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UTILIZATION OF ETHANOLAMINE AS CARBON DIOXIDE ABSORBER FOR ESTIMATING OF CORAL AGE FROM LANGKAI ISLAND VIA LSC (*Liquid Scintillation Counting*) METHOD

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ABSTRACT

Utilization of ethanolamine as carbon dioxide absober for estimating of coral age from langkai island via LSC (Liquid Scintillation Counting) method has been done. Focus is to analyze coral reefs taken from Langkai island surface which is relatively far from the influence of human activities. Chemical preparation was carried out by using a mixture of NaOH with H_2O_2 30% followed by a mixture of $HClO_4$ with H_2O_2 30%, and finally with HCl solution to produce a clean sample with 8.6% weight reduction. Carbonate matrix samples as CO_2 is produced by reaction with HCl 10% and absorbed by ethanolamine solution 30% as carbamate complex. The total carbon in the sample solution is 4.542 grams obtained through decreased method after and before absorbtion process. Total carbon in 8 mL sample is 0.2477 grams. Radiocarbon dating method based on the measurement of the specific activity of the samples acquired from the result of LSC (Liquid Scintilation Counter) Hidex 300 SL counting. Age of coral reefs was counted from specific activities data and average activities of modern carbon by using radioisotope decay rate formula. The spesific activities of ^{14}C in coral reefs from Langkai island is 14.55 ± 1.1 dpm/gC. Finally the age of coral reefs was estimated 415.01 ± 91.08 years.

Keywords: Coral reefs, LSC (Liquid Scintilation Counting), radiocarbon dating, Spermonde islands.

INTRODUCTION

Marine ecosystem is the largest aquatic systems on the planet with the physical and chemical environment complete. Sea area has the largest wealth and biodiversities in the world (Aulia, 2012).

Indonesia is one of country that has a very wide sea area, with an area of ocean waters more than 75% to reach 5.8 million square kilometers (Manapa, 2011). According Boekschoten and Best (1988), one of the richest sources of marine biodiversity Indonesia is Spermonde islands. Spermonde islands reefs has area approximately 60,000 ha (Rauf and Joseph, 2004).

Estimating the age of the coral reefs in the waters has enormous benefits in studying the geography of origin of marine coral samples, for example to trace and study the formation of a rock formation on a beach and also can be used to estimate the apparent radiocarbon age of sea water (Yuliati and Akhadi, 2005).

Age reefs can be estimated by radiocarbon dating method. Radiocarbon dating method is a method that is based on the calculation of the ^{14}C activity was contained in a sample. The value obtained from the calculation of ^{14}C activity which is converted to be age when compared to the standard (Pratikno et al, 2009).

Therefore, for the purposes of counting the radiation emitted by ^{14}C requires special counter with a very low background radiation so that the results would be obtained with high accuracy. Counter who has the ability namely LSC (Liquid scintillation Counter) with approximately 99.99% counting efficiency (Tjahaja and Mutiah, 2000).

Absorption of sample pretreatment method is most often applied in estimating age of coral reefs through measurements of ^{14}C activity by using the LSC (Liquid Scintillation Counter). Carbon dioxide absorption method has a high effectiveness, good product quality and relatively easy and cheap (Naibaho, 2012).

Amine compound is the most widely used as solvent in CO_2 absorption process, which is as an absorber for the amine compound can react with CO_2 to form complex compounds (carbamate ions) with a weak chemical bonds. Amine compound can be regarded as an efficient solvent in the operational CO_2 absorption process (Wang et al, 2004). According to Yu et al (1985), one of the amine compound which has a good ability to absorb CO_2, the absorption rate is fast and easy to be regenerated is ethanolamine.

Under these condition, research by using ethanolamine as a CO_2 absorber in age estimating of coral reefs in the archipelago Spermonde through LSC method (Liquid scintillation Counting) has been done.

MATERIALS 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.

Washing Coral Reef

Washing is done in two stages: physical washing and chemical washing.

Samples of coral reefs washed in running water with brushed several times, followed by rinsing with distilled water until clean. After the physical washing, samples were placed in a container of coral reefs and dried. Then reef cut into small pieces and weighed to determine the initial weight before washing chemicals (Adkins et al, 2002).

Chemical leaching begins with soaking samples of coral reefs in a 50/50 mixture of H_2O_2 30% and 1 N NaOH in 100 mL beaker and was ultrasonicated for ± 10 minutes. After that, the sample is separated from the wash solution and rinsed with distilled water until the foam disappears. Furthermore, samples of coral reefs soaked in a 50/50 mixture of H_2O_2 30% and 1 N $HClO_4$ in a 100 mL beaker for 30 seconds-2 minutes. Furthermore, the sample is separated from the wash solution and rinsed with distilled water ± 3 times. The last process in the chemical leaching is sampled coral reefs immersed in 10 mL

of HCl 10% for 15-60 seconds. Then the samples were dried in an oven coral reefs at 105^0C temperature until dry and weighed again to determine the sample weight lost during the washing process chemistry (Adkins et al, 2002).

The sample pretreatment

Each piece of dry coral reefs that have weighed wet weight crushed into powder with a mortar until smooth. For the preparation of the analysis of the content of ^{14}C in the sample, prepared a series of tools that CO_2 absorption associated with N_2 gas cylinder. Furthermore, the round-bottom flask put 50 grams of sample.

After that, a series of flowing N_2 gas absorption apparatus to achieve the absorption column which contains ethanolamine then the valve of the gas cylinder is closed. Furthermore, the funnel valve is opened so that HCl 10% can react with the sample to calcium carbonate contained in the sauce completely reacted. In the reaction of CO_2 will be produced through the following reaction:

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

CO_2 gas generated in the circuit flows through the impinger absorption apparatus that each - each containing a filter paper soaked in $AgNO_3$ and Silica gel. At the end of the series, the samples collected in the absorption column.

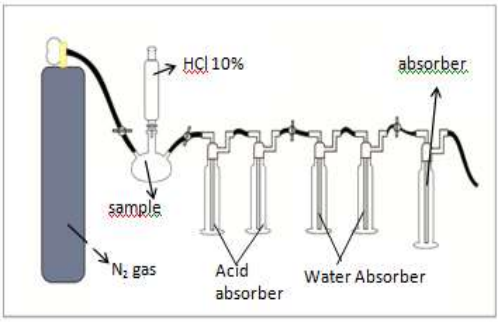

Figure 1. Design Tool carbonate as CO_2 separation of samples of coral reefs

During the absorption process, there will be heat until it reaches a temperature of 50^oC. After a saturated aqueous solution reached temperature decreases to return to room temperature and changes color to yellow. After the absorption process is complete, as many as 8 mL pipette solution into 20 mL vial bottle was then added 12 mL Aqualight LLT. Scheme absorbasi tool CO_2 in the samples of coral reefs can be seen in Figure 1tersebut.

Measurement of ^{14}C activity in the Coral Reef

Carbon-14 activity in the sample is expressed in units of activity, which is the decay every minute (DPM) of carbon-14. Sample enumeration with liquid scintillation counter Hidex 300 SL generate data in units of CPM (chopped per minute) and TDCR (Triple To Double Coincidance Ratio) or known as counting efficiency (E).

$$E = \frac{Cpm}{Dpm} \text{x } 100\%$$

Statistical calculations using the radioactive sample enumeration LSC is very natural decay calculations on radioactive element that emits pure beta particles every time (random decay).

Determination of the activity of carbon-14 in samples of coral reefs can be seen through the LSC sample pencachan Hidex 300 SL. Homogeneous mixture of sample and scintillator enumerated by the LSC Hidex 300 SL at the time of enumeration 1-1440 minutes. The same thing is done in the background enumeration by filling 12 ml scintillator into 20 mL vials and counted by LSC Hidex 300 SL.

Age Estimating of Coral Reefs

Age samples of coral reefs can be calculated based on the ratio of the specific activity of modern carbon (15.3 ± 0.1 bpm / GRC) on the specific activity of the sample obtained from the enumeration by using radiocarbon decay rate equation:

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

A = Radioactivity of 14C isotope in the sample

Ao = Radioactivity isotope 14C at the time of the plant or animal life (15.3 ± 0.1) DPM (Libby, 1960)

Λ = Constant of radioactive decay; $t_{1/2} = 1 / \lambda$

$t_{1/2}$ = Half-life = 5730 ± 40 years

ln2 = 0.693

RESULTS AND DISCUSSION

Intake Coral Reef

Samples obtained from the location of coral reefs located on the island Langkai. Langkai Island is one part of a group of islands Spermonde, South Sulawesi. Sampling was carried out in the coral reefs of the island because the condition is relatively quiet and relatively preserved from human activity so that the coral reefs around the island are generally still very good. Location Langkai island is 36 km from the city of Makassar. The sample used coral reefs can be seen in Figure 2 below.

Figure 2. Sample of coral reef origin Langkai island archipelago Spermonde.

Location sampling is done around the coral reef island archipelago Langkai Spermonde at coordinates S: 05^0 01 '47.055 "E: 119 ^{0} 05' 50, 272 " with a depth of 4-5 meters from the sea surface with the aid of SCUBA divers. Samples of coral reefs comes from the island will be determined Langkai age through radiocarbon dating method LSC.

Radiocarbon dating method is selected based on the assumption that the proportion of cosmogenic radionuclides ^{14}C in the living body is always constant because the income, expenditure and decay takes place continuously. After living creatures do not show the activity of life, income ^{14}C does not happen again. However, due to the nature of the radioactive ^{14}C, the radionuclide decays so that the amount of ^{14}C decreases exponentially with time. By determining residual ^{14}C activity contained by samples of coral reefs will be correlated with age starting from the sample no longer shows the activity of life. Age can be calculated with the use of a half-life decay of the isotope ^{14}C.

There are several series of the process that must be done to determine the activity of ^{14}C in samples of coral reefs through the method of LSC. The process includes the step of sample preparation includes washing the sample, both physically and chemically, as well as absorption of CO_2 from the sample by using an appropriate absorber and ^{14}C activity measurements to determine the age of a sample of coral reefs.

Coral Reef Washing

Sample preparation is very important to note that age obtained through the method of LSC (liquid scintillation Counting) has high efficiency. Washing

the sample is part of the sample preparation. In general, the goal is to separate the sample leaching carbon of all organic and inorganic impurities so that the sample is free of carbon originating from impurities that result from the activities of pure chopped ^{14}C derived from the sample.

Washing the sample consists of two phases, namely physical and chemical leaching. Physical washing begins by using flowing water is used to remove impurities that are easily lost as the ground. The next stage is the chemical leaching, preceded by soaking samples of coral reefs to a solution of H_2O_2 30% and NaOH 1 N (50/50) in a 100 mL beaker was placed in an ultrasonic tool for ± 10 minutes. The use of ultrasound to eliminate stains attached to the narrowest blemish coral reefs through the provision of vibrations to the base and walls of the sample container during the soaking process takes place.

Furthermore, washing with a solution of H_2O_2 30% and 1 N $HClO_4$ in a 100 mL beaker for 2 minutes intended to oxidize the impurities other sources that have not been lost and also removes organic dye brown / yellow attached to the coral polyps to be pure white . At the time of immersion with $HClO_4$ only done about 30 seconds to 2 minutes because at the time range $HClO_4$ capable of dissolving 5-6% by weight of the sample (Adkins, 2002).

Final washing using HCl 6 N which serves to reduce the CO_2 absorbent modern adsorbed on the surface of the sample during the washing process. The results of this activity is not much different from the results of deep-sea coral sample cleanup conducted by Adkins et al, (2002). In addition, leaching with acid adsorbed able to eliminate secondary carbonate accumulated during sample storage. Washing with HCl 6 N was conducted submarine aims for 15-60 seconds natural contaminants that accumulate over coral reefs in contact with air and the surrounding environment.

Loss of impurities and carbon source during the washing known by weighing the dry weight of the sample reef before laundering is 276.505 grams and impurities are lost by 8.62% as can be seen in Table 1. Difference in weight of the two samples is the number of sample weight lost during washing. Sample weight lost is not much different from the one described by Adkinds et al (2002) that the process of washing the sample with chemical compounds as above can eliminate the weight of the samples ranged 5-10% of the previous weight.

Table 1. Data comparison weight Langkai island archipelago of coral reefs Spermonde before and after the washing process.

Coral Reefs	Before Washing	After Washing
Sample Weight (g)	276,505	252,653

The sample pretreatment

The main constituent is a carbonate reef. Carbonate contained in the coral reefs can be separated by treatment with HCl 10% in 40 grams of powder samples in a round bottom flask. The sample used in the form of a fine powder obtained by grinding using a mortar. The form of the resulting sample contact area between HCl 10% with the sample becomes more widespread and the reaction can take place quickly. When samples of coral reefs

reacted with HCl 10% will produce CO_2 gas.

The next process is the CO_2 gas flow through the impinger tubes containing filter paper that had drops of $AgNO_3$, intended to absorb the excess acid produced during the reaction between CaCO3 and HCl 10% occurs, while the silica gel in the next impinger tube serves to absorb excess water.

In the absorption column, the CO_2 will be absorbed by ethanolamine. CO_2 absorbed gas will react with ethanolamine produce carbamate compounds. In this process, not all the CO_2 gas is passed into a solution of ethanolamine capable captured characterized by the presence of CO_2 gas bubbles through the surface of the absorber solution. The reaction is as follows:

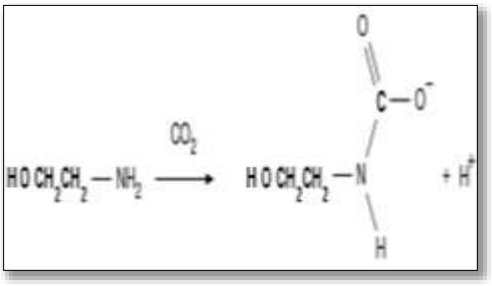

Figure 3. Ethanolamine and carbon dioxide reaction

The reaction of ethanolamine and carbon dioxide. The reaction between the ethanolamine solution with CO_2 gas causes the heterogenous reaction. Carbamate compounds formed will be measured by LSC (Liquid scintillation Counting) which aims to determine the amount of ^{14}C activity.

To determine the amount of CO_2 that is absorbed in 8 mL absorber, can be determined by determining the total carbon. The amount of CO_2 that is successfully absorbed by 4.542 g while the CO_2 contained in the sample of 8.333 g. The efficiency of absorption of CO_2 by ethanolamine ie 51.19%. The amount of CO_2 that is not absorbed as much as 48.81% has no effect because that is used in the calculation of the specific activity is the total carbon in 8 mL of sample. Measurement of ^{14}C activity in the Coral Reef Enumerators liquid scintillation have specific privileges compared to other count tool, which has a system software MikroWin 2000 which is able to provide absolute chopped results. Tools LSC (Liquid Scintillation counter) Hidex 300 SL was instrumental in detecting β particle emission of ^{14}C in the sample.

β -emitting radioisotopes in this enumeration method works on the basis of the interaction of a solution of organic compounds that can berfluorisensi when interacting with radiation (Salam, 1993). In this case, the carbamate compounds formed from the absorption by ethanolamine to CO_2. If you interact with the radiation will berfluorisensi carbamate compounds.

In the enumeration process takes 8 mL of sample and 12 ml of scintillator were mixed into a 20 mL vial. The process of mixing the sample solution and the scintillator, avoiding contamination by free air containing CO_2-free. Enumeration with LSC Hidex 300 SL done in a span of 1-240 minutes. Analysis of samples by this method involves the scintillator solution that will collide with solvent molecules to excited. At this point the energy will be released in the form of photons or light flicker. Flicker of light has a specific wavelength and when it reaches the layer fotokatode in PMT (Photo Multiplier Tube) will release electrons from the layer. These electrons will be multiplied by dinode-dinode contained in PMT and in

the end these electrons will be collected on anodenya in the form of electrical pulses.

Sample enumeration is done in two stages, namely, the step of determining the optimum time of enumeration and the step of determining the average value of the sample count values at the optimum time. Sample counting is done in two stages, determining the counting optimum time and average value of the sample counting at the optimum time. The results of determining the counting optimum time of ^{14}C activity contained in the sample can be seen in Figure 3.

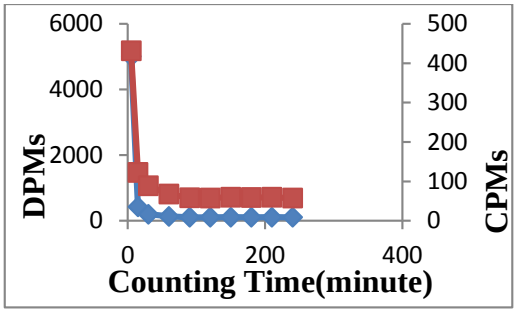

Figure 3. Graph relation DPM and CPM sample reefs vs time

Table 1 showed a counting optimum time, 150 minutes. The results of counting at optimum time can be seen in Table 1.

Table 1. Data from sample counting at optimum time

No.	Sample: Shredded Time (minutes)	CPM	DPM	TDCR
1.	150	53,310	107,440	0,496
2.	150	50,350	95,360	0,528
3.	150	51,580	96,550	0,534
4.	150	51,020	99,350	0,513
5.	150	50,070	92,110	0,543
6.	150	51,150	98,150	0,521
7.	150	49,920	93,310	0,534
Average		51,057	97,467	0,524

In this study, the background used is marble. When the marble indicates the persistence of the radioactivity of ^{14}C then allegedly ^{14}C specific activity of coral reef diverged by the specific activity of ^{14}C in the marble. The results of background counting to determine the optimum time was shown in figure 4.

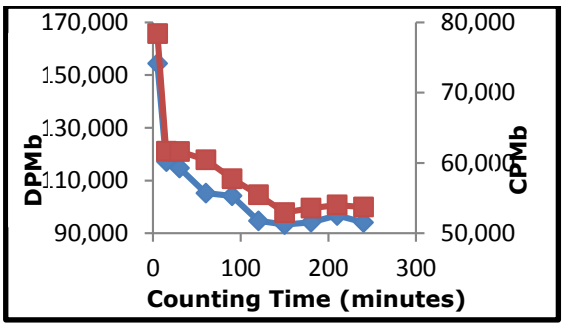

Figure 4. Graph relation DPM and CPM sample reefs vs time

These results are then used to determine ^{14}C activity in background by using optimum shredded time, 150 minutes, which can be seen in Table 2.

Table 2. Data of ^{14}C activity in background by using optimum shredded time

Background				
No.	**Shredded Time (minutes)**	**CPM**	**DPM**	**TDCR**
1.	150	54,720	98,880	0,553
2.	150	53,380	93,220	0,570
3.	150	52,940	91,790	0,576
4.	150	53,550	93,050	0,575
5.	150	52,940	93,320	0,567
6.	150	53,360	93,090	0,573
7.	150	53,540	93,290	0,573
Average		53,490	93,806	0,570

The results of ^{14}C activity measurements with LSC Hidex 300 SL in the form of Count Per Minute (CPM), which indicates the amount of β particles produced from ^{14}C in the sample reef every minute, and the value of Disintegration Per Minute (DPM), which indicates the amount of ^{14}C atoms that decay in sampled every minute.

Estimating the age of the sample was based on ^{14}C specific activity in the sample. Age of coral reefs by using ethanolamine as the absorber in the absorption process is 415.01 ± 91.08 years.

The results of the determination of the age of samples of coral reefs through the liquid scintillation method to measure the activity of ^{14}C provides the results of the sample aged 415.01 ± 91.08 years.

If the terms of the results of research conducted Buddemeier and Kinzie (1976) that the growth rate of coral reefs are classified as maximum growth ranges from 10-12 mm / year, then the age of coral reefs have been obtained in accordance with the results of research Buddemeier and Kinzie because the sample in this study was taken at a depth of 4-5 m mean age of the coral reefs of the island should Langkai 333.33 to 500 years for the growth of 10-12 mm / year.In general, the average annual growth rate of coral reefs in the maritime Spermonde it ranged from 9.9 to 11.1 mm / year with samples derived from Samalona island, islands and islets Bone Stem-Lae Lae (Rani et al, 2004). Age reef island Langkai taken at a depth of 4-5 m ranged from 360.4 to 505.1 years if it is based on an average annual growth rate of coral reef islands Spermonde above.

Jauhari (2013) also examined the coral reefs in the island archipelago Lanjukang Spermonde based on measurements of 14C activity by the method of LSC (liquid scintillation Counting). From the study of coral reefs from the island of measurement results obtained Lanjukang age 669, 484 ± 20 years. If the count is in the range of 649.484 to 669.484 years of age.

Lanjukang Island 5.5 miles from the island Langkai, mean age of the coral reefs

of the island is not much different.The results of the determination of the age of the sample coral reefs of the island Langkai through LSC method that has been done to give the age of the sample 415.01 ± 91.08 years. If the count is in the range of 323.93 to 506.09 years of age. Age indicates that the age obtained in accordance with the age range of the results of previous studies and not much different from the life of the coral reefs of the island Langkai.

CONCLUSION

Carbon dioxide gas is absorbed by ethanolamine 0.5041 CO_2/mol absorber. The specific activity of coral reefs 14, 55 ± 1.1 dpm/gC. Age of coral reef calculated based on the specific activity using ethanolamine is 415.01 ± 91.08 years.

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