



COMPARISON OF MEA, DEA AND TEA AS CO₂ ABSORBENTS FOR MEASUREMENT OF CARBON-14 ACTIVITY IN CORAL REEF SAMPLE FROM SPERMONDE ISLANDS

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ABSTRACT

Comparison of MEA, DEA and TEA as CO₂ absorbent to measure carbon-14 activity of coral sample has been performed. This research aimed to Determine the age of coral reef sample of Spermonde Islands by measuring the activity of carbon-14 using the method Liquid Scintillation Counting (LSC). The sample of coral reef were collected in Langkai Island. The research were conducted by following steps of sample preparation, the CO₂ absorption using the solutions of MEA, DEA and TEA. The measurement of the carbon-14 activities was performed using the Liquid Scintillation Counter (LSC) Hidex 300 SL. The research results indicated that the absorption capacities of MEA, DEA and TEA were 0.5180, 0.5903 and 0.2608 mol CO₂/mol amine respectively. The specific activity of the coral reef sample using the absorbents of MEA, DEA and TEA were 14.44, 14.59, and 14.42 DPM/g C respectively. The age of the coral reef sample, which was calculated based on the specific activity values using the absorbents of MEA, DEA and TEA were 480.15 ± 37; 390.11 ± 60 and 488.22 ± 87 years respectively.

Keywords :LSC (Liquid Scintillation Counter), Carbon-14, CO₂ Absorption, Alkanolamine, Langkai Island

INTRODUCTION

Spermonde Islands is one area of coral reefs spread evenly wide. Recently, the study of the genesis and historiography of Spermonde islands as coral-based exposure remains a mystery, especially in the initial information reveals the formation of the reef .

Determination of the age of the coral reefs in the waters has a huge benefit in studying the geography of marine origin such coral samples to trace and study the formation sector in coastal rock formations, especially if an area is an area of islands with very high coral reef biodiversity levels (Yuliaty and Akhadi, 2005).

Radiosiotop ¹⁴C is a radioactive isotope that is most commonly used for dating hydrology, geology and archeology samples. Age determination using ¹⁴C often referred to as radiocarbon dating, a

method based on the calculation of the ¹⁴C activity was contained in a sample. This value is then converted into age after the activity compared to modern reference standard (Satrio and Abidin, 2007; Satrio and Sidauruk, 2010).

Carbon-14 measurements by liquid scintillation counting method is based on two methods of pretreatment, the method of synthesis of benzene and CO₂ absorption method (Satrio and Abidin, 2007). CO₂ absorption method is an alternative pretreatment method in the last two decades. It was developed for measuring the Carbon-14 in various environmental samples such as soil, river water, sediment and coral reefs (Varlam et al., 2007; Mazeika et al., 2009; Varlam, et al., 2010; Faurescu et al., 2010; Satrio and Sidauruk, 2010; Maming, et al., 2014).

CO₂ absorption approach is based on the same basic principle as the benzene-LSC method. The main difference is the CO₂ produced from the sample is absorbed directly into the appropriate cocktail with high CO₂ affinity and directly counted by LSC without further changes. The method is simple, safe, and significantly reducing time analysis and cost compared to conventional methods.

Alkanolamine compounds such as monoethanolamine (MEA), diethanolamine (DEA) and triethanolamine (TEA) is a reactive CO₂ absorbent. Alkanolamine compound has the advantage of absorbing CO₂ due to rapid absorption rate, low cost and high heat absorption (Vaidya and Mahajani, 2006; Kim, et al. 2013).

According to research conducted by Kim, et al (2013), CO₂ absorption capability of a solution of 30 % MEA, 30% DEA and 30 % TEA are 0.565; 0.658 and 0.486 mol CO₂ / mol amine respectively. CO₂ absorption capability allows the use of relatively large alkanolamine compounds as alternative CO₂ absorbent for Carbon-14 measurements.

Carbon-14 analysis which is correct and accountable is the most important factor in assessing the status of a coral reef. Therefore, in this study will be conducted to determine the capacity of MEA, DEA and TEA as CO₂ absorbent for radiocarbon measurements in coral sample.

MATERIAL AND METHOD

Materials

The materials of this study was 30% H₂O₂, HClO₄ 1 N, 1 N NaOH, ethanolamine, N₂ gas HP (High Purity), 10% HCl, AgNO₃, 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, 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

Coral sample taken at seawater near one of the islands in the Spermonde Archipelago, which is in Langkai Island at a depth about 4-5 m. Langkai Island located on coordinate S: 05° 01' 47,055" E: 119° 05' 50,272".

Physical and Chemical Cleaning

Cleaning methods are designed to remove contaminating carbon sources that accumulate both while the specimen is on the sea floor and while it is stored on land after collection. Water rinses and scrubbing with a brush remove sediment from inside the coral and between the septa. Samples are then immersed in a 1:1 mixture of 30% H₂O₂ and 1N NaOH and ultrasonicated for 15 minutes. However, this process often leaves a brownish/orange organic stain on the CaCO₃. Quick dips (30 seconds to 2 minutes) in a 1:1 mixture of 30% H₂O₂ and 1N HClO₄ effectively remove this stain. After the dilute perchloric step, samples are rinsed thoroughly with clean distilled water. For the second acid wash, pre-weighed samples are dipped into 6N HCl for 15–60 seconds followed by rinses in two separate beakers of distilled H₂O. After drying for several minutes in a 60 °C oven, the samples are cooled and reweighed to determine the percent of sample removed. Samples are then crushed in an agate mortar and pestle to facilitate dissolution in the reaction flasks (Adkins, et al., 2002)

Carbon Dioxide Absorption

Dried coral were transferred to flask that connected to a separation funnel as hydrochloric acid reservoir. Prior to carbon dioxide absorption, the nitrogen

gas was streamed along the system. Solution of 10 % HCl was added by drops to the sample until bubbles formed (Fig.1). Gas is channeled into an impinger contains 40 mL of 30 % MEA, DEA or TEA as CO₂ absorber after passed acid trap and water trap. The process was stopped when the gas not formed by adding the hydrochloric acid. Concentration of CO₂ absorbed was quantified from the difference of weight before and after absorption process

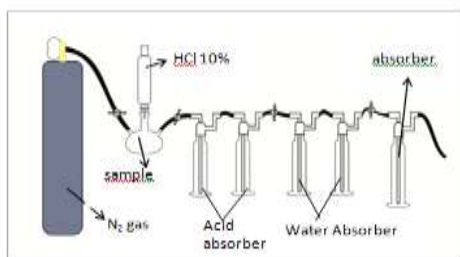


Figure 1. Design of absorption system of carbon dioxide from coral sample

The same method is used to absorb CO₂ from Marble for use in the measurement of the Background

Carbon-14 Counting

Approximately 8 mL of sample or background mixture with 12 mL scintillator in 20 mL vial. The mixture was homogenated by shaking and saved from light exposure, and then lied on 20 mL vial plate tray. Counting the sample as protocol LSC Hidex 300 SL and it was counted at 5-240 minutes in range.

RESULT AND DISCUSSION

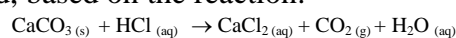
Physical and Chemical Cleaning

Coral sampel that have been physically and chemically cleaned looked clean and white. The chemical cleaning removed

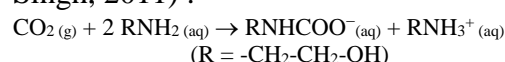
impurities and carbon source on the surface up to 8,63 %. The result of these experiments are not much different from the result of deep-sea coral sample cleanup was done by Adkins et al. (2002) and Maming et al. (2014). The missing part of the sample is a natural contaminant that accumulates over the coral reef waters and dissolved matrix surface.

Carbon Dioxide Absorption

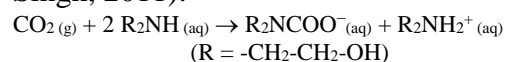
The main component coral as carbonate that have been grinded are separated by reaction with hydrochloric acid, based on the reaction:



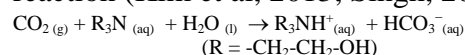
Carbonate in this reaction is released as CO₂ gas when the sample react with acid. Carbon dioxide is absorbed by MEA through chemical reaction as carbamate, based on the reaction (Kim et al, 2013; Singh, 2011) :



Carbon dioxide is absorbed by DEA through chemical reaction as carbamate, based on the reaction (Kim et al, 2013; Singh, 2011):



TEA, a tertiary amine, cannot directly react with CO₂. TEA acts as a base catalyst to form bicarbonate ions, based on the reaction (Kim et al, 2013; Singh, 2011):



The existence of carbamate or bicarbonate ions as reaction products is identified by the difference of solution weight before and after absorption. The correlation between weight of CO₂ absorbed using MEA, DEA and TEA to the weight of sample is showing on the figure 2.

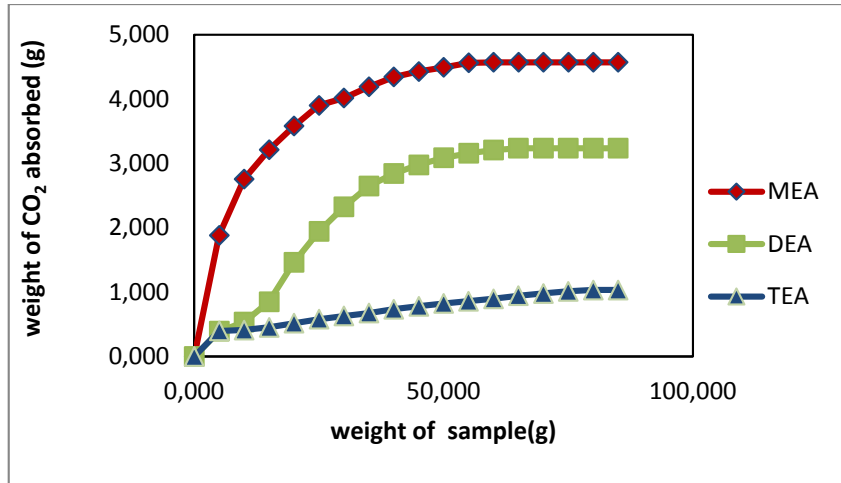


Figure 2. Correlation between weight of sample with amount of CO₂ absorbed using MEA, DEA and TEA

Table 1. The optimum amount of CO₂ absorbed by MEA, DEA and TEA

Absorbent	Amount of CO ₂	
	Weight of CO ₂ (g)	mol CO ₂ /mol alkanolamine
MEA 30 %	4,572	0,5180
DEA 30 %	3,236	0,5903
TEA 30 %	1,033	0,2608

The optimum amount of CO₂ absorbed by MEA, DEA and TEA are listed on the table 1. These results are not much different from the results obtained by Kim et al. (2013)

Carbon-14 Counting

The results of measurements of ¹⁴C activity measured on the instrument is expressed in units of Count Per Minute (CPM) which shows the number of β particles produced from ¹⁴C in coral sample in every minute, and the activity of coral sample is expressed in units Disintegration Per Minute (DPM) which shows the actual number of atoms ¹⁴C decays in the coral samples in every minute.

The relationship between the value of DPM and the value CPM is expressed as a form of efficiency in units of enumeration which stated Triple Double Coincidence Ratio (TDCR).

Measurement of Carbon-14 activity of 30% MEA, DEA and TEA solution also investigated as background. MEA, DEA and TEA background activity measurement results show the value of the carbon-14 activity is relatively higher than the activity of the sample. This is due to the difference in the interaction between the solution with scintillator due to the formation of carbamate or bicarbonate ions in the sample solution. Therefore, it needs a chemical treatment to equalize the conditions of the sample solution and the background. For this purpose, it is done by the CO₂ absorption using marble as a source of CO₂ background (Canducci et al, 2013; Varlam et al, 2007). Marble is a carbon source with old age that is considered to contain carbon-14 with very low activity. Comparison of activity measurements of carbon-14 in the sample and background are shown in Figure 3, 4 and 5.

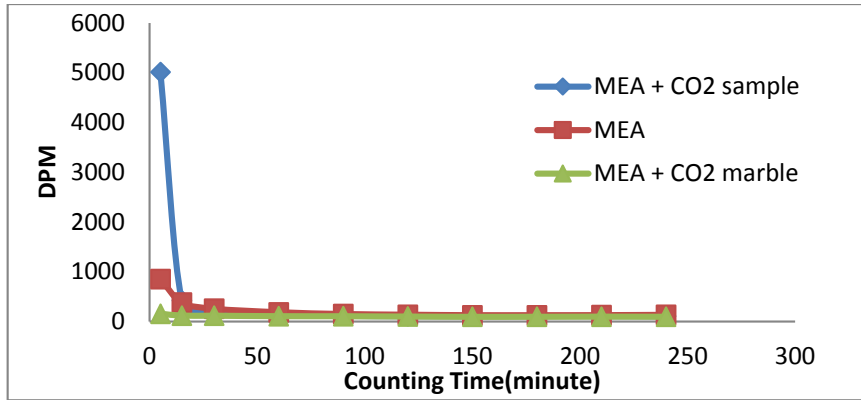


Figure 3. Comparison of activity measurements of carbon-14 in the sample and background using MEA absorbent

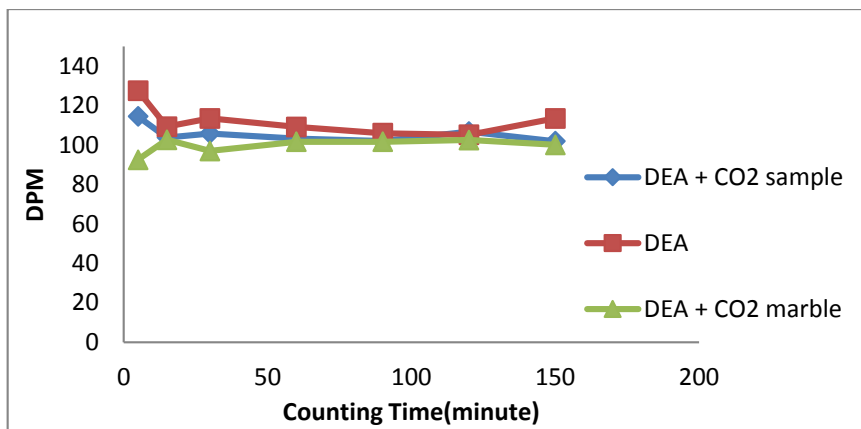


Figure 4. Comparison of activity measurements of carbon-14 in the sample and background using DEA absorbent

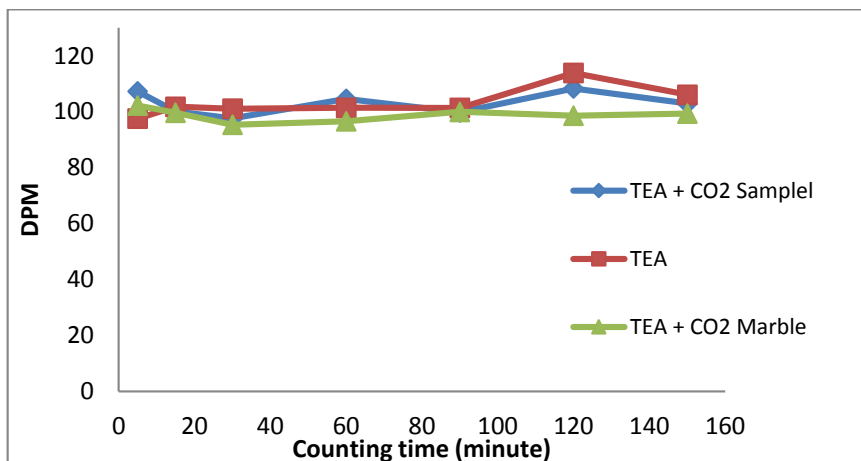


Figure 5. Comparison of activity measurements of carbon-14 in the sample and background using TEA absorbent

In figure 3,4 and 5 shows that the measurement of Carbon-14 marble as background showed lower activity than the sample. Therefore, the Carbon-14

activity of marble background is used to correct activity of Carbon-14 from samples.

Comparison of activity measurements of carbon-14 in the sample and

background are shown in Table 2.

Table 2. Activity of ¹⁴C of sample and background

Absorbent	CPM		DPM		TDCR	
	CPMs	CPMb	DPMs	DPMb	TDCRs	TDCRb
MEA 30 %	50,804	53,394	96,554	92,968	0,526	0,573
DEA 30 %	57,230	56,464	101,520	98,944	0,563	0,571
TEA 30 %	60,330	60,090	100,298	99,486	0,601	0,604

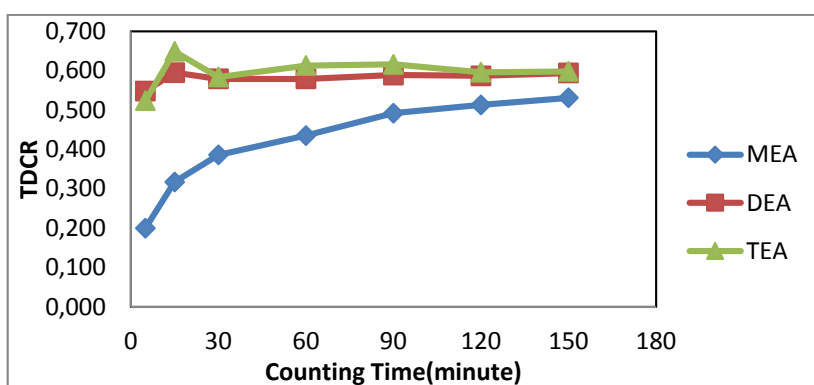


Figure 6. Comparison of TDCR counting of MEA, DEA and TEA

From Table 2 shows that the efficiency of the order of enumeration (TDCR) using absorbent MEA, DEA and TEA are TEA> DEA> MEA. The order of enumeration efficiency is influenced by the type of ions generated in the process of CO₂ absorption. DEA and MEA absorb CO₂ as carbamate ions while the TEA produces bicarbonate ions. The order of stability of the species which resulted from CO₂ absorption is MEA-carbamate ion> DEA-carbamate ion> bicarbonate ion (Singh, 2011). Differences in the type and stability of the species causes the difference of interaction with the solvent in the scintillator and give an effect on the count rate. Figure 6 shows a comparison of the efficiency of enumeration (TDCR) absorbent MEA, DEA and TEA to time. From the graph shows that the value

TDCR for MEA absorbent less stable in the early minutes when compared to the DEA and TEA TDCR absorbent.

Specific Activity and Coral Age Estimation

Determination of specific activities are needed in order to determining the age of the sample. The specific activity is the basis for calculating the age of the coral sample obtained from the activity value of DPM divided by the total carbon weight of sample mixed with scintillator. The value of specific activity expressed in units of DPM per unit mass. Specific activity data of coral sample is shown in Table 3. The specific activity value (As) shows the actual number of ¹⁴C atoms which disintegration per minute (dpm) in each gram of the element carbon.

Table 3. Specific activity data of coral samples from Langkai Island

Absorbent	DPM	C-total (g)	As (DPM/gC)	As C-14 life* 5
MEA 30 %	3,576	0,2477	14,44 ± 1,12	15,30 ± 0,1
DEA 30 %	2,576	0,1765	14,59 ± 2,23	15,30 ± 0,1
TEA 30 %	0,812	0,0563	14,42 ± 2,58	15,30 ± 0,1

Based on the following equation can be obtained The Age estimation of coral sample is obtained based on the specific activities that have been obtained previously.

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

Where:

A = Radioactive ¹⁴C in the sample
 A₀ = Radioactivity of ¹⁴C isotopes in living organisms 15.3 DPM / gC⁵
 t_{1/2} = half-life = 5730 years
 ln2 = 0.693

The age of coral sample calculated from the specific activity using absorbent MEA, DEA and TEA was 480.15 ± 37; 390.11 ± 60 and 488.22 ± 87 years respectively.

CONCLUSION

In this study concluded that the Absorption capacity of MEA, DEA and TEA was 0.5180; 0.5903 and 0.2608 mol CO₂/mol amine, respectively. The specific activity of coral sample using absorbent MEA, DEA and TEA was 14.44; 14.59; and 14.42 DPM/g C, respectively. The age of coral sample calculated from the specific activity using absorbent MEA, DEA and TEA was 480.15 ± 37; 390.11 ± 60 and 488.22 ± 87 years, respectively.

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