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Chemical Effects of the Nuclear Reaction  $N^{14}(n,p)C^{14}$   
In Various Nitrogenous Compounds

by

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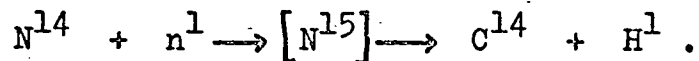
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## I. BACKGROUND AND SCOPE OF THE RESEARCH

### A. Background

When compounds containing nitrogen are subjected to thermal neutron irradiation, the following nuclear reaction occurs:



The recoil energy of the product  $\text{C}^{14}$  atom is 40 Kev., about  $10^4$  times chemical bond energies. This large recoil ensures rupture of all residual chemical bonds, i.e., chemical bonds originally attached to  $\text{N}^{14}$ . The recoiling  $\text{C}^{14}$  atom may then enter chemical combination after dissipating most of its kinetic energy through collisional interactions with atoms, ions, or molecules of the target material. This nuclear reaction and others that produce radioactive carbon provide unique ways to study the chemistry of atomic carbon under varying environmental conditions. The possible chemical combinations of the recoil atom depend initially and principally upon the atomic and molecular constitution of the target and its state of aggregation.<sup>1,2,3</sup> The ultimate distribution of labeled products may depend as well upon concomitant radiation during the neutron irradiation and upon post-irradiation treatment of the target, such as the dissolution of solid targets in solvents.<sup>2,3</sup>

Carbon hot atom chemistry has been studied by nuclear reactions that produce  $\text{C}^{11}$  and  $\text{C}^{14}$ . Wolf and co-workers<sup>4,5,6</sup> at Brookhaven determined the distribution of labeled carbon compounds in ammonia using the reactions  $\text{N}^{14}(\text{p}, \alpha)\text{C}^{11}$  and  $\text{N}^{14}(\text{n}, \text{p})\text{C}^{14}$ .  $\text{C}^{14}$  has a very long half-life (5600 years) and  $\text{C}^{11}$  a very short one (20 minutes). Consequently, the time required for irradiation of the targets is many times greater for the (n,p) than the (p,  $\alpha$ ) reaction, in order that sufficient radioactive product be produced. The extraneous radiation is therefore always large for (n,p) irradiations but can be varied from small to large for the (p,  $\alpha$ ) process, depending upon the proton flux. Cacace and Wolf<sup>6</sup> subjected gaseous, liquid, and solid ammonia to varying proton flux. The carbon-11 products were methylamine, methyleneimine,

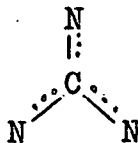
and methane. Increases in radiation dose was attended by a decrease in methylamine and a corresponding increase in methane production. Under comparable proton flux, the ratio of methylamine and methane was larger in liquid and solid ammonia than in gaseous ammonia, suggesting that the radiolytic conversion of methylamine to methane is diffusion controlled. In pile irradiated gaseous ammonia, Yang and Wolf<sup>4</sup> found mainly  $C^{14}H_4$  and small amounts of  $C^{14}H_3NH_2$ , indicating that the large gamma and x-ray flux attending the pile irradiation affected the conversion of methylamine to methane.<sup>2</sup> Cacace and Wolf concluded that methylamine and methyleneimine are produced by hot reactions in ammonia, and that methane is produced primarily in thermal reactions and secondarily in radiolytic reactions.

Yankwich and Vaughan<sup>2</sup> studied the chemistry of  $C^{14}$  produced in crystalline ammonium bromide. The distribution of labeled products provides an interesting parallel with that of  $C^{11}$  in low dose proton irradiated solid ammonia.<sup>6</sup> The yields of methylamine were 79 % and 75 % in ammonium bromide and solid ammonia, respectively, and the yields of methane were 7.5 % and 9 % for these targets, respectively. In addition, formaldehyde was found when the crystalline ammonium bromide was dissolved in water, which suggests that methyleneimine could have been the precursor in the crystals prior to their dissolution.<sup>2</sup> This parallel supports the contention that the radiolytic effect upon the distribution of labeled products is diffusion controlled, and that this diffusion is of negligible consequence in high melting ionic salts.

Considerable insight into the mechanisms of carbon atom reactions has been provided by the gas phase studies of Wolfgang, MacKay, and co-workers,<sup>5</sup> using the nuclear reaction  $C^{12}(\alpha, n)C^{11}$  in hydrocarbon targets. Labeled products were attributed to addition (to multiple bonds), insertion into single bonds, and abstraction reactions.<sup>5,8</sup>

The chemistry of recoil  $C^{14}$  in high melting crystalline targets is complicated by the necessity to dissolve the target in a suitable solvent in order to release the labeled products.

The identity of the entrapped primary recoil product is masked by the possibility of secondary reactions between these products and the solvent. Thus, neutron-irradiated crystalline  $\text{Be}_3\text{N}_2$ <sup>9</sup> dissolved in aqueous sulfuric acid yielded significant proportions of labeled methane, carbon dioxide, formic acid, formaldehyde, hydrogen cyanide, cyanamide, guanidine, urea, and methylamine, each of which was a secondary product of the reaction of crystal-entrapped precursors and the solvent. The presence of guanidine and urea among the post-solution products indicates the existence of surprisingly stable polyatomic precursors,<sup>9</sup> which are



probably pi stabilized.

The spectrum of carbon-14 products of neutron irradiated crystalline nitrogenous targets (aqueous dissolution) depends markedly upon the specific chemical natures of the targets. In ammonium sulfate,<sup>10</sup> the main products were methylamine, formic acid, formaldehyde, and methane. In hydrazine sulfate ( $\text{N}_2\text{H}_6\text{SO}_4$ ),<sup>3</sup> these products plus large yields of guanidine, urea, cyanamide, methylene diamine, and formamidine were found. The richer spectrum of nitrogen compounds produced in hydrazine sulfate is attributable to the weak N-N link in the  $\text{N}_2\text{H}_6^{++}$  ion and to the possible carbon atom insertion in N-H or N-N bonds in  $\text{N}_2\text{H}_6^{++}$ .

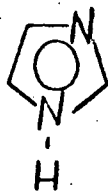
### B. Objectives

The research described in this report is concerned with uncovering the detailed chemistry of recoil carbon-14 in crystalline compounds of nitrogen. The targets currently being studied are the alkali azides ( $\text{NaN}_3$ ,  $\text{KN}_3$ , and  $\text{CsN}_3$ ), hydrazine dihydrochloride ( $\text{N}_2\text{H}_6\text{Cl}_2$ ), and certain nitrogen heterocycles (eg., imidazole). The azides are especially interesting targets for the following reasons: (1) Like  $\text{Be}_3\text{N}_2$ , the possible atomic combinations of the recoil  $\text{C}^{14}$  atom is restricted to nitrogen

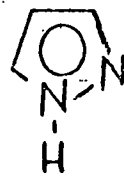
and to a metal atom. (2) Like  $\text{Be}_3\text{N}_2$ , a rich spectrum of post-solution labeled products is observed (see Results, Section A). (3) Unlike  $\text{Be}_3\text{N}_2$ , the alkali azides exhibit high solubility in a number of solvents. Accordingly, the method of selective dissolution can be applied. The chosen target is dissolved in several solvents and the radiocarbon distribution determined in each. Water, liquid ammonia, and liquid sulfur dioxide are suitable solvents for alkali azide targets; at this time, the distribution of labeled products produced by the aqueous dissolution of neutron-irradiated  $\text{KN}_3$  is being studied. Changes in the distribution of products hopefully will give evidence of their crystal-entrapped precursors. Knowledge of the precursors will permit formulation of mechanisms for their formation in the crystal and for their reactions with various solvents.

Unlike the alkali azides, it is possible for stable one-carbon compounds to be formed intact in hydrazine dihydrochloride. The purpose of the present investigation of this target is to separate such products from those produced in reactions with the solvent. Two techniques are being used for this purpose: (1) Selective dissolution, as described above. (2) Thermal decomposition of the target in oxidizing ( $\text{O}_2$ ) and reducing ( $\text{H}_2$ ) atmospheres, followed by gas chromatographic analysis of the resulting products. At this time, the distribution of products of crystalline hydrazine dihydrochloride dissolved in water is being studied.

Rose, MacKay, and Wolfgang<sup>11</sup> discovered  $\text{C}^{11}$ -labeled benzene in gamma irradiated cyclopentadiene ( $\text{C}^{12}(\gamma, n)\text{C}^{11}$ ). This result suggests that  $\text{C}^{14}$ -labeled diazines could be products in thermal neutron irradiated imidazole (I) and pyrazole(II).



(I)



(II)

At this writing, imidazole is being purified preliminary to pile irradiation at Los Alamos.



## II. EXPERIMENTAL PROCEDURES

### A. Irradiation of Targets

1. Potassium Azide. Eastman Kodak  $\text{KN}_3$  (white crystals) was recrystallized three times from thrice distilled water and reagent grade ethanol. The recrystallized product was then oven dried overnight at  $110^\circ \text{C}$ , transferred to the dry box, ground finely in a mortar (Helium atmosphere), and transferred into a quartz ampoule. The quartz ampoule was sealed into the vacuum system (by means of a graded quartz-borosilicate glass seal) and subjected to high vacuum ( $\sim 10^{-5}$  mm.) for eight days. The ampoule was then sealed off (under vacuum) and shipped to Los Alamos for irradiation where it was subjected to thermal neutron irradiation in the Los Alamos Omega West reactor for 120 hours at  $5 \times 10^{12}$   $\text{n cm}^{-1} \text{ sec}^{-1}$ . The ambient reactor temperature was  $90^\circ \text{C}$ . The first specimens sent for irradiation (1 g  $\text{KN}_3$  each) were broken in handling and discarded. In the second attempt, the ampoule was made large enough to accommodate 10 g of  $\text{KN}_3$ ; the irradiation was concluded successfully. The irradiated ampoule was opened in the dry box (helium atmosphere), and stored between experiments under helium in a desiccator inside the dry box.

The radiolysis of  $\text{KN}_3$  in a pile reactor has been studied by Cunningham,<sup>12</sup> who collected the gaseous ( $\text{N}_2$ ) evolute. We calculated the pressure of nitrogen produced by 120 hours of irradiation from Cunningham's results to be  $\sim 1.0$  atm per cc of dead space in the ampoule. When the ampoule was opened in the dry box, no pressure differential was discerned, in good agreement with the calculation.

2. Hydrazine Dihydrochloride. Fisher Certified Reagent  $\text{N}_2\text{H}_6\text{Cl}_2$  was ground finely in a mortar under helium in the dry box, transferred to a quartz ampoule, then vacuum dried ( $< 10^{-5}$  mm) with infrared heating for eight days. The irradiation and post-irradiation treatment was identical to that of the potassium azide. A 10 g specimen was irradiated and is being studied currently.

3. Imidazole. Aldrich Chemical Company Imidazole was recrystallized three times from benzene, air dried for several days, then stored in a desiccator. We plan to encapsulate the sample within the next month in quartz prior to irradiation at Los Alamos.

B. Procedures for Assay of Recoil Carbon Products-Aqueous Dissolution

1. Separation into Classes. Because of the wide spectrum of possible one-carbon products, it is helpful to separate them according to classes, based upon chemical and physical similarities. A sample of target (ca. 0.1 g) is dissolved in water, representative carriers are added, and these carriers are then separated along with carrier-free radiocarbon products having like properties. The following classes are recognized:

Gases: Carriers -  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$ .

Bases: Carriers -  $\text{CH}_3\text{NH}_2$ ,  $\text{H}_2\text{NCN}$ .

Non-Bases: Carriers -  $\text{HCOOH}$ ,  $\text{HCHO}$ .

Non-Gases: Carriers -  $\text{CH}_3\text{NH}_2$ ,  $\text{H}_2\text{NCN}$ ,  $\text{HCOOH}$ ,  $\text{HCHO}$ .

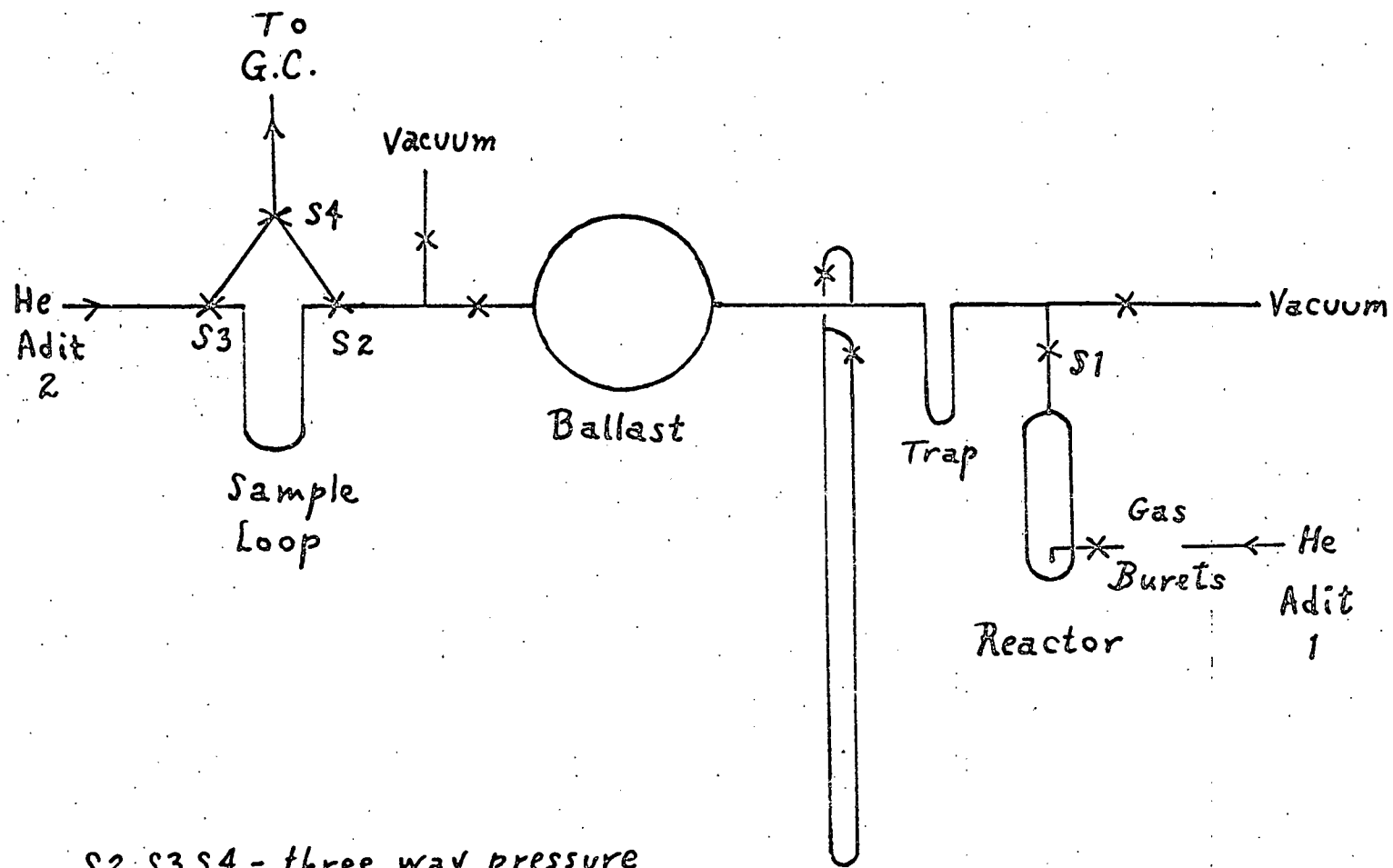
To separate the gases, the target solution is acidified and  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{CH}_4$  are swept through the solution with oxygen into a combustion furnace at  $800^\circ\text{C}$  and into aqueous sodium hydroxide. The gaseous fraction is then collected as barium carbonate. The degassed solution is adjusted to 100 ml and a 25 ml aliquot is oxidized to carbonate by alkaline permanganate and collected as  $\text{BaCO}_3$ . This is the non-gaseous fraction. The remaining solution is then distilled to dryness and the residue and distillate converted to  $\text{BaCO}_3$ . These constitute the basic and non-basic fractions. The radioactivity of each class is determined by converting  $\text{BaCO}_3$  to gaseous  $\text{CO}_2$  in the vacuum line where it is transferred to an ionization chamber for determination by the vibrating reed electrometer.

2. Subdivision of Classes.

a) Gas Chromatographic Method. This procedure is

highly selective and rapid and the radioassay may be carrier-free. The applicability of the method is limited to stable, volatile compounds such as methylamine. Unstable species, such as cyanic acid and methylene diamine, may be estimated from their expected hydrolytic products. The total volatile activity can be determined by "bypass" assay.<sup>6</sup> We are set up to apply this procedure to samples of dissolved azide and hydrazine dihydrochloride targets. The instrumentation consists of a Hewlett-Packard (F. and M.) Model 700-0019 F gas chromatograph, a Cary Model 31 vibrating reed electrometer, and a Cary-Loenco ion chamber oven and high temperature ion chamber (see Equipment Report, Section IV). We have made tests of the chromatographic separation of aqueous solutions of non-radioactive methylamine, formic acid, formaldehyde, and methanol using standard  $\frac{1}{4}$  in x 6 ft stainless steel columns packed with 30 % tricresylphosphate, 10 % diisodecyl phthalate, 10 % SE 30, and 10 % carbowax (all supported by Chromosorb W). Oven temperatures to 135° C were tried. In every case, the large solvent (water) peak masked wholly or partially the solute peaks. To improve the resolution, we plan to lengthen the columns and try other packing materials, such as 20 % cetyl alcohol on KOH-washed firebrick<sup>6</sup> and 20 % diethylhexyl sebacate on Celite.<sup>6</sup>

To assay gases, we have designed and constructed a glass gas sampling system, illustrated schematically in Figure 1. The reactor consists of a flask fitted with a break seal and a sintered glass frit. A weighed sample of target is placed below the break seal, and solvent above it. When the break seal is broken, solvent falls onto and dissolves the sample. Helium gas at one atmosphere pressure is then added through the frit, together with CO<sub>2</sub>, CO, and CH<sub>4</sub> carriers from the gas burets. Stopcock S1 is opened and the sweep gas passes through the trap (-80° C) into the ballast until the pressure within is one atmosphere. Gas samples may then be taken into the sample loop and then swept into the gas chromatograph by helium from Adit 2. The moles of the gas sample is calculable from the calibrated volumes of the system and the



S2, S3, S4 - three way pressure stopcocks

Figure 1. Gas Sampling System

measured pressures of the ballast before and after sampling. The chromatograph output passes first through a TC detector and then through a flow ionization chamber. This system is now ready to be tested.

b) Specific Identification of Individual Labeled Products. In some cases, it is desirable to identify and determine quantitatively certain products. For example, guanidine is relatively non-volatile and is not readily determined gas chromatographically under conditions suitable for more volatile products. Accordingly, the picrate of guanidine may be prepared (with added guanidine carrier), recrystallized repeatedly, and then converted to carbon dioxide in a combustion furnace. Specific procedures for all likely one carbon radioproducts are given in reference 3.

C. Procedures for Assay of Recoil Carbon Products-Non-Aqueous Dissolution

After completing the assay of products in the aqueous solutions of a target, we propose to dissolve samples of the target in liquid ammonia and in liquid sulfur dioxide, and then to introduce these solutions into the chromatograph. Design of a manifold for the vacuum system for the handling of condensable solvents and for dissolving target samples is under consideration. If some products of the dissolution prove to be non-volatile or unstable, it may be necessary to convert from a non-aqueous to an aqueous system for specific assay of such products.

D. Total C<sup>14</sup> Specific Activity of Target Specimens

To determine the total carbon-14 activity per gram of target, about 0.2 g of target is mixed with 0.2 g of oxalic acid and the whole oxidized to carbonate in a combustion furnace. The carbon dioxide is collected as barium carbonate and converted back to carbon dioxide in the vacuum line for radioassay. This procedure is designed to yield all of the carbon-14 activity per gram of target and is then used to compute percent activities of given labeled products per gram of target.

III. RESULTSA. Potassium Azide

Irradiated  $\text{KN}_3$  (0.40 g) was dissolved in water, degassed, and fractionated into classes as described in Section II. The results are given in Table I. These results are preliminary

Table I

Distribution of  $\text{C}^{14}$ -Labeled Products in Potassium Azide: Aqueous Dissolution

<u>Labeled Products</u>	<u>Dis. <math>\text{sec}^{-1} \text{g}^{-1} \text{KN}_3</math></u>	<u>% Activity<sup>d</sup></u>
$\text{CO}_2$	202.9	0.7
$\text{CO} + \text{CH}_4$	409.7	1.3
Total Non-Gaseous	30,329.4	98.0
Total Basic	14,221.4	53.2
$\text{CNNH}_2^{\text{a}}$	8,000	25
Total Non-Basic	16,451.8	46.0
$\text{HCOOH}^{\text{b}}$	1675.8	5.4
$\text{HCHO}^{\text{c}}$	4676.4	15.1
$\text{CO}_2 + \text{CO} + \text{CH}_4 +$ Total Non-Gaseous	30,942.0	

a. Precipitated from ammoniacal  $\text{AgNO}_3$  (ref. 3,10).

b. Mercuric Acetate Oxidation (ref. 2).

c. Hydrogen Peroxide Oxidation (ref. 2).

d. Based upon the sum of the gaseous and non-gaseous activity.

indications of the products produced with the irradiated target dissolved in water. The small yields of the gaseous products  $\text{CO}_2$  and  $\text{CH}_4$  indicates that there is small tendency for the crystal-entrapped entities to undergo either complete oxidation (to  $\text{CO}_2$ ) or complete reduction (to  $\text{CH}_4$ ) by the solvent. The essentially uniform distribution between basic and non-basic products and the comparatively small percentage activities of formic acid, formalde-

hyde, and the intermediate percentage activity of cyanamide indicate a strong resemblance to irradiated beryllium nitride, aqueous sulfuric acid dissolution.<sup>9</sup> The fact that cyanamide does not account for all the basic activity, nor formic acid and formaldehyde the non-basic activity, strongly suggests a rich spectrum of dissolved products. Once this spectrum of products produced by aqueous dissolution is known in full, we can draw preliminary conclusions regarding their precursors in the crystal. Thus, the presence of cyanamide in aqueous solution requires that there be a precursor that contains carbon linked to at least two nitrogen atoms. This same precursor cannot produce cyanamide in a solvent that does not contain hydrogen, and may also react with ammonia in a different way than with water to give a different final product.

#### B. Hydrazine Dihydrochloride

The total activity of  $N_2H_6Cl_2$  was determined by burning two samples of about 0.1 g each in a combustion furnace; oxalic acid was used to supply carbonate (see Section II D). The resulting carbonate was counted as carbon dioxide in an ionization chamber. The total specific activity of the target was found to be  $2.292 \times 10^4 \pm 0.003$  dis.  $sec^{-1} g^{-1}$ . A third sample of 0.20 g target was dissolved in water, degassed, and the degassed solution oxidized to carbonate by alkaline permanganate. The percent activities found for this sample (based upon the independently determined total specific activity) were  $CO_2$ : 7.5 %,  $CO + CH_4$ : 5.0 %, and the total non-gaseous fraction: 29.7 %. About 58 % of the activity was not found. A qualitative radioassay of the  $MnO_2$  residue of the total non-gaseous fraction did not reveal the unrecovered activity. This experiment is currently being repeated. The presence of  $CO_2$  as a dissolution product in the rigorously dried target clearly indicates that some of the final labeled products result from reaction of crystal precursors with the solvent.

Between runs, both samples are stored in glass stoppered bottles in a desiccator within a helium-filled dry box.

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