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THE RECOVERY OF C^{14} FROM IRRADIATED BERYLLIUM NITRIDE.

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I. Introduction.

Several advantages are apparent in the use of Be_3N_2 as a source of nitrogen for the reaction $N^{14}(n,p)C^{14}$. From the chemical standpoint Be_3N_2 is a stable, solid compound containing 50% nitrogen by weight. From the nuclear standpoint the presence of Be in the compound is satisfactory because of the low capture cross-section of Be.

Methods for the recovery of C^{14} from Be_3N_2 were based on solution in acid and alkali. It has been shown by Libby⁽¹⁾ and Yankwich⁽²⁾ that upon aqueous solution of irradiated Be_3N_2 , the C^{14} activity is distributed among several single carbon atom compounds, the most important of which are CH_4 and $HCOOH$. In the recovery studies reported here means were employed for separating various C^{14} activities in order to obtain C^{14} of the highest specific activities. A recommended procedure is offered.

II. Alkaline Dissolution of Be_3N_2 .

The method for the differential analysis of Be_3N_2 ⁽²⁾ was adapted to a larger scale with certain modifications. In the original method a small sample (50 mg.) of Be_3N_2 together with traces of CN^- , CO_3^{2-} , $HCHO$, $HCOOH$ and CH_3OH carriers is placed in a 3-necked flask fitted with a cold-water condenser, a mercury-sealed stirrer and a combination gas and liquid delivery system. The Be_3N_2 is dissolved by the addition of a large excess of 6N NaOH and heating. Oxygen gas is swept through the system constantly. The gas first passes through a CuO-filled combustion tube at 325-350°C which selectively oxidizes CO to CO_2 but allows CH_4 to pass unreacted. After passing through a 1N NaOH

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absorption bottle, the gas passes through a second combustion tube at 660°C where the CH_4 is oxidized, then collected in a NaOH trap. Several hours of gas sweeping are employed to insure complete collection of C^{14} activity. The remaining C^{14} activities are then obtained by oxidization with KMnO_4 in the hot alkaline solution. The solution was cooled, acidified with 18N H_2SO_4 , reheated and the CO_2 swept out in the O_2 stream through the combustion tube.

The dissolution of one mole of Be_3N_2 requires six moles of NaOH and simultaneously liberates two moles of NH_3 .

The presence of this large volume of NH_3 is a serious difficulty since either it must be absorbed in an acid trap or allowed to be oxidized to nitrogen and water in the combustion tube. The generation of a large volume of gas also makes pressure regulation within the system difficult to control. Several test runs with 5 and 10 grams of inactive Be_3N_2 indicated that because of the exothermic reaction, the Be_3N_2 must be slurried with water and the slurry brought to a boil before adding NaOH. The addition of NaOH must be very slow in order to control the pressure satisfactorily. A tracer run with 10 gms. of inactive Be_3N_2 and 70 mg. of active Be_3N_2 gave an overall C^{14} recovery of 89%.

A large scale run with 58.86 gms. of Be_3N_2 prepared at Berkeley, containing about 6.4 millicuries of C^{14} was then begun. The Be_3N_2 was placed in a two liter, 3-necked flask and slurried with 150 ml. of water. The system was flushed out with O_2 gas for 1/2 hour, after which the NaOH absorption bottles were placed in the system. An H_2SO_4 absorption bottle was located between the dissolving flask and the combustion tube in order to remove NH_3 . The slurry was brought to boiling and the addition of saturated NaOH solution begun. After the first few ml.

of NaOH had been added, the whole slurry caked up while the pressure within the system built up and some gas was lost through the mercury seal of the stirrer. The flask was cooled and additional water added to the solid mass to make the water/ Be_3N_2 ratio about 10 ml./gm. The reaction was again started and after the addition of about 1/10 the required NaOH the reaction became too vigorous and again gas was lost. The experiment was stopped and the C^{14} collected in the NaOH trap was precipitated as BaCO_3 after adding some Na_2CO_3 as carrier. A new NaOH trap was then set in place and the experiment started once more. By very slow addition of NaOH the Be_3N_2 was finally dissolved. A total of about 15 ml. of saturated NaOH was required per gram of Be_3N_2 . The C^{14} collected by sweeping the boiling solution with O_2 overnight was precipitated as BaCO_3 with no added carrier. These fractions collected contained both CH_4 and CO activities.

To the cooled alkaline solution in the dissolving flask traces of all the carriers were added, followed by 25 gms. of KMnO_4 . This quantity of KMnO_4 should represent a considerable excess. On heating the solution the green color of MnO_4^- appeared so that additional KMnO_4 was added. Even after 130 gms. of KMnO_4 (nearly 1 mole) had been added in several portions no permanent purple coloration was obtained, however, no further addition was made. The solution was acidified with 18N H_2SO_4 , heated to boiling and the CO_2 collected and precipitated. The activities collected in this fraction contained CO_2 , CN^- and all the oxidizable compounds.

Table I summarizes the experimental results. In each case where a CO_2 sample was collected, two NaOH traps were placed in series. While as much as 10^8 counts were found in the first trap, the second trap contained only a few thousand counts and hence these results were not included in the table. The overall C^{14} recovery in this experiment was 67%, the remainder undoubtedly having been lost as a result of the accidents noted.

The alkaline dissolution method for Be_3N_2 was discarded at this point

for several reasons. First, the liberation of NH_3 during the reaction makes pressure control very difficult. Secondly, the KMnO_4 requirement for oxidation was unusually large. The need for nearly one mole of KMnO_4 cannot be accounted for on the basis of the oxidation of carbon compounds. One possible explanation for this amount of KMnO_4 is that the nitrogen was not all converted to NH_3 but rather to hydrazine (for example) which was then oxidized. A third feature against the alkaline procedure is that about 15 cc. of saturated NaOH solution is required per gram of Be_3N_2 and the amount of C^{12} introduced as carbonate impurity in this very large amount of NaOH is appreciable even though saturated NaOH (carbonate-free) is used.

TABLE I

RECOVERY OF C^{14} FROM IRRADIATED Be_3N_2 Sample 51-A (58.86 gms.)

Sample No.	Carbon Fraction	BaCO_3 Weight mg.	BaCO_3 Specific Activity - c/m/mg*	Total C^{14} c/m
51-A-4A	Volatile(CH_4 -CO)** (first portion)	839.4	1.99×10^5	1.67×10^8
51-A-4B	Volatile (CH_4 -CO) (second portion)	318.8	4.84×10^5	1.38×10^8
51-A-4B†	From supernatant of 51-A-4B***	226.5	7.42×10^4	2.68×10^6
51-A-4D	Oxidizable	6416.3	5.43×10^4	3.42×10^8
51-A-4D†	From supernatant of 51-A-4D***	177.3	4.98×10^2	8.84×10^4

* Counted with efficiency of 14.5 disintegrations per count.

** Na_2CO_3 carrier added at time of precipitation of BaCO_3 .

*** Sufficient C^{14} is left in the supernatant solution from a BaCO_3 precipitation to justify its recovery in these cases. This is done by forming a "pre-formed precipitate" of BaCO_3 by the slow addition of dilute Na_2CO_3 to the supernatant solution and stirring the resultant precipitate for at least one hour.

III. Acid Dissolution of Be_3N_2

The dissolution of Be_3N_2 in acid solution eliminates the generation

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of NH_3 gas and, hence, makes pressure control in the dissolving system feasible. The elimination of NaOH also reduces the amount of carbon introduced in the form of carbonate. Several test runs were made with 10 grams of inactive Be_3N_2 and a few mg. of active Be_3N_2 . These preliminary tests indicated that the reaction is carried out most easily when the Be_3N_2 is first slurried with 10 ml. of water per gram of Be_3N_2 and the slurry brought to a boil before adding H_2SO_4 . The H_2SO_4 must be added slowly because of the heat generation of the reaction. The dissolution requires 8 equivalents of H^+ per mole of Be_3N_2 :

About 100 ml. of 18N H_2SO_4 is added per 10 gms. of Be_3N_2 to complete the dissolution. Additional 18-24N H_2SO_4 is added until the solution is about 6N H_2SO_4 . Since there is some Be metal in the Be_3N_2 , N_2 gas is used to sweep the system, otherwise the H_2 gas resulting from the solution of Be would explode in the combustion tube. When the solution of Be_3N_2 is complete, O_2 gas is used for the rest of the experiment. Some separation of C^{14} activities were made in the subsequent recoveries. A NaOH trap was placed before the combustion tube to remove CO_2 and HCN, while CH_4 and CO were oxidized in the combustion tube and collected in a NaOH trap after the tube. These fractions were collected after sweeping the boiling solution overnight. In the first trap AgCN was precipitated (NaCN carrier added) after first precipitating BaCO_3 . The AgCN was burned in a combustion tube and the carbon activity recovered as CO_2 . After the collection of the above activities, traces of CH_3OH , HCOOH and CH_2O carriers were added followed by enough CrO_3 (dissolved in a few ml. of water) to make the solution 0.2 M in CrO_3 . The solution was kept boiling and O_2 sweeping was continued overnight.

Several samples of Be_3N_2 irradiated at Clinton were used to practice this method before recovering some very active material.

Table II summarizes the results obtained on the recovery of C^{14} from

53.5 grams of Be_3N_2 prepared at Argonne and irradiated at Clinton for one month. No separation of activities was made in this experiment. Since no analysis was made on the sample originally, the overall recovery of the experiment was not determined.

A total of 0.12 millicuries of C^{14} was recovered in this sample.

TABLE II

RECOVERY OF C^{14} FROM ONE MONTH CLINTON IRRADIATED Be_3N_2 Sample CP-1 (53.5 gms.)

Sample No.	Carbon Fraction	BaCO_3 Weight mg.	BaCO_3 Specific Activity - c/m/mg*	Total C^{14} c/m
CP-1-A	All activities	498.4	3.52×10^4	1.75×10^7

* Counted with efficiency of 14.5 disintegrations per count.

Table III lists the results obtained from an experiment with 5.12 grams of Argonne prepared Be_3N_2 . Separation into several fractions was made but the overall recovery was not determined.

A total of .43 millicuries of C^{14} was recovered here.

TABLE III

RECOVERY OF C^{14} IRRADIATED Be_3N_2 Sample H-3 (5.12 gms.)

Sample No.	Carbon Fraction	BaCO_3 Weight mg.	BaCO_3 Specific Activity - c/m/mg*	Total C^{14} c/m
H-3-A	CO_2^{**}	146.2	2.02×10^4	2.95×10^6
H-3-AC	HCN	431.	1.19×10^4	5.12×10^6
H-3-B	$\text{CH}_4\text{-CO}$	500.4	9.39×10^4	4.69×10^7
H-3-C	Oxidizable	126.6	1.45×10^5	1.84×10^7
H-3-D	Cleanup***	145.8	5.42×10^3	7.91×10^5

* Counted with efficiency of 12.9 disintegrations per count.

** Na_2CO_3 carrier added at time of precipitation of BaCO_3 .

*** Includes supernatant solutions from H-3-A and H-3-C BaCO_3 precipitations.

Table IV records the results obtained from a 9.67 gram sample of Be_3N_2 . This material was the same as that recorded in Table III, however, the Be_3N_2 in this experiment had been decanned from aluminum by dissolution of the Al in NaOH whereas in the former experiment the Al had been removed mechanically. No Na_2CO_3 carrier was added in the precipitation of the CO_2 sample since this Be_3N_2 was expected to be contaminated with inactive Na_2CO_3 .

A total of 0.67 millicuries was recovered from this sample.

TABLE IV

RECOVERY OF C^{14} FROM IRRADIATED Be_3N_2 Sample H-4 (9.67 gms.)

Sample No.	Carbon Fraction	BaCO_3 Weight mg.	BaCO_3 Specific Activity - c/m/mg *	Total C^{14} c/m
H-4-A	CO_2	159.2	4.40×10^4	7.00×10^6
H-4-AC	HCN	175.8	1.82×10^4	1.37×10^7
H-4-B	$\text{CH}_4\text{-CO}$	195.4	3.42×10^5	6.68×10^7
H-4-C	Oxidizable	151.1	1.55×10^5	2.34×10^7
H-4-D	Cleanup **	236.8	1.59×10^4	3.76×10^6

* Counted with an efficiency of 12.9 disintegrations per count.

** Includes supernatant solutions from H-4-A and H-4-C BaCO_3 precipitations.

The recovery of C^{14} from 57.95 gms. of irradiated Berkeley-prepared Be_3N_2 is shown in Table V. Previous analysis of this sample showed that 12.2 millicuries of C^{14} were present.

The C^{14} recovered here amounted to 11.3 millicuries or 93%.

TABLE V

RECOVERY OF C^{14} FROM Be_3N_2 Sample 51-B. (57.95 gms.)

Sample No.	Carbon Fraction	$BaCO_3$ Weight mg.	$BaCO_3$ Specific Activity - c/m/mg*	Total C^{14} c/m
51-B-7A	CO_2	25.1	4.14×10^5	1.04×10^7
51-B-7AC	HCN	3971**	3.34×10^3	1.33×10^7
51-B-7B	CH_4 -CO	1012.	1.51×10^6	1.23×10^9
51-B-7C	Oxidizable	807.	5.39×10^5	4.35×10^8
51-B-7D	Cleanup***	150.	4.57×10^4	6.86×10^6

* Counted with an efficiency of 12.9 disintegrations per count.

** The AgCN precipitate was collected on filter paper and the precipitate and paper ignited together.

*** Includes supernatant solution from 51-B-7A and 51-B-7C.

The last C^{14} recovery was from 57.83 gms. of irradiated Berkeley Be_3N_2 .

The results are recorded in Table VI. Analysis of this material indicated that 19.7 millicuries were present. In this experiment after the boiling CrO_3 solution had been swept with O_2 gas overnight, a small amount of additional carriers were added to be oxidized and the sweeping continued another 24 hours.

The total C^{14} recovery was 18.7 millicuries or 95.0%.

TABLE VI

RECOVERY OF C^{14} FROM Be_3N_2 Sample 51-C. (57.83 gms.)

Sample No.	Carbon Fraction	$BaCO_3$ Weight mg.	$BaCO_3$ Specific Activity - c/m/mg*	Total C^{14} c/m
51-C-4A	CO_2	135.4	1.05×10^6	1.42×10^8
51-C-4AC	HCN	178.2	6.31×10^5	8.71×10^7
51-C-4B	CH_4 -CO	1363.7	1.75×10^6	2.39×10^9
51-C-4C	Oxidizable (first portion)	890.5	6.18×10^5	5.50×10^8
51-C-4E	Oxidizable (second portion)	148.2	1.71×10^5	2.53×10^7
51-C-4D	Cleanup**	143.0	3.33×10^4	4.77×10^6

* Counted with an efficiency of 12.9 disintegrations per count.

** Includes supernatant solutions from 51-C-7A and 51-C-7C.

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IV. C^{12} Contamination of Be_3N_2

One of the original purposes in separating the various C^{14} activities was to prepare high specific activity samples of C^{14} . Since some 60% of the C^{14} activity may be separated in the form of CH_4 (or $CH_4 + CO$), this offers a means for obtaining such specific activities. The initial experiments with Be_3N_2 , however, indicated that appreciable amounts of C^{12} contamination were appearing in this fraction, and only a small part of this contamination came from the NaOH used for the absorption of the CO_2 . In those experiments where N_2 gas sweeping was employed, it was found that the nitrogen (oil-pumped) contained some carbon. This carbon content was eliminated by first passing the N_2 through a combustion tube and NaOH trap before entering the rest of the system. However, this did not completely eliminate the carbon contamination. When a 10 gram sample of Be metal (from which the Be_3N_2 prepared at Berkeley was made) was dissolved in H_2SO_4 and otherwise treated the same as Be_3N_2 , C^{12} was found in volatile fractions. About 0.1% C^{12} was thus present in the Be metal, probably in the form of Be_2C . The amount of C^{12} apparently present in this form both in Berkeley and Argonne prepared Be_3N_2 amounted to about 0.1%. Since Be_3N_2 is 50% by weight Be, it would appear that half the C in the Be_3N_2 is introduced from the N_2 used in the nitride preparation. In order, then, that high specific activities be obtained, purified N_2 and Be metal should be employed.

V. Analytical Notes.

All sample counting was done using a thin (2 mg/cm^2) mica window counter and mounting $BaCO_3$ on plates according to the method described by Yankwich⁽²⁾.

For diluting samples of $BaCO_3$ too active to count directly, a rapid dilution procedure was adopted. A Warburg-type vessel was designed for this purpose. In the inner cup 2 cc. of 6N NaOH was introduced. A small amount (0.1-20 mg.) of active $BaCO_3$ was weighed in a platinum boat and the boat plus

sample placed in the outer portion of the vessel and 5 cc. of water added. Into a small sidearm on the vessel 0.5-1 ml. of 70% HClO_4 was added to be used for the liberation of CO_2 . The cap of the vessel, a 34/28 ground joint fitted with a stopcock, was then put in place and the flask evacuated to 20 cm. Hg absolute pressure. By tipping the vessel the HClO_4 was added to the BaCO_3 suspension. Gently shaking of the vessel on a mechanical shaker for one hour assured complete absorption of the CO_2 into the NaOH. The NaOH was pipetted into a 125 ml. Erlenmeyer flask, the required amount of diluting carbon added as Na_2CO_3 and the BaCO_3 precipitated.

VI. Final Recommended Procedure for C^{14} Recovery from Be_3N_2

The dissolution of Be_3N_2 in H_2SO_4 may be carried out in the following manner in which the C^{14} activity is collected into two fractions, a volatile fraction containing CH_4 , CO , CO_2 and HCN and an oxidizable fraction containing HCOOH , CH_3OH and HCHO .

1. Be_3N_2 is slurried with water in the ratio of 10 ml. water per gram of Be_3N_2 .
2. The slurry is brought to a boil and 8 ml. of 18N H_2SO_4 per gram of Be_3N_2 is slowly added to the boiling solution, while sweeping the system with N_2 . The gas stream is carried through a CuO -filled combustion tube into a 1N NaOH absorption bottle.
3. When all the H_2SO_4 has been added and dissolution appears complete, N_2 sweeping is replaced by O_2 sweeping. An additional amount of 18N-24N H_2SO_4 is added such as to make the solution 6N in H_2SO_4 . The solution is kept boiling and gas sweeping continued for 24 hours, after which the NaOH trap is disconnected and BaCO_3 precipitated.
4. A new NaOH absorption bottle is placed in the system and sufficient CrO_3 is added to the solution to make it 0.2M in CrO_3 . Traces of carriers may be added just before the CrO_3 if desired.

5. The solution is kept boiling and swept with O_2 for 24 hours after which the NaOH trap is disconnected and $BaCO_3$ precipitated.

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- (1) W. F. Libby first reported the production of a relatively large amount of active methane.
 - (2) P. E. Yankwich, "Chemical Forms Assumed by C^{14} Produced by Neutron Irradiation of Beryllium Nitride", BC-36, Feb. 3, 1947.

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