

SYNTHESIS OF BUTHYL BROMIDE LABELED ^{82}Br FOR LEAKAGE DETECTION APPLICATION IN INDUSTRIAL PIPELINE SYSTEM

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ABSTRACT

SYNTHESIS OF BUTHYL BROMIDE LABELED ^{82}Br FOR LEAKAGE DETECTION APPLICATION IN INDUSTRIAL PIPELINE SYSTEM. The detection of a leakage in an installation or pipeline in industrial complex is difficult to be done because related to security, safety, and operation condition. With expanded radioisotope application as a tracer in industry, hence a leakage in a pipe can be detected easily and quickly without needed excavation or stop the production process. The selection of radioisotope labeled compound as radiotracer should be examined carefully to determine the appropriate and well mixed radiotracer with the material passing through the pipeline system. Radioisotope labeled compound butyl bromide-82 ($\text{C}_4\text{H}_9^{82}\text{Br}$) as a radiotracer can be synthesized by reacting K^{82}Br with 1-butanol and sulphuric acid (H_2SO_4) as a catalyst. The experiment result shows that synthesized $\text{C}_4\text{H}_9^{82}\text{Br}$ by composition of 15 mL K^{82}Br solution (0.1 gr/mL KBr) and 10 mL 1-butanol gave the highest percentage of reactions amount 40,95% & 50,00%. Characterization by FTIR showed that the product has absorption band for C-Br at 514,99-738,74 cm^{-1} . GCMS analysis showed the peak of $\text{C}_4\text{H}_9^{82}\text{Br}$ together with other 7 peaks of impurities with 43.03% percentage of $\text{C}_4\text{H}_9^{82}\text{Br}$ peak. In distribution coefficient determination of $\text{C}_4\text{H}_9^{82}\text{Br}$ in the test solution from industry (ethylene dichloride), Kd value of 5,1350 was obtained and more than 98% $\text{C}_4\text{H}_9^{82}\text{Br}$ distilled together with ethylene dichloride in 110°C distillation process whereas no radioactivity detected in distillation flask if K^{82}Br was used. Based on these results, $\text{C}_4\text{H}_9^{82}\text{Br}$ is suitable to be applied as radiotracer for leakage detection in pipeline system with organic compounds as passing liquid including ethylene dichloride.

Keywords: Bromine-82, Buthyl Bromide, Radiotracer, Leakage Detection.

ABSTRAK

SINTESIS BUTIL BROMIDA BERTANDA ^{82}Br UNTUK APLIKASI PENDETEKSI KEBOCORAN DI SISTEM PERPIPAAN INDUSTRI. Deteksi kebocoran pada rangkaian atau jalur pipa di area industri sulit dilakukan terkait dengan faktor keamanan, keselamatan, dan kondisi operasi. Dengan ekspansi aplikasi radioisotop sebagai pelacak dalam industri, maka kebocoran pada pipa dapat dideteksi dengan mudah dan cepat tanpa perlu penggalian atau menghentikan proses produksi. Pemilihan senyawa bertanda sebagai radioperunut harus dikaji dengan cermat untuk menentukan perunut yang sesuai dan tercampur baik dengan bahan yang melewati sistem pipa. Radioisotop berlabel senyawa butil brom-82 ($\text{C}_4\text{H}_9^{82}\text{Br}$) sebagai perunut dapat disintesis dengan mereaksikan K^{82}Br dengan 1-butanol dan asam sulfat (H_2SO_4) sebagai katalis. Hasil percobaan menunjukkan bahwa $\text{C}_4\text{H}_9^{82}\text{Br}$ yang disintesis dengan komposisi 15 mL larutan K^{82}Br (0,1 gr / mL KBr) dan 10 mL 1-butanol memberikan persentase reaksi tertinggi yaitu 40,95% & 50,00%. Karakterisasi oleh FTIR menunjukkan bahwa produk memiliki pita serap untuk C-Br pada 514,99-738,74 cm^{-1} . Analisis GCMS menunjukkan puncak $\text{C}_4\text{H}_9^{82}\text{Br}$ bersama dengan 7 puncak pengotor lainnya dengan 43,03% persentase puncak $\text{C}_4\text{H}_9^{82}\text{Br}$. Dalam penentuan

koefisien distribusi $C_4H_9^{82}Br$ dalam larutan uji dari industri (etilena diklorida), nilai K_d 5.1350 diperoleh dan lebih dari 98% $C_4H_9^{82}Br$ didistilasi bersama-sama dengan etilen diklorida dalam proses distilasi $110^\circ C$ sedangkan radioaktivitas tidak terdeteksi dalam labu destilasi jika $K^{82}Br$ digunakan. Berdasarkan hasil ini, $C_4H_9^{82}Br$ cocok untuk diaplikasikan sebagai perunut untuk deteksi kebocoran dalam sistem pipa dengan senyawa organik sebagai cairan yang lewat termasuk etilen diklorida.

Kata kunci : Brom-82, Butil Bromida, Radioperunut, Deteksi Kebocoran.

1. INTRODUCTION

Radiotracer is one of radioisotopes utilization in industrial application. Radiotracer utilizes its gamma radiation as a beam or signal to be traced by the examiner. Bromine-82 (^{82}Br) with half life 35 hours, emits high energy gamma radiation at keV. This gamma radiation enable high detection sensitivity because of ability of gamma radiation to penetrate thick matter. Meanwhile, short half life of ^{82}Br reduces the risk of long radiation exposure. Bromine itself, is easy to be converted in many chemical form with different characteristics. Those reasons bolster up ^{82}Br as favorable radiotracer for online detection in industrial application [1].

^{82}Br is usually produced by neutron activation of natural bromine target in some chemical form, usually potassium bromide, ammonium bromide and dibromobenzene. In TRIGA 2000 Reactor, ^{82}Br was produced by neutron irradiation of KBr (natural isotope) target. ^{82}Br was obtained as $K^{82}Br$ solution. This radioisotope solution is suitable for detection of water flow or fluids in the range of room temperature [2]. When the $K^{82}Br$ is used for high temperature fluid, for instance the heat exchanger system, there is a concern about $K^{82}Br$ deposit when evaporation of solution happens, as a result

$K^{82}Br$ radiotracer will not resemble the fluid system [3].

Some common detection methods, for example hydrostatic pressure, chemical reagent, bubble, dye penetrant, acoustic emission and helium tracer are not available for online monitoring for leakage detection of bank of heat exchanger, therefore a shutdown process is a mandatory. This action sometimes interferes plant operation schedule.

The use of radioisotopes as a tracer in detecting leakage of these pipes must meet certain requirements, which must be appropriate and can be mixed with compounds that flow in the pipe. Based on research conducted by Setiawan [4], one of the radioisotopes as a radioactive tracer that is used to determine leakage of oil-filled pipes is radioisotopes in the form of methyl bromide-82 compounds ($CH_3^{82}Br$). In use, the methyl bromide-82 compound is volatile because it has a very low boiling point of $3.56^\circ C$ at room pressure. Therefore, the development of the synthesis of radioisotope butyl bromide-82 is carried out, so that the product can have high usability and can be utilized in the relevant field. Utilization of butyl bromide-82 is based on the characteristics of its boiling point which is not too low so it is not volatile when applied and has a relatively short half-life of 35.30 hours so that the

radiation contamination generated will be immediately lost through its decay.

2. EXPERIMENTAL SECTION

Materials

Potassium bromide (KBr) p.a was used as target material for neutron irradiation, 1-butanol p.a and sulfuric acid (H_2SO_4) 98% were purchased from Merck. Aluminium capsule was made in house and used as target material container. Aqua demineralized and water ice was produced by indigenous system. Reflux apparatus consists of 250 mL three necks rounded flask and equipped with thermometer. Reflux condenser was placed in vertical neck of the flask and distillation condenser was installed on another neck. Lead container was purchased from PTKRN BATAN. Reflux and distillation process were carried out in radioisotope processing box shielded with lead under sufficient negative air pressure condition.

Production of K^{82}Br

5 grams of KBr was weighed and transferred into quartz ampoule then it was sealed by glass welding. Ampoules were packed into capped aluminium capsule before inserted into irradiation position at TRIGA 2000 research reactor Bandung. KBr was irradiated for 72 hours with 1.63×10^{13} $\text{n}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ neutron flux. At the end of irradiation, target was cooled for 48 hours then transferred into radioisotope processing box. K^{82}Br in glass ampoule was crushed in sealed system before addition of 50 mL water. As a final step, K^{82}Br solution was transferred into sealed quartz vial and it was transported within lead container to other processing box

with reflux system installed. Radioactivity of ^{82}Br was measured by dose calibrator.

Synthesis of $^{82}\text{Bromobutane}$ ($\text{C}_4\text{H}_9\text{-}^{82}\text{Br}$)

Radioactivity of 7.5 mL, 15 mL and 30 mL K^{82}Br solution was measured first using dose calibrator before addition of 5 mL, 10 mL and 20 mL 1-butanol in each separated batch respectively. The mixture of K^{82}Br and 1-butanol was cooled in water ice bath prior to addition of concentrated sulfuric acid. Sulfuric acid should be added slowly into the solution in cool addition to prevent Br_2 loss. After addition of sulfuric acid, reaction was initiated by heating at 90 – 120 °C for 1 hour. Heating mantle was turned off after one hour mark and cooled until the system reached room temperature. Distillation began after reflux condenser's stop cock was closed and distillation condenser was opened. Distillation was carried out with heating at 110 °C until no liquid dropped from the distillation condenser or until no change of dose rate in reactor flask and receiver flask. Distillate was measured by dose calibrator at ^{82}Br dial energy.

Separation of water and organic layer

Distillate from synthesis step of $^{82}\text{Bromobutane}$ consists of butanol, bromobutane itself, water, by product and unreacted chemical. Those composition was observed divided into two layers, organic and water layers. Each layer was separated using separating funnel. To determine the type of the layers, an aliquot of each separated layer was added and mixed into one mL of water. If the aliquot mixed well with the water then it should be water layer, otherwise it was organic layer. Radioactivity of organic layer

was determined by dose calibrator and this layer was subjected for further analysis.

Labeling yield of ^{82}Br was calculated as ratio of radioactivity of organic layer (A_{org}) versus initial radioactivity of K^{82}Br added (A_{initial})

$$\text{Labeling yield} = \frac{A_{\text{org}} (\text{mCi})}{A_{\text{initial}} (\text{mCi})} \times 100\%$$

Characterization of $\text{C}_4\text{H}_9\text{-}^{82}\text{Br}$ Functional Group Analysis

$\text{C}_4\text{H}_9\text{-}^{82}\text{Br}$ radiolabelled compound was analyzed by FTIR followed by GCMS to understand its chemical characteristics and confirm the substitution reaction of 1-butanol with bromine.

Determination of Distribution Coefficient of $\text{C}_4\text{H}_9\text{-}^{82}\text{Br}$ in Ethylene Dichloride and water system

Ethylene dichloride was used as industrial sample to be traced by Bromobutane-82. The interaction of K^{82}Br solution and butyl bromide-82 can be seen from the distribution coefficient. The distribution coefficient can be stated as follows :

$$K_d = \frac{C_{\text{organic}}}{C_{\text{water}}}$$

C_{org} = Concentration (number of counts) in the organic phase

C_{water} = Concentration (number of counts) in the water phase

A total of 0.2 mL K^{82}Br (radioactive) was added to the mixture of 1 mL of ethylene dichloride and 1 mL of water, then shaken using a shaker for 5 minutes. The organic phase and the formed water phase are separated. Each phase is counted using a Single Channel Analyzer (SCA). Same

procedure was applied to 0.2 mL of Bromobutane-82.

3. RESULTS AND DISCUSSION

The Synthesis of butyl bromide-82 carried out in this study is based on the substitution reaction. Substitution reaction is the replacement reaction of atoms or atomic groups in a molecule. In the process, the -OH group on butanol is replaced by the radioactive bromide ion (^{82}Br) which is a halogen element. So the reaction process that occurs can also be called a halogenation reaction.

Production of K^{82}Br

^{82}Br radioisotopes used in this research has a chemical form of a K^{82}Br solution. The solution was obtained from the dissolution of the K^{82}Br solid as a result of irradiation of potassium bromide (KBr) which was carried out at the Bandung TRIGA 2000 Reactor with a neutron flux of $3.16 \times 10^{13} \text{ n.cm}^{-2}.\text{s}^{-1}$ for 72 hours. Selection of potassium bromide as a target for irradiation was based on consideration that it could easily dissolved especially in water and also has a high melting point that is resistant to the heat generated during irradiation process. In addition, according to [5], the presence of potassium bromide in nature is quite abundant, which is around 49.31%. Then, potassium bromide can be used as an irradiation target to obtain ^{82}Br in the form of K^{82}Br . From irradiation of 5 gr KBr target, 11,21 Ci of ^{82}Br as K^{82}Br was obtained as K^{82}Br in 20 mL of water.

Synthesis and Characterization of Bromobutane-82

Bromobutane-82 can be obtained from a substitution reaction by reacting a number of K^{82}Br solutions with butanol ($\text{C}_4\text{H}_9\text{OH}$). The synthesis reaction of butyl bromide runs slowly, so sulfuric acid (H_2SO_4) was used as a catalyst to accelerate the reaction. The use of sulfuric acid caused protonation of butanol, thus forming H_2O which was a better leaving group compared to the hydroxyl group ($-\text{OH}$) because H_2O is a weak base compared to the hydroxyl group ($-\text{OH}$). Bromide ions derived from the K^{82}Br acted as nucleophiles in a substitution reaction between the leaving group (H_2O) with the bromide ion ($^{82}\text{Br}^-$) and produce butyl bromide ($\text{C}_4\text{H}_9\text{-}^{82}\text{Br}$) and water (H_2O) as a by-product. To optimize the substitution process, reaction was carried out in closed reflux system followed by distillation and layer separation of product. The temperature used in the reflux process was around $90\text{-}120^\circ\text{C}$. Table 1 shows labelling efficiency of $\text{C}_4\text{H}_9\text{-}^{82}\text{Br}$ in varied radioactivity and K^{82}Br volume. Molar ratio between KBr and 1-butanol was kept in stoichiometric condition for each reaction. 15 mL of K^{82}Br yielded highest labelling efficiency despite different radioactivity of K^{82}Br used.

Tabel 1. Labeling Efficiency of $\text{C}_4\text{H}_9\text{-}^{82}\text{Br}$ in various volume and radioactivity of K^{82}Br .

Batch	K^{82}Br (mL)	Initial radioactivity (mCi)	radioactivity obtained (mCi)	Labeling Efficiency (%)
1	7,5	8,72	1,235	14,16
1	7,5	0,033	0,008	24,24
1	15	0,028	0,014	50,00
3	15	1050	430	40,95
2	30	3990	1098	27,52
2	30	14	3,97	28,36

Identification of functional groups of $\text{C}_4\text{H}_9\text{-}^{82}\text{Br}$ labelled compounds was analyzed using FTIR spectroscopy. Analysis using FTIR spectroscopy aims to determine the absorption of functional groups contained in organic layer after separation of two layer. Figure 1 depicts FTIR spectrum of $\text{C}_4\text{H}_9\text{-}^{82}\text{Br}$.

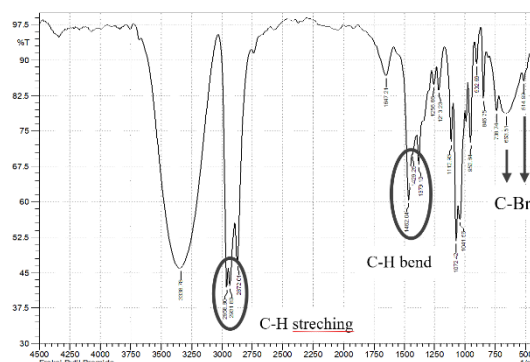


Figure 1. FTIR spectrum of separated organic fraction in $\text{C}_4\text{H}_9\text{-}^{82}\text{Br}$ synthesis.

Based on Figure 1, it can be identified that the functional groups contained in the organic phase are stretching of C-H, bending of C-H, and C-Br bonding. The stretching of CH group identified by absorption peaks in wave number $2958.80\text{-}2872.01\text{ cm}^{-1}$ with a range of $2960\text{-}2850\text{ cm}^{-1}$ and the bending of CH group is in the wave number $1462.04\text{ -}1379.10\text{ cm}^{-1}$ with a range $1450\text{-}1375\text{ cm}^{-1}$. While the absorption band for the C-Br bond which is characteristic of butyl bromide was found in wave numbers 514.99 cm^{-1} and 663.51 cm^{-1} . The absorption band or peak formed is caused by stretching C-Br at wave number $680\text{-}500\text{ cm}^{-1}$ [6].

In FTIR spectrum pattern, there was also absorption bands of hydroxyl groups (OH) at wave number 3338.78 cm^{-1} with a range of wave numbers $3550\text{-}3200\text{ cm}^{-1}$ [7] and CO groups at wave numbers 1255.66-

1041, 56 cm^{-1} with a range of wave numbers 1260-1000 cm^{-1} . The existence of the group indicates that the butyl bromide product produced contains impurities that might come from the residual butanol or water as the unreacted starting material.

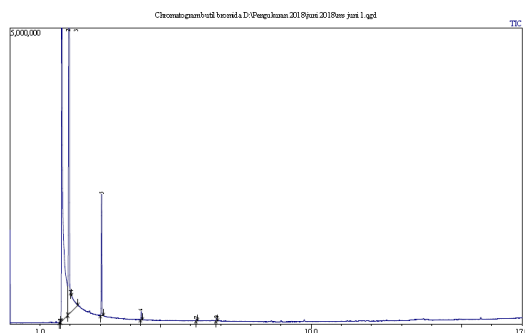


Figure 2. Gas chromatogram of of obtained organic fraction in $\text{C}_4\text{H}_9\text{-}^{82}\text{Br}$ synthesis.

Figure 2 shows there are eight peak of compounds that are present in the synthesized butyl bromide phase. The chromatogram percent area in table 2 shows the percentage ratio of the total area of a compound with the total area of the all peaks produced. The compounds that have the largest area are butanol (1-butanol) (50.37%) and butyl bromide (1-bromobutane) (43.03%). Based on the results of the analysis, it was found that there was a peak for butyl bromide with a retention time of 1,965 minutes [8]. Butyl bromide or 1-bromobutane is the main compound of the desired product, while 1-butanol is the starting material used in the synthesis process.

Tabel 2. Gas chromatogram analysis of organic phase by GCMS

Peak	R.Time	Area	%Area	Height	A/H	Predicted m/z
1	1,720	22600738	50,37	7692484	2,94	1-butanol
2	1,965	19306472	43,03	9727753	1,98	1-bromobutane
3	3,040	2618207	5,83	2055824	1,27	n-butyl ether

From the MS result, there were 3 main molecules detected. The first one with a molecular weight of 136 g / mol indicating the presence of butyl bromide. The presence of the Br halogen group was detected by the release of Br which results in a peak at m/z 57. The mass spectrum produced was similar to the data library shown by the Similarity Index (SI) value close to 100, which is 98 [9]. Second molecule was defined as 1-butanol, with m/z 74 and SI value of 98. The last one was n-butyl ether as by product of halogenation substitution reaction between 1-butanol and bromine.

Application of $\text{C}_4\text{H}_9\text{-}^{82}\text{Br}$

Ethylene dichloride (EDC) is used widely in chemical company as both end product or starting material. Some chemical factories use ethylene dichloride as cooling liquid [10]. EDC has thermodynamic properties with tendency of solidification under drastic temperature and pressure change, which led to accumulation and blockage in pipeline system [11]. Leakage detection of pipeline contain by radiotracer requires radiolabelled compound with similar characteristic with EDC. In this work, the miscibility of $\text{C}_4\text{H}_9\text{-}^{82}\text{Br}$ radiolabelled compound was examined by determination of

distribution coefficient (Kd) of $\text{C}_4\text{H}_9\text{-}^{82}\text{Br}$ in EDC liquid. Table 3 shows Kd of $\text{C}_4\text{H}_9\text{-}^{82}\text{Br}$ in EDC and compared with K^{82}Br aqueous solution. It can be conclude that $\text{C}_4\text{H}_9\text{-}^{82}\text{Br}$ more distributed in EDC than K^{82}Br .

Tabel 3. Distribution coefficient of $\text{C}_4\text{H}_9\text{-}^{82}\text{Br}$ and K^{82}Br in ethylene dichloride solution

Sample	Distribution Coefficient (Kd)	
	$\text{C}_4\text{H}_9\text{-}^{82}\text{Br}$	$\text{K}^{82}\text{Br}_{(\text{aq})}$
1	4,1723	0,0018
2	4,7161	0,0020
3	6,5166	0,0029
Average	5,1350	0,0022
Deviation	1,2270	0,0006

When used as cooling liquid in heat exchanger system in one of the chemical factories in Indonesia, EDC would turn into gaseous from at temperature range of 110 – 120°C. We simulated this condition by distillation process of the mixture of EDC and $\text{C}_4\text{H}_9\text{-}^{82}\text{Br}$. Table 4 shows the distillation percentage of radioactivity of distilled mixture after full distillation process at 110°C. Aqueous K^{82}Br remained as salt in residual flask whereas most of $\text{C}_4\text{H}_9\text{-}^{82}\text{Br}$ and EDC evaporated and recovered in distilled flask with recovery percentage more than 98%.

Tabel 4. Distillation percentage of EDC + $\text{C}_4\text{H}_9\text{-}^{82}\text{Br}$ mixture and EDC + K^{82}Br mixture after distillation process at 110°C

Sample	Radioactivity (mCi)					
	EDC + $\text{C}_4\text{H}_9\text{-}^{82}\text{Br}$			EDC + $\text{K}^{82}\text{Br}_{(\text{aq})}$		
	Residual Flask	Distilled Flask	% Distillation	Residual Flask	Distilled Flask	% Distillation
Initial	10.20	-		11.39	-	
Final (3 hours)	0.10	9.81	98.99	10.71	n.d	0%

4. CONCLUSION

$\text{C}_4\text{H}_9\text{-}^{82}\text{Br}$ was successfully synthesized in this research. Although the product still contains the impurities of 1-butanol and some trace of by product compounds, $\text{C}_4\text{H}_9\text{-}^{82}\text{Br}$ synthesized in this research mixed well with ethylene dichloride. Similar characteristic of $\text{C}_4\text{H}_9\text{-}^{82}\text{Br}$ and ethylene dichloride made this labelled compound suitable as radiotracer to analyze the leakage in industrial pipeline system which utilizes ethylene dichloride as passing liquid.

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