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Age Determination of Marine Sediment in Spermonde Archipel Via Activity Measurement of ^{14}C by LSC (Liquid Scintillation Counting)

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Abstract. A research on Age Determination of Sea Sediment of Spermonde Islands through Activity Measurements of ^{14}C with LSC (*Liquid Scintillation Counting*) method has been performed. The sample of sediment was taken at the island of Lae-Lae, Spermonde Islands where it is relatively close to the influence of human activities. This study aims to determine the activity of ^{14}C in the sediment sample and calculate the age through measurement of ^{14}C specific activities of sediment sample. Preparation is done both physically and chemically by using a mixture of solution of the acid and alkaline: NaOH, H_2O_2, $HClO_4$, and HCl to produce sediment sample which was white and clean with a weight reduction of up to 5 %. Carbonate matrix sample was separated as CO_2 using 1 N KOH absorber with H_3PO_4 85 %. Carbon content of the sample solution is 1.172 g/8 mL. The ^{14}C activity of the sample was analyzed using LSC (*Liquid Scintillation Counting*) as an analysis technique. The specific activity sediment sample was 13.85g/C. The age of sediment sample calculated from the specific activity was 821,0822 year.

INTRODUCTION

Indonesia is an archipelago with vast sea area of more than 75% to reach 5.8 million km2, there are more than 17500 islands with the second longest coastline in the world after Canada, which is about 81,000 km (Murdianto 2004 in Wibowo, 2012). Lae-Lae Island is one of the coral islands formed in Spermonde Islands, Indonesia with an area of approximately 8774 m^2. Spermonde Islands is one of a cluster of islands located in the Makassar Strait. Spermonde Islands waters are shoal located in the southwest, South Sulawesi (Rashid, J.A and Ibrahim, 2013). Spermonde Islands waters are shoal located in the southwest, South Sulawesi (Rashid, J.A and Ibrahim, 2013).

The waters around the island of Lae-Lae relatively shallow, or have less depth of 7.5 meters, except at building a breakwater at the northeast side with water depths of up to 9 meters (Rashid, J.A and Ibrahim, 2013).
Lae-Lae Island first is a dike that extends from north to south along the 1 km that serves to dampen the waves coming into the port area of Makassar. However, because of the sedimentation process occurs continuously and lasts a

long time as well as the various activities around the community, so that on the north side of the dike in the accumulation of white sand which gradually getting bigger and expand to form islands (Usman, 2012).

Sediment is the result of the deposition process in the natural ingredients which are usually influenced by the transport agent and the environment, while sedimentation is a natural process of sediment deposition is influenced by transport agents such as wind, waves, currents, and the deposition environment. (Suhendar, 1979 in Anwar, 2005).

In terms of their origin, derived from marine sediments of the river that carries water supply inorganic materials (minerals) and organic compounds. The flow of water from urban areas also brings the kind of material that is derived from household waste, industrial, and transportation. These materials will be towards the sea and eventually a time will settle as sediment (Rustiah, 2002).

According to Gross (1990) in Kalay (2009) defined as the accumulation of marine sediment minerals and rock fragments mixed with crushed shells and bones of marine organisms and other particles that are formed through chemical processes that occur in the ocean. Sediments formed from material derived from the demolition of the stones, and shells of mollusks (shell), as well as the rest of the framework of marine organisms (Supriyadi, 1996).

Distribution of beach sediment is sediment movement in coastal areas caused by waves and currents. Turbulence from breaking waves, changed the basic sediment (bed load) into a suspension (suspended load). When the breaking waves and currents cause huge turbulence that can move the bottom sediments (Rifardi, 2012).

Carbon-14 (14C) is a pure beta-emitting radionuclides low energy (E_β = 0.155 MeV) with a very low specific activity (Yuliati and Akhadi, 2005). Radioisotope ^{14}C is one of the radioisotopes that are commonly used in the determination of the age of a sample containing carbon (Satria and Abidin, 2007). Sample can be either organic materials (fossils, shells, wood) and inorganic (in the form of extracts groundwater $BaCO_3$, marine sediments, and carbonate rocks) (Gupta, 1985 in Padley, 2009). To be content $^{14}_{6}C$ can be measured, the carbon in a sample of an organism that died after an interval (t) is usually converted into a gas such as carbon dioxide which is then inserted in the detector is sensitive to beta rays (Wiyatmo, 2009).

The activity of a radioactive nucleus is the number of disintegrations per second that occur in radioactive footage. Unit activity is commonly used Curie (Ci). International Commission of Physical Chemistry set 1 Curie (Ci) = 37 x 10^9 dps (disintegration per second) (Anthony, 1995). The specific activity is the activity per unit mass of material is observed (Agussalim, 2004).

Scintillation liquid (Liquid Scintillation) is a solution of fluorine compounds in organic solvents. Radioisotope sample to be measured must be in a state dissolved in this solution (Noor, 2003). Liquid scintillation enumerator is the most popular tool currently working trace trace radiation or radioisotopes, particularly in β- isotopes, such as ^3H and ^{14}C. This tool works on the basis of the interaction of organic compound solution can berflouresensi with high-energy particles produce beams flouresensi with high-energy particles produce beams flouresensi (Tjahaja and Mutia, 2000). Liquid scintillation enumerator used for chopping samples only dead and not used for chopping samples in the form of living organisms.

MATERIALS AND METHODS

TIME AND PLACE RESEARCH

This study was conducted in August-November 2013 in the Laboratory of Radiation Chemistry, Department of Chemistry, Faculty of Mathematics and Natural Sciences, Hasanuddin University.

RESEARCH TOOL

LSC (Liquid Scintillation Counting) Hidex 300, The pipe, Rope, Tape measure.

MATERIALS RESEARCH

Sediments were taken from Lae-Lae Island, Makassar, 1N NaOH, 37% HCl, 6N HCl, 30% H_2O_2, $HClO_4$ 1N, aqualite scintillator solution, distilled water, 5M HCl, H_3PO_4 85%, 1M KOH, 10% $BaCl_2$, Methyl Indicator orange (MO), Phenol Indicator Thalein (PP).

Wash Sample

Washing process is done in two stages, namely the physical and chemical leaching. Chemical leaching of sediment carried by soaking in a mixture of 30% H_2O_2 and NaOH 1N (1: 1). Ultrasonic for ± 10 minutes, then the solution is separated from the sediment sample. Sediment was rinsed with distilled water several times until clean. Sediment dipped back into the mix of 30% H_2O_2 and 1N $HClO_4$ (1: 1) for ± 30 seconds. Sediment sample was separated again from the solution (H_2O_2, and $HClO_4$) and rinsed with distilled water times. Furthermore sediment samples put in 6N HCl solution for ± 15-60 seconds and separated again from the wash solution. Sediment sample was rinsed with distilled water again. Furthermore, sediment sample was dried in an oven with a temperature of 60 ^{0}C.

Separation of Carbonate Samples Carbonate sediment derived from sediment sample separated as CO_2 by the addition of phosphoric acid (H_3PO_4) 85% in 10 grams of the sample (Figure 1). This reaction should run perfectly until the calcium carbonate actually completely reacted with phosphoric acid. Furthermore, the resulting CO_2 gas flowed into 40 mL of 1M KOH solution. CO_2 reacts with KOH produces K_2CO_3 dissolved. The equation can be seen as follows:

$$CaCO_{3\,(s)} + H_3PO_{4\,(l)} \rightarrow CaHPO_4\downarrow + CO_{2(g)} + H_2O_{(g}$$

$$2\,KOH_{(l)} + CO_{2\,(g)} \rightarrow K_2CO_{3(aq)} + H_2O_{(l)}$$

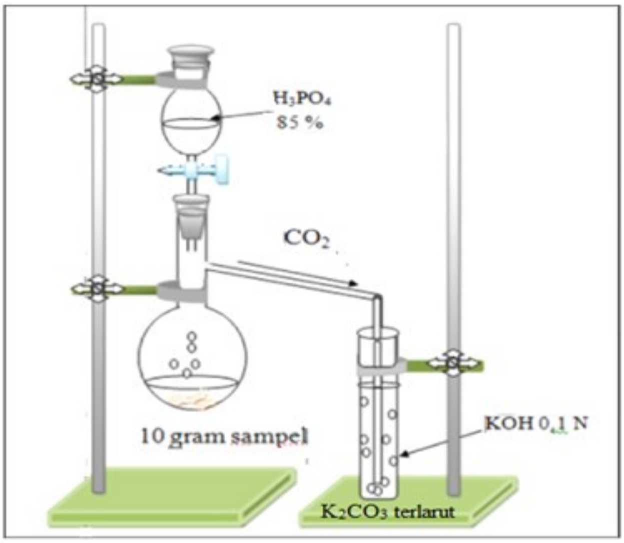

Figure 1. Schematic separation of carbonate sample.

Determination of Total Carbon

Next step is the determination of total carbon. K_2CO_3 solution was pipetted to 20 ml, further dilution with distilled water.

Titration performed with 5 M HCl and the addition of MO indicator. Titration was conducted to determine the total base KOH and K_2CO_3. Then the solution was filtered and the filtrate was re-added with 10% $BaCl_2$. The filtrate was pipetted 10 mL and added to the erlenmeyer and added with a few drops of indicator PP, then back titrated with HCl 5 M. The titration is then performed to determine the total alkaline OH.

Enumeration background / blank Sediment

Sample

Before the sediment sample enumeration, enumeration first blank solution. Blank solution was enumerated with ten repetitions. Further enumeration sample into a glass vial containing 12 mL of scintillator each with a variation of up to 24 hours. Determination of radioactive activity in sediment samples specified in units of activity CPM (Count Per Minute), DPM (Disintegration Per Minute). The relationship between the results of counts and the activity of a radioactive known as the counting efficiency is expressed in units of TDCR (Triple Double Coincidence Ratio).

$$\text{Efisiensi} = \frac{\text{Cpm}}{\text{Dpm}} \text{ x}100\% \qquad (1)$$

Calculation of Age

Calculation of age sediment carried by using the formula :

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

Specification:

A = Radioactive ^{14}C in the sample

Ao = Radioactivity of ^{14}C isotopes in living organisms 15.3 DPM / gC (Libby, 1960)

t1/2 = half-life = 5730 years

ln2 = 0.693

Results and Discussion

Sediment sampling conducted in Lae-Lae Island with a distance of 4 meters from the shoreline and is done during the day when the tide is low. Here sediment sampling sites was taken at the point and 119°23'24,6"BT 05°08'08,1"LS with a depth of 1 meter.

Activity Measurements ^{14}C Sediment Sample

Sample that have been prepared previously taken 8 mL and 12 mL scintillator was added. The results of measurements of ^{14}C activity measured on the instrument is expressed in units of Count Per Minute (CPM) which shows the amount / number of β particles produced from ^{14}C in sediment sample in every minute, and the activity of sediment sample is expressed in units Disintegration Per Minute (DPM) which shows the actual number of atoms in the ^{14}C decays sediment samples in every minute.

The relationship between the value of Disintegration Per Minute (DPM) and the value of Count Per Minute (CPM) is expressed as a form of efficiency in units of enumeration which stated Triple Double Coincidence Ratio (TDCR). Value measurement of the activity and efficiency of ^{14}C measurements was analyzed sediment sample is presented in Table 1.

Table 1. Value of activity and efficiency of counting ^{14}C in sediment sample

Time (Minutes)	**^{14}C activity of the sample is measured (CPM)**	**^{14}C counting efficiency of the samples was measured (TDCR)**
1	129,000	0,294
15	99,400	0,415
30	87,060	0,429
60	71,710	0,517
120	70,610	0,531
108	63,440	0,578
240	64,959	0,583
300	66,970	0,593
480	64,870	0,595
705	64,050	0,590
960	65,060	0,593
1080	65,290	0,599
1440	66,310	0,597

Based on Table 1, obtained by counting the activity chart and counting efficiency of ^{14}C in marine sediment sample with a range of time between 1 min - 1440 minutes each can be seen in Figure 2 and Figure 3.

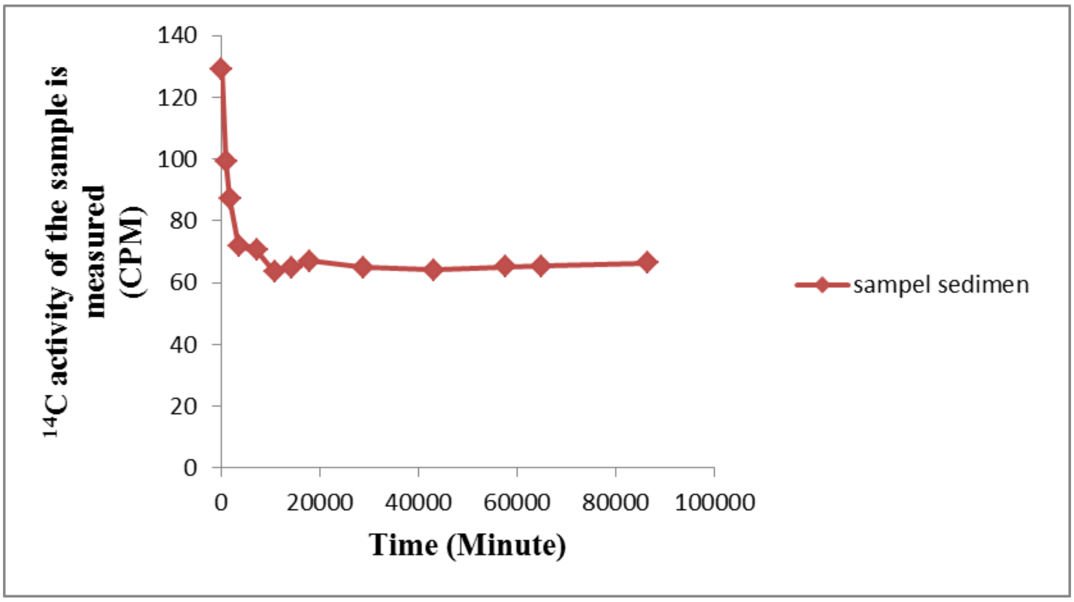

Figure 2. Activity enumeration of ^{14}C in marine sediment with a range between 1 min - 1440 minutes.

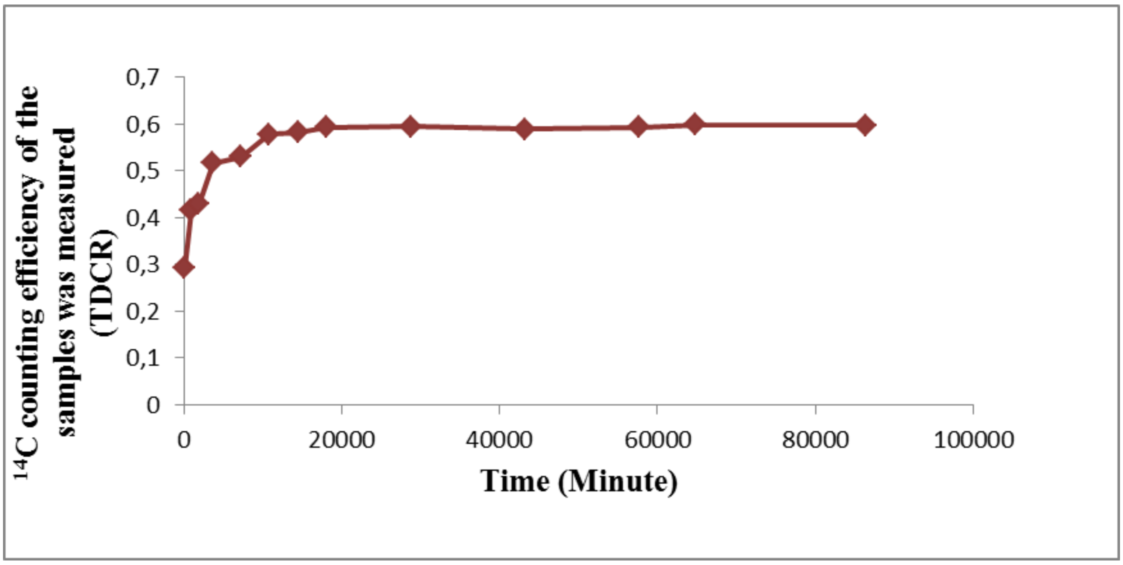

Figure 3. The efficiency of counting ^{14}C in marine sediments with a range of time between 1 mi

Based on Figure 2 and Figure 3 shows the data on sediment samples enumeration activity that began in ke- minute 1 to minute 30, appears an increase in the value of 14C activity resulting data obtained fluctuate. But the minute ^{14}C activity values ranging 60-1440 achieve stability in the value of 63440-71710 CPM. This is due to the presence of chemical glow effect (*chemiluminescence*) during the enumeration process takes place, and the phase instability of the sample solution at The start of the enumeration which caused the outage (*Quenching*). The outage (*Quenching*) also play a role in influencing the efficiency of the enumeration. Reduction of enumeration efficiency caused by the outage (*Quenching*) sourced from the oxygen or impurities in the bottle / vial were dissolved in the sample. At the time of minutes to 60-1440 enumeration value ^{14}C activity appears to begin to achieve stability in the value of 93470-97740 CPM, this is because the physical and chemical condition of the sample solution that has been relatively more stable. Counting efficiency values are expressed in units TDCR (Triple Double Coincidence Ratio) at minute 1 to minute 30 visible data generated fluctuate so much of the efficiency limit value of 0.6. But in the time of minutes 60 to minute 1440 (24 hours) appears stable again, this is clearly due to the stability of the TDCR to approach a value of about 0.6 with a value of around 63-71 CPM activity. The stability of the activity of counts / decay it is important to gain chopped exponential graphs.

Determination of Specific Activity Sediment Sample

Determination of specific activities are needed in order to further the process of determining the age of the sample. The specific activity is the basis for calculating the age of the sediment sample obtained from the activity value of Disintegration / Decay Per Minute (DPM) divided by the total sample weight of carbon mixed with scintillator. As the value of (activity / specific disintegration rate) expressed in units of DPM (disintegration / decay Per Minute) per unit mass. Specific activity data of sediment sample is shown in Table 2.

Table 2. Specific activity data of sediment samples Lae-Lae Island, Islands Spermonde

Sample	DPM	C-total (gram)	As (DPM/gr C)
Sediment	16,23	1,172	13,85 ± 4,58

The specific activity value (As) shows the actual number of ^{14}C atoms which disintegration per minute (dpm) in each gram of the element carbon.

Age Determination of Sediment Sample

Age determination of sediment samples is determined based on the specific activities that have been obtained previously. Based on the following equation can be obtained age sediment sample :

Specification:

A = Radioactive ^{14}C in the sample
Ao = Radioactivity of ^{14}C isotopes in living organisms 15.3 DPM / gC (Libby, 1960)
t1/2 = half-life = 5730 years
ln2 = 0.693

Based on the equations derived age marine sediment taken from Lae-Lae Island, Islands Spermonde at 821.0822 Year. This illustrates the length of the sedimentation process in Lae-Lae Island.

CONCLUSION

Based on the research that has been done, some conclusions can be drawn, namely:

1. The specific activity value (As) Lae-Lae Island sediment obtained 13.85 ± 4.58 Dpm/gram of carbon.

2. Age sediment contained in Lae-Lae Island based measurements of ^{14}C activity is 821.0822 Year.

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