0,671 |
| 210 | 276,270 | 411,720 | 0,671 |
| 240 | 274,290 | 408,220 | 0,671 |

Source: Data base Determination of marble background optimum time with LSC Hidex 300 SL, September 2016

DPM value fluctuates in instability solution phase both in the physical and chemical conditions of the solution when the emulsion is formed during analysis. Optimum time for background enumeration is 90th minute, CPM is 276,120; DPM value is 418,350 and efficiency of enumeration (TDCR) is 0.660 or 66.9%. When compared with the sample DPM value, background DPM using marble has a lower DPM value, so this enumeration data can be used to correct the count of 14C activity in the

sample. The optimum time of background is used to find average value of $^{14}C$ activities with 10 repetitions. Data background in Table 5:

**Table 5**. Data on Enumeration Results at Optimum background using LSC HIDEX 300 SL in 10 repetitions

| Time (Minutes) | CPM | DPM | TDCR |
|---|---|---|---|
| 90 | 172,920 | 361,410 | 0,478 |
| 90 | 169,490 | 354,920 | 0,477 |
| 90 | 171,660 | 358,780 | 0,478 |
| 90 | 171,590 | 360,110 | 0,476 |
| 90 | 171,560 | 365,230 | 0,469 |
| 90 | 173,320 | 372,120 | 0,465 |
| 90 | 174,310 | 369,620 | 0,471 |
| 90 | 173,040 | 362,500 | 0,477 |
| 90 | 174,110 | 367,680 | 0,473 |
| 90 | 174,200 | 364,610 | 0,477 |
| Average | 172,62 | 363,698 | 0,474 |

Source: Data from enumeration with LSC Hidex 300 SL, April 2018

Average from background enumeration are used to obtain the $^{14}C$ disintegration per minute (DPM) in the sample.

**Determine Specivic Activity (As)**

Based on the calculation, specific activity from sample is 12.0541 lower than value of $^{14}C$ atmosphere 15.3 [14]. This shows that there has been decay in the nucleus of the carbon atom in the sample when the sample died. The average specific activity of $^{14}C$ obtained shows the disintegration per minute (DPM).

**Table 6.** Calculation Specific Activities (As) of Coral Reefs from Selayar Islands

| DPMs | DPMb | DPMs-DPMb (DPMk) | DPMk/g C ($A_S$) |
|---|---|---|---|
| 372,460 | 372,120 | 0,34 | 6,27306273 |
| 368,580 | 367,680 | 0,9 | 16,6051661 |
| 362,130 | 361,410 | 0,72 | 13,2841328 |
| Average Specific Activity (As) | | | 12,0541205 |

**Calculation Age of Coral Reefs**

The age of coral reef is determined by comparison with $^{14}C$ radioactivity from living sample or standard (Ao) and Radioactivity $^{14}C$ in the sample (At).

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

where

t = Sample age

$t_{1/2}$ = half-live radiocarbon (5730 40 years)

At = Isotop activity of sample (DPM)

Ao = Isotop activity of standard (15,3 ± 0,1)

ln2 = 0,693

From equation, it is used to calculate the age of the sample coral reefs from Selayar islands through calculations. The results obtained are presented in the following Table 7:

**Table 7.** Age Calculation for Coral Reef samples

| Sample | Age |
|---|---|
| Coral reefs | 1971,728 years |

## 4. CONCLUSIONS

Based on the results, analysis samples (coral reefs) of Selayar islands with LSC (Liquid Scintillation Counting) method, can be concluded:

1. The efficiency of KOH as a carbosorb is 58.99%.
2. The Age of the coral reefs in Selayar islands is 1971,728 years.

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