

Attachment C

Description of Tritium Labeling Process and of Low-Level Radioactive and Mixed Waste Generated from Tritium Labeling Activities at the National Tritium Labeling Facility

The basic tritium reaction processes used at the NTLF are described below, along with the NTLF waste streams. All tritium handling processes at the NTLF are conducted in a set of gloved containment boxes and hoods in LBNL Building 75, Room 103, or in the adjacent chemistry laboratory, Room 75-107. The various pieces of apparatus involved in the high-level tritium handling processes are hard-plumbed to facilitate efficient and safe transfer of material and to prevent release of tritium.

Figures C-1, C-2, and C-3 are three process flow diagrams. In addition, Figure C-4 shows the floor plan of the NTLF, and Figures C-5 through C-8 are photos of the rooms of the NTLF. All figures are appended to this text.

Tritium Labeling Reaction

The tritium incorporation reactions used at the NTLF can be summarized as follows: The compound to be labeled with tritium is dissolved in 1–2 mL of solvent within a small reaction vessel (the largest reaction vessel easily fits in the palm of one's hand). Examples of solvents used in tritium labeling reactions and subsequent chemical derivations include:

acetic acid, acetone, benzene, butane, chloroform, cyclohexene, cyanogen bromide, dibromomethane, dimethoxyethane, dimethyl acetamide, dimethyl formamide, dimethylsulfoxide, dioxane, ethyl acetate, ethanol, heptafluorobutyric anhydride, methanol, methylene chloride, methylmorpholine, pentane, propanolamine, quinoline, tetrahydrofuran, tetramethylethylene diamine, thionyl chloride, toluene, triethylamine, triethylborane, trifluoroacetic acid, and water.

Only a few solvents (usually not more than two) are used in the tritium labeling step of reactions leading to a tritium labeled compound. Many of the solvents listed above are used rarely; e.g., benzene is used only one to four times a year.

Tritium gas is introduced; in many cases a noble metal catalyst (such as palladium on barium sulfate, palladium oxide, etc.) is used; and the labeling reaction takes place, during which tritium atoms are transferred from the tritium gas onto the target substrate (i.e., are incorporated into the structure of the substrate).

Integral Processes and Associated Waste Streams

To complete the tritium labeling process (i.e., to yield a "usable" tritiated product), at least the following additional steps must occur after the tritium incorporation reaction:

- a. The excess tritium gas is separated from the product/solvent solution by transfer onto a carbon trap for eventual capture on a uranium bed and recycling.
- b. The solvent is then separated from the product by evaporation under vacuum and collection in a cold trap for management as mixed waste.
- c. Labile tritium is then removed from the labeled compound and catalyst by rinsing with methanol, which is also evaporated under vacuum and collected in the cold trap.
- d. The catalyst is then separated from the product by filtration using a solvent that is directed to the cold trap.

- e. Sample purification is performed [often using high-pressure liquid chromatography (HPLC)], after which purification solvents are removed from the labeled product by evaporation (also collected in a cold trap and managed as mixed waste).

As part of the overall labeling reaction and equipment cleanup process, tritium gas and the contents of the carbon trap and the plumbing are pumped into a storage tank prior to oxidation using a copper oxide furnace. These waste streams are described in more detail below.

Low-Level Radioactive Waste Streams

Silica Gel. This waste stream is used silica gel contaminated with tritiated water, which has three sources:

Silica Gel 1. During the tritium incorporation process and subsequent manipulations, ambient air in the gloved containment boxes in Room 103 is vented through silica gel to remove tritiated water vapor and thereby minimize air emissions. Used silica gel is periodically replaced with fresh silica gel, and the used silica gel is disposed of in sealed one-gallon metal cans.

Silica Gel 2. Silica gel is used to remove tritiated water vapor from the vacuum pump exhaust. The vacuum pumps are used to evacuate a range of tritium-containing equipment, such as the tritiation reaction equipment, process plumbing, copper oxide furnace, and storage tank. Used silica gel is periodically replaced with fresh silica gel, and the used silica gel is disposed of in sealed one-gallon metal cans.

Silica Gel 3. Silica gel is used to immobilize tritiated water. The copper oxide furnace is used to convert tritium gas into tritiated water to recover residual unreacted tritium and to minimize tritium air emissions. Tritium gas evacuated from the plumbing after the tritiation reaction is stored in a metal storage tank. The gaseous contents of this tank are circulated repeatedly for 16–48 hours through a closed loop over a copper oxide furnace at approximately 550–600°C to completely oxidize the tritium gas to tritium oxide (water). During this process, water vapor is condensed continuously in a cold trap that is part of the closed-loop system. This tritiated water is absorbed onto silica gel in 250-mL bottles, and a sample of the water is taken for documenting tritium content. The bottle is sealed into a plastic bag and placed inside a one-quart can, and the void space is filled with silica gel.

Dry Waste 1. This waste stream consists of normal laboratory dry waste contaminated with tritium during routine laboratory work, and is intended to be compacted. This dry waste consists of Kimwipes™, pipettes, filters, paper, gloves, glass vials or tubes, non-lead metal devices, etc.

Dry Waste 2. This waste stream consists of miscellaneous dry material that becomes contaminated with tritium during workup, analysis, or purification procedures, and contains levels of tritium that cannot be placed into the normal low-level dry waste. This dry waste consists of Kimwipes™, pipettes, filters, paper, glass vials and tubes, stainless steel washers, etc. The waste is placed into one quart ice cream cartons, wrapped in a plastic bag, and then sealed into a one-gallon metal can with silica gel as the void space filler.

Carbon Bed Waste 1. Carbon absorption of tritium gas was introduced in 1990 as a waste minimization step and as a means of further reducing tritium emissions. After the tritium incorporation reaction, approximately 50–80% of the unreacted tritium is transferred from the reaction vessel under vacuum and absorbed onto the liquid-nitrogen-cooled carbon bed. After being closed off from the tritiation reaction vessel, the carbon trap is warmed to room temperature, releasing the tritium gas. The tritium gas is then absorbed onto a uranium bed. Ultimately, the tritium from this bed is returned to the manufacturer for recycling. This process reduces the amount of tritium directed to the copper oxide furnace for oxidation and therefore reduces tritium emissions to the air. The carbon bed is periodically replaced, and the glass ampoule containing the used carbon (about 5 g), contaminated with tritium, is flame-sealed for

disposal. The sealed carbon bed is placed into a one-quart can, the void space is filled with silica gel, and the can is sealed.

It is possible that some of the wastes described above might contain trace organics. Such trace organics, if present, would be in amounts insufficient to cause a characteristic hazardous waste designation. In addition, such trace organics, if present, would not cause an F-listing. Any possible remaining trace solvents would originally have been (1) minute contaminants released during processing; (2) trace residuals left over on equipment during processing and after removal of the spent solvents to the mixed waste stream; and/or (3) in an uncontained gaseous form, and therefore were not spent solvents when they contaminated the wastes. EPA has repeatedly stated in various guidance memoranda that process wastes that become contaminated with small amounts of solvents during processing are not within the scope of the spent solvent listings or mixture rule.

Low-Level Radioactive Mixed Waste Streams

There are three sources of mixed waste generated from the tritium labeling, purification, and analysis processes at the NTLF.

Mixed Waste Solvents in Ampoules or Bottles (Inventory Waste). This waste stream was a mixture of silica gel and organic solvents from the tritiation reaction and sample purification (STP LB-W125 inventory waste). Organic solvents from the labeling reaction were transferred under vacuum and collected into glass ampoules or bottles (containers). Solvents from several reactions were generally captured in the same container of silica gel, with 0.5–10 mL of solvent generated from each reaction. Methanol was generally used to wash the product after the tritiation reaction in order to remove labile tritium from the reactant. The used methanol was also transferred under vacuum and collected in the same container. In addition, solvents from purification processes (HPLC, column chromatography, etc.) were transferred under vacuum and collected in the same container. Each container was sealed after the tritiated solvents were added to silica gel. The container was placed inside a one-quart can, the void space was filled with silica gel, and the can was sealed.

Characterization. Both radiological and chemical characterization of this waste are based on process knowledge and sample analysis. During the treatability study, the ampoules or bottles were broken inside a vacuum extraction vessel (see Figure 1 in the Delisting Petition), and the spent solvent mixtures were extracted from the silica gel using a vacuum extraction system. The solvent mixtures were then oxidized using the catalytic chemical oxidation (CCO) system. Chemical constituents identified in the collected liquid mixtures included:

acetic acid, acetic anhydride, acetone, acetonitrile, benzene, chloroform, cyclohexylamine, dibromomethane, dimethyl formamide (DMF), dioxane, ethyl acetate, ethanol, hexane, isopropanol, methanol, methyl acetate, methylene chloride, pyridine, tetrahydrofuran (THF), tetramethylethylene diamine (TMEDA), toluene, triethylamine, water

Generation rate. This waste stream was LBNL inventory waste and was oxidized during the treatability study, which commenced in June 1996. The complete inventory consisted of 59 cans of waste generated from 1993 through to February 1996.

Mixed Waste Solvents. This waste stream includes organic solvents from the tritiation reaction and sample purification. Organic solvents from the labeling reaction are transferred under vacuum into a cold trap. Solvents from several reactions are generally accumulated, with 0.5–10 mL of solvent generated from each reaction. Methanol is generally used to wash the product after the tritiation reaction in order to remove labile tritium from the reactant. The used methanol is also transferred under vacuum and collected in the same container. In addition, solvents from purification processes (HPLC, column chromatography, etc.) are transferred under vacuum and collected in the same cold trap. At regular intervals the contents of the cold

trap are transferred through a sealed transfer line to an appropriate container for analysis followed by oxidation.

Characterization. Chemical characterization of this waste stream is based on both process knowledge of which chemicals are being used in tritium labeling and purification processes and GC/MS analysis of the spent solvents. Chemical constituents identified in the spent solvent mixtures are similar to those identified above. The solvent mixtures are oxidized using the catalytic chemical oxidation (CCO) system.

Generation rate. We anticipate generation of approximately 1–4 liters of high-tritium-content liquid mixed waste per year.

Synthetic Reactions, Purification, and Analysis Solvents. After tritium incorporation, further reactions may be conducted with the labeled material. These reactions create mixed waste with lower tritium content than the labeling solvents. The tritium-labeled product is usually purified by some type of chromatography, often high-pressure liquid chromatography (HPLC). Reverse-phase HPLC analyses often rely on methanol/water or acetonitrile/water mixtures to effect separations. In some cases a methanol (< 100%), water, and 0.1% trifluoroacetic acid or acetic acid mixture is used as the HPLC solvent. Normal phase separations rely on solvents such as hexane, THF, ethyl acetate, or ethyl ether. In rare instances, chlorinated solvents such as chloroform or methylene chloride are required as the HPLC solvent. NMR analyses are generally conducted in deuterated solvents, including methanol, benzene, water, THF, or dioxane.

Characterization. The waste generated from synthetic reactions, purification processes, and analytical activities is a mixture of flammable solvents and water. Documentation of the chemical constituents of the waste are based on a combination of process knowledge and GC/MS analytical information.

The constituents of this waste are flammable solvents and water, with the bulk of the volume being acetonitrile and methanol, but also including hexane, tetrahydrofuran, benzene, ethyl acetate, and isopropanol. Acids such as acetic acid and trifluoroacetic acid are used to improve HPLC separations, and are found at low concentrations in the waste (e.g., 0.1%). On rare occasions chlorinated solvents such as chloroform and methylene chloride are used.

Waste is placed in either a glass or plastic container for transfer to the HWHF. The tritium activity per container is assessed by liquid scintillation counting, and the chemical constituents are verified by GC/MS analysis.

Generation Rate. The NTLF will generate approximately 80 liters of liquid waste per year from synthetic reactions, purification and analyses.

Figure C-1

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Figure C-2

Figure C-3

**Figure C-4. Floor Plan of the NTLF.
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Figure C-5. NTLF Room 75-103: Treatability Study Glove Box

Figure C-6. NTLF Room 75-107: NTLF Instrument Laboratory

Figure C-7. NTLF Room 75-106: NTLF NMR Laboratory

Figure C-8. NTLF Room 75-103: NTLF Tritiation Reaction Glove Boxes