

TRITIUM BASICS & REGULATORY INFORMATION

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Exam Preview:

- 1. According to the reference material, tritium has a low coefficient of diffusion. It readily diffuses through porous substances such as rubber and can also diffuse through metals.
 - a. True
 - b. False
- 2. As tritium decays in a container of constant volume at a constant temperature, the tritium partial pressure decreases and the partial pressure of ³He increase. The pressure in the container approaches _____ that of the original container pressure.
 - a. 2X
 - b. 3X
 - c. 4X
 - d. 6X
- 3. Tritium in the form of T2O may be difficult to store for long periods in part due to its corrosive properties. Experiments with T2O indicate that pure T2O is corrosive and as the percentage of T2O in the subject water increases so does its corrosivity.
 - a. True
 - b. False
- 4. According to the reference material, Radioactive hydrogen, referred to as tritium has one proton and _____ neutrons in the nucleus.
 - a. 4
 - b. 3
 - c. 5
 - d. 2

- 5. The Hazard Category of a nuclear facility is based on threshold quantities of radiological material inventory. According to the reference material, to be classified as a Category II nuclear facility, the facility tritium inventory must be > ___ grams.
 - a. 10
 - b. 20
 - **c.** 30
 - d. 40
- 6. Tritium at high concentrations in liquid form is generally measured using scintillation counter. Low concentrations of tritium in liquid form are generally measured by using calorimetry.
 - a. True
 - b. False
- 7. Due to the body's ready adsorption of tritium in the form of tritiated water, exposure to tritiated water in air is on the order of ______ times more hazardous than exposure to gaseous tritium (HT, DT, and T2).
 - a. 5,000
 - b. 10,000
 - **c**. **15,**000
 - d. 20,000
- 8. Gaseous tritium at high pressure takes up less space but is more difficult to contain in part due to the potential for tritium and helium embrittlement of the vessel materials. This embrittlement increases the probability of a tritium leak or catastrophic container failure.
 - a. True
 - b. False
- 9. According to the disposal conditions section of the reference material, depending on the initial pressure, the water loading on the sieve and the tritium concentration in the water, the overpressure can exceed 1.5 atmospheres within _____. LANL is developing a path forward concerning transportation and disposal associated with this issue on molecular sieve.
 - a. Hours
 - b. Days
 - c. Months
 - d. Years
- 10. Ignitable wastes are solid wastes that exhibit any of the following properties: liquids with a flashpoint of less than _____°F; solids that are capable of causing fires through friction, absorption of moisture, or spontaneous chemical changes; ignitable compressed gases, as defined in 49 CFR 173.300; or oxidizers, as defined in 49 CFR 173.151.
 - a. 95
 - b. 100
 - **c.** 120
 - d. 140

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FOREWORD

Tritium handling practices have evolved over several decades at Department of Energy (DOE) tritium facilities. The objective has been to accomplish required tritium work while minimizing and controlling the exposure of workers, the public, and the environment to tritium. This document provides guidance for the handling, storing, and shipping of tritium.

This Standard is approved for use by all DOE elements and their contractors. DOE technical standards, such as this Standard, do not establish requirements. However, all or part of the provisions in a DOE standard can become requirements if either they are explicitly stated to be requirements in a DOE requirements document or the organization makes a commitment to meet the Standard in a contract or in an implementation or program plan. The DOE implementation plan to address the Defense Nuclear Facilities Safety Board (DNFSB) Recommendation 2005-1 committed to implement interim storage packaging provisions for tritiated materials, which are discussed in Section 6.6. These packaging provisions are requirements for tritium facilities under the auspices of the National Nuclear Security Administration (NNSA) and the Environmental Management Program Office (EM).

The author of the Standard, Bill Weaver of DOE Office of the Chief of Nuclear Safety (CNS), wishes to acknowledge the contributions of the Savannah River National Laboratory (SRNL) and the Savannah River Site (SRS) staff, Paul Blanton, Paul Korinko, Greg Staack, and Steve Xiao; Ken Keeler and Mike Rogers of the Los Alamos National Laboratory (LANL); Diane Spencer of the Lawrence Livermore National Laboratory (LLNL); CNS staff members Steve McDuffie, Marlene Fitzpatrick, and Elaine Beacom; Nazir Kherani of the University of Toronto; Armando Antoniazzi of Kinectrics, Inc.; Genevieve Weaver of Penn State; Tracy Getz, Robin Henderson and Robert Waxman of Office of The General Counsel; and Steve Zobel, a staff member from the DOE Office of the Associate Under Secretary for Environment, Health, Safety and Security.

ACRONYMS

AEA	Atomic Energy Act of 1954				
AI	Alveolar-Interstitial region				
ALARA	As Low As Reasonably Achievable				
ALI	Annual Limit on Intake				
AMAD	Activity median aerodynamic diameter				
AMD	Activity median diameter				
ASCE	American Society of Civil Engineers				
ASME	American Society of Mechanical Engineers				
ASN	French Nuclear Safety Authority				
ANSI	American National Standards Institute				
ARAR	Applicable or Relevant and Appropriate (CERCLA)				
AU	Office of the Associate Under Secretary for Environment, Health, Safety and Security				
AWQC	Ambient water quality criteria				
bb	bronchiolar region				
BB	Bronchial region				
Bq	Becquerel				
BS	Bone surface				
BTSP	Bulk Tritium Shipping Package				
BZA	Breathing zone air (sampler)				
CANDU	CANada Deuterium Uranium pressurized reactor				
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act				
CFR	Code of Federal Regulations				
Ci	Curie				
CMD	Count median diameter				
CoC	Certificate of Compliance				
CRC	Combustion Research Center				
CWA	Clean Water Act				
DCS	Derived Concentration StandardD&D Decontamination and Decommissioning				
DAC	Derived Air Concentration				
DBA	Design Basis Accident				
DBE	Design Basis Earthquake				
DCF	Dose Conversion Factor				
DCFo	Dose Conversion Factor based on observed activity				
DCG	Derived Concentration Guide				
DNFSB	Defense Nuclear Facilities Safety Board				
DOE	U.S. Department of Energy				
DOT	U.S. Department of Transportation				

DPM	Disintegrations per minute				
DSA	Documented Safety Analysis				
E ₅₀	Committed Effective Dose				
EDL	Economic Discard Limit				
EPCRA	Emergency Planning and Community Right-to-Know Act				
EPDM	Ethylene Propylene Diene Monomer				
EPA	Environmental Protection Agency				
EH	Office of Environment, Safety and Health				
EIS	Environmental Impact Statement				
EM	Office of Environmental Management				
ET	Extrathoracic				
f ₁	fraction of radionuclide absorbed from the GI tract				
FCA	Fire Control Area				
FDTAS	Field Deployable Tritium Analysis System				
FY	Fiscal Year				
GI	Gastrointestinal				
HEPA	High-Efficiency Particulate Air				
HDPE	High-Density Polyethylene				
HIVES	Highly Invulnerable Encased Safe				
HMR	Hazardous Material Regulations				
HSV	Hydride Storage Vessel				
HSWA	Hazardous and Solid Waste Amendments				
HTV	Hydride Transport Vessel				
HVAC	Heating, Ventilation, and Air Conditioning				
IAEA	International Atomic Energy Agency				
IATA	International Air Transport Association				
ICRP	International Commission on Radiological Protection				
IMT	Insoluble Metal Tritide				
INL	Idaho National Laboratory				
ISM	Integrated Safety Management				
ITER	International Thermonuclear Experimental Reactor				
ITP	Insoluble Tritiated Particulate				
keV	Kiloelectron volt				
LANL	Los Alamos National Laboratory				
LDPE	Low-Density Polyethylene				
LDR	Land Disposal Restriction				
LLD	Lower Limit of Detection				
LLI	Lower Large Intestine				
LLNL	Lawrence Livermore National Laboratory				
LN	Lymph Node				
LSA	Low Specific Activity				
LSC	Liquid Scintillation Counting				

LLW	Low-level waste
MAR	Material at Risk
mCi	Millicurie
MCL	Maximum Contaminant Level
mm	Millimeter
mrem	Millirem
NFPA	National Fire Protection Association
NMMSS	Nuclear Materials Management and Safeguards System
NNSS	Nevada National Security Site
NP	Nasal Passage Region
NPDWR	National Primary Drinking Water Regulation
NPH	Natural Phenomena Hazard
NRC	U.S. Nuclear Regulatory Commission
NRPB	National Radiological Protection Board
OBT	Organically Bound Tritium
OPI	Office of Primary Interest
ORR	Operational Readiness Review
OH-	Hydroxide
Р	Pulmonary Parenchyma Region
PC	Performance Category
РСВ	Polychlorinated biphenyl
PMR	Palladium Membrane Reactor
PPE	Personal Protective Equipment
PPPL	Princeton Plasma Physics Laboratory
psia	pounds per square inch absolute
psig	pounds per square inch gauge
PSO	Program Secretarial Officer
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl chloride
PV	Product Vessel
RCRA	Resource Conservation and Recovery Act
RCS	Radiological Control Standard
RM	Remainder Organ
RMA	Radioactive Materials Area
RTF	Replacement Tritium Facility
RWP	Radiological Work Permit
S	Stomach or specific source organ (used with SEE)
SAES	Societá Apparecchi Elettrici e Scientifici
SAF	Self Absorption Factor
SAM	Surface Activity Monitor
SAR	Safety Analysis Report
SCO	Surface Contaminated Object

SDWA	Safe Drinking Water Act
SEE	Specific Effective Energy
SEL	Seismic Equipment List
SEM	Scanning Electron Microscope
SEP	Seismic Evaluation Procedure
SI	Small Intestine
SMT	Stable Metal Tritide
SNL	Sandia National Laboratory
SNLL	Sandia National Laboratory, Livermore
SNM	Special Nuclear Material
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
SSCs	Structures, Systems, and Components
STC	Special Tritium Compound
Sv	Sievert
Т	Tissue
ТВ	Trachea and Bronchial Region
TFG	Tritium Focus Group
TRL	Tritium Research Laboratory, Sandia National Laboratory
TWD	Technical Work Document
TSD	Treatment, Storage, and Disposal
TSR	Technical Safety Requirement
UB	Urinary Bladder
UHMWPE	Ultra-High-Molecular-Weight Polyethylene
ULI	Upper Large Intestine
WETF	Weapons Engineering Tritium Facility, Los Alamos National Laboratory
WSRC	Washington Savannah River Company

1.0 INTRODUCTION

There are several tritium-handling publications, including International Atomic Energy Agency (IAEA) Technical Report Series, Number 324, *Safe Handling of Tritium*, published in 1991, in addition to the French Nuclear Safety Authority (ASN) and U.S. Department of Energy (DOE) publications. Furthermore there are internal documents associated with ITER. Most of the tritium publications are written from a radiological protection perspective. This Standard provides more extensive guidance and advice on the full range of tritium operations, shipping, and storage.

1.1 Purpose

This Standard can be used by personnel involved in the full range of tritium handling, from receipt to ultimate disposal. Issues are addressed at each stage of handling.

1.2 Scope

This Standard provides useful information for establishing processes and procedures for the receipt, storage, assay, handling, packaging, and shipping of tritium and tritiated wastes. It includes discussions and advice on compliance-based issues and adds insight to those areas in which DOE guidance is unclear. It is intended to be a "living document" that is revised periodically. For example, planning for and implementing contamination control as part of normal operation and maintenance activities are important functions in any tritium facility. The best practices from around the DOE complex are planned for inclusion in each revision of this Standard.

1.3 Applicability

DOE facilities range from small facilities engaged in operations using a few millicuries (mCi)to largescale Hazard Category II Nuclear Facilities.. Guidance in this Standard applies to any scale of operations.

1.4 Key References

- DOE G 151.1-4, Response Elements.
- DOE O 151.1C, Comprehensive Emergency Management System.
- DOE O 232.2, Occurrence Reporting and Processing of Operations Information
- DOE O 243.1B, Chg. 1, Records Management Program.
- DOE O 410.2, Management of Nuclear Materials
- DOE O 420.1C, Facility Safety.
- DOE G 420.1-1A, Nonreactor Nuclear Safety Design Guide for use with DOE O 420.1C, Facility Safety.
- DOE O 435.1, Chg. 1, Radioactive Waste Management.
- DOE M 441.1-1, Nuclear Material Packaging Manual.
- DOE G 441.1-1C, Admin Chg. 1, Radiation Protection Programs Guide for Use with Title 10, Code of Federal Regulations, Part 835, Occupational Radiation Protection.
- DOE G 450.4-1C, Integrated Safety Management System Guide.
- DOE O 450.2, Integrated Safety Management.
- DOE P 450.4A, Integrated Safety Management System Policy.
- DOE O 458.1, Admin Chg. 3, Radiation Protection of the Public and the Environment.
- DOE O 460.1C, Packaging and Transportation Safety.
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- DOE-STD-1121-2008, Internal Dosimetry.
- DOE-STD-3009-2014, Preparation Guide for U.S. Department of Energy Nonreactor Nuclear Facility Safety Analyses.
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- DOE/MLM-3719, Health Physics Manual of Good Practices for Tritium Facilities.
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- DNFSB/TECH 34, Confinement of Radioactive Materials at Defense Nuclear Facilities.
- American National Standard. N 13.14 1994. Internal Dosimetry Programs for Tritium Exposure -Minimum Requirements
- ANSI N13-1-1999, Sampling and Monitoring of Airborne Radioactive Substances from the Stacks and Ducts of Nuclear Facilities
- ANSI N13.12-1999, Surface and Volume Radioactivity Standards for Clearance.
- ANSI N14.5-2014, Leakage Tests on Packages for Shipment.
- ANSI Z88.2, Practices for Respiratory Protection.
- ASCE 7-95, Minimum Design Loads for Buildings and Other Structures.
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- 10 CFR Part 71, Packaging and transportation of radioactive material.
- 10 CFR 71 Subpart H, Quality Assurance
- 10 CFR Part 830, Nuclear safety management.
- 10 CFR Part 835, Occupational radiation protection.
- 36 CFR, Chapter XII, National Archives and Records Administration.
- 40 CFR Part 61, National emission standards for hazardous air pollutants.40 CFR Part 261, Identification and listing of hazardous waste.40 CFR Part 262, Standards applicable to generators of hazardous waste.
- 40 CFR 302.4, Designation of hazardous substances.
- 49 CFR Part 172, Hazardous Materials Table, Special Provisions, Hazardous Materials Communication, Emergency Response Information, Training Requirements, and Security Plans.
- 49 CFR Parts 100-180, DOT Hazardous Materials Regulations.
- 49 CFR 171.8, Definitions and Abbreviations.
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2.0 TRITIUM

Isotopes are elements that have the same atomic number (same number of protons in the nucleus) but different atomic mass (i.e., the total of protons and neutrons in the nucleus). There are three naturally occurring isotopes of hydrogen. Ordinary hydrogen, referred to as protium $\begin{pmatrix} 1 \\ 1 \end{pmatrix}$ H, atomic mass of 1), is the most abundant element in the universe and has one proton in the nucleus. Heavy hydrogen, referred to as deuterium $\begin{pmatrix} 2 \\ 1 \end{pmatrix}$ H or D, atomic mass of 2), makes up about 0.015 percent of the hydrogen, and has one proton and one neutron in the nucleus. Radioactive hydrogen, referred to as tritium $\begin{pmatrix} 3 \\ 1 \end{pmatrix}$ H or T, atomic mass of 3), has one proton and two neutrons in the nucleus. Refer to Appendix A for basic information on tritium, its properties, and compounds.

2.1 Radioactive Properties

Tritium is a beta emitter. It decays to ³He by emitting a beta particle (electron) and an antineutrino from one of the neutrons in the nucleus. The energy of the beta particle varies from 0 to 18.6 kiloelectron-volts (keV) with an average energy of 5.69 keV. For scientific purposes, the generally accepted value for the half-life of tritium, as measured by Mound Laboratories, is 12.323 ± 0.004 years (4500.88 ± 1.46 days). For DOE accountability purposes, the half-life of tritium is 12.33 + 0.006 years. Figure 2-1 shows the rate of decay of one mole of tritium over six half-lives.



1) Figure 2-1: the rate of decay of one mole of tritium over six half-lives

2.2 Physical Properties

Tritium gas is colorless, odorless, tasteless, and radioactive. Tritium has a high coefficient of diffusion. It readily diffuses through porous substances such as rubber and can also diffuse through metals.

As tritium decays in a container of constant volume at a constant temperature, the tritium partial pressure decreases and the partial pressure of ³He increase. The pressure in the container approaches twice that of the original container pressure. The rate of pressure change over time is shown in Figure 2-2.



2) Figure 2-2: Pressure versus time in a container of tritium

Other properties of tritium are listed below. Additional characteristics are given in Appendix A.

- Atomic weight = 3.01605
- Gram molecular weight = 6.03210
- Diameter of a tritium atom (approximate) = 1.1 Angstroms
- Dissociation energy, T₂ to 2T = 4.59 eV
- Ionization energy, T to T+ e^- = 13.55 eV
- Half-life = 12.323 +/- 0.004 years

In this Standard, tritium in the form of the oxide (HTO, DTO, and T_2O), unless otherwise specified, is HTO. Likewise, tritium in its elemental form (HT, DT, and T_2) is HT.

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2.3 Chemical Properties

2.3.1 General Properties

The electronic configuration of tritium is the same as protium and deuterium. The chemical properties of the isotopes are also the same. The rates of reaction vary for the different isotopes due to the difference in the atomic masses. Additionally, the energy provided by the radioactive decay of tritium provides the activation energy required so that some reactions will occur with tritium that will not occur with deuterium or hydrogen.

Hydrogen is present in almost all materials. If tritium is present in a material containing hydrogen, the tritium atoms will exchange with hydrogen atoms to form a tritiated molecule of the material.

2.3.2 General Behavior

A chemical restatement of Newton's Third Law of Motion, Le Chatelier's Principle, states that when a system at equilibrium is subjected to a perturbation, the response will be such that the system eliminates the perturbation by establishing a new equilibrium. When applied to situations when the background tritium levels are increased in nature the reactions will be shifted to the right in order to adjust to the new equilibrium conditions by readjusting to the isotopic ratios.

 $CH_4 + 2T_2 \iff CT_4 + 2H_2$ $2H_2O + T_2 \iff 2HTO + H_2$

The inverse situation also applies in that, when the background tritium levels are decreased, the reactions will be shifted back to the left, by again readjusting to the isotopic ratios; i.e.,

 $CH_4 + 2T_2 \iff CT_4 + 2H_2$ $2H_2O + T_2 \iff 2HTO + H_2$

When Le Chatelier's Principle is applied to a sequential set of reactions like those depicted above, it shows that exchange reactions tend to behave as springs, constantly flexing back-and-forth, readjusting to changing energy requirements, in a constantly changing attempt to establish a new set of equilibrium conditions. Since elemental hydrogen, regardless of its form can be expected to dissolve to some extent in virtually any material, Le Chatelier's Principle can be applied to the solubility reactions as well on solubility reactions.

2.3.3 Behavior Model

Starting with the assumption that all three hydrogen isotopes are in equilibrium with each other, in the nominal isotopic ratios and applying Le Chatelier's Principle. From both, we get the relationship,

 $2H_2 + 2D_2 + 2T_2 \iff H_2 + HD + D_2 + HT + DT + T_2$

In the Environment, virtually all of the tritium exists as water vapor. Applying this situation for the natural conversion to water and/or water vapor gives

 $2H_2O + 2D_2O + 2T_2O \iff H_2O + HDO + D_2O + HTO + DTO + T_2O$

Furthermore, assume that the surfaces of all bound objects are coated with a series of monomolecular layers of water vapor and that the innermost layers of water vapor are very tightly bound to the actual surface, that the intermediate layers of water vapor are relatively tightly to relatively loosely bound, and that the outermost layers of water vapor are very loosely bound.

When an overpressure of tritium is added to the system, a perturbation is introduced and Le Chatelier's Principle indicates that the tritium levels in the mono-molecular layers of water will be shifted to the right. Tritium is incorporated first into the loosely bound, outer layers, then into the intermediate layers, and finally into the very tightly bound, near surface layers.

When the overpressure is removed, the system experiences a new perturbation. In this case, however, the perturbation is in the negative direction, and the system becomes the entity that contains the excess tritium. Le Chatelier's Principle, in this case, indicates that the tritium levels in the mono-molecular layers of water will be shifted back to the left. The tritium that had previously been incorporated into the mono-molecular layers now begins to move out of the layers, in an attempt to return to background levels. The movement of tritium into the mono-molecular layers of water vapor is generically referred to as "plate-out." The movement of tritium out of the mono-molecular layers of water vapor is generically referred to as "outgassing."

2.3.4. Plate-Out

When the concentration gradients have been small and/or the exposure times have been short, only the outermost, loosely bound, mono-molecular layers of water vapor will be affected. Under such circumstances, the surface contamination levels will range from no detectable activity to very low levels; that is, up to a few tens of disintegrations per minute per 100 square centimeters (dpm/100 cm^2). Since only the outermost mono-molecular layers are affected, and since these layers are easily removed by a simple wiping, the mechanical efforts expended to perform decontamination on

such surfaces will, if any, be minimal. When the concentration gradients have been relatively large and/or the exposure times have been relatively long, the affected mono-molecular layers will range down into the intermediately bound layers (i.e., the relatively tightly to relatively loosely bound layers). Under such circumstances, the surface contamination levels will range from relatively low to relatively high (i.e., from a few hundred to a few thousand dpm/100 cm²). Because the tritium has now penetrated beyond those levels that would normally be easily removed, mechanical efforts expended to decontaminate such surfaces will become more difficult. When the concentration gradients have been large and/or the exposure times have been long, the affected mono-molecular layers will range all the way down into the very tightly bound layers. The tritium will have penetrated down into the actual surface of the material. Under such circumstances, the surface contamination will range from relatively high to very high levels (i.e., from a few tens of thousands to several hundred thousand dpm/100 cm²), and that mechanical efforts expended to decontaminate such surfaces could be very difficult.

2.3.5 Outgassing

The phenomenon of outgassing is rarely a problem under the first of the exposure situations described above (i.e., situations in which the concentration gradients have been small and/or the exposure times have been short). However, when systems that have been exposed to even small amounts of tritium for long-to-very-long periods of time are suddenly introduced to room air, or any sudden change in its equilibrium situation, reactions can be thought of as springs, and the initial phenomenon of outgassing can be described as damped harmonic motion. Under such circumstances, therefore, a relatively large, initial "puff" of HTO will be released from the monomolecular layers of water vapor, followed by a relatively long, much smaller trailing release. Because several curies of HTO can be released in a few seconds, and several tens of curies can be released in a few minutes, the speed of the "puff" portion of the release is quick. The duration of the trailing portion of the release can be lengthy. Depending on the concentration gradients involved and/or the time frames involved in the plate-out portion of the exposure, the trailing portion of the release can easily last from several days to several months or even years. The general derivation of tritium room concentration discussed in section 4.1.2 includes terms associated with a long outgassing period although they are commonly ignored in most practical applications. As the trailing portion of the release asymptotically approaches zero, the outgassing part of the release becomes too small to measure on a real-time basis, and the tritium levels involved in any given release can only be measured by surface contamination measurement techniques.

2.3.6 Material Contamination

When an overpressure of tritium is added to the system (i.e., the surface of an idealized material), Le Chatelier's Principle indicates that the tritium levels in the mono-molecular layers of water will be shifted to the right; that is,

$$2H_2O + 2D_2O + 2T_2O \rightarrow H_2O + HDO + D_2O + HTO + DTO + T_2O$$

22 ENGINEERING-PDH.COM | NUC-132 | Tritium is incorporated first into the loosely bound, outer layers, then into the intermediate layers, and finally into the very tightly bound, near-surface layers. As the tritium loading in the nearsurface layers builds, the disassociation processes that proceed normally as a result of the tritium decay make an overpressure of tritium available in a mono-molecular form (i.e., as T). Relative to the normal amounts of elemental hydrogen that can be expected to be dissolved in the material, the availability of excess tritium in the mono-molecular form represents a different type of perturbation on a system, and the available tritium begins to dissolve into the actual surface of the bulk material. As the local saturation sites in the surface of the bulk material begin to fill, the tritium dissolved in the surface begins to diffuse into the body of the bulk material; at that point, the behavior of the tritium in the body of the bulk material becomes totally dependent on the material in guestion. Elemental hydrogen, regardless of its form (H2, D2, T2, and all combinations thereof), can be expected to dissolve to some extent in virtually all materials. As a general rule, the solubility of tritium in pure metals and/or ceramics has a minimal effect, at normal room temperatures and pressures, except for the possibility of hydrogen embrittlement. For alloyed metals, such as stainless steel, similar considerations apply, again, at normal room temperatures and pressures. For alloyed metals, however, additional consideration is given to the possible leaching of impurities from the alloyed metal, even at normal room temperatures and pressures. In LP-50 containment vessels, for example, the formation of relatively large amounts of tritiated methane (i.e., up to 0.75 percent mole percent of CT4) has been noted after containers of high-purity tritium have been left undisturbed for several years. The formation of the tritiated methane, in this case, has long been attributed to the leaching of carbon from the body of the stainless steel containment vessel.

Under increased pressures (e.g., from a few tens to several hundred atmospheres), however, the general rules no longer apply for, in addition to the possibility of hydrogen embrittlement and possible leaching effects, helium embrittlement is also possible. Helium embrittlement tends to occur as a result of the dissolved tritium decaying within the body of the material, the resultant migration of the helium-3 atoms to the grain boundaries of the material, the localized agglomerations of the helium-3 atoms at the grain boundaries, and the resultant high-pressure build-ups at these localized agglomerations. Under increased temperature situations, the matrix of solubility considerations becomes even more complicated because virtually all solubility reactions are exponentially dependent on temperature. In the case of diffusional flow through the walls of a containment vessel, for example, it can be assumed that steady-state permeation will have been reached when

$$\frac{D*t}{L} = 0.045$$

where D = the diffusion rate in cm^2/sec , t = the time in seconds, and L = the thickness of the diffusion barrier. For type 316 stainless steel, the value for the diffusion rate is

$$D = 4.7 * 10^{-3} e^{\left(-\frac{12,900}{RT}\right)}$$

23 ENGINEERING-PDH.COM | NUC-132 | and the corresponding value for R, in the appropriate units, is 1.987 cal/mole K. With a nominal wall thickness of 0.125 inches (i.e., 0.318 cm), this Equation indicates that it will take about 875 years to reach steady-state permeation, at a temperature of 25° C. At 100° C, the time frame will be reduced to about 11-years, and at 500° C, it only takes about 12-hours.

2.4 Biological Properties

2.4.1 Gaseous Tritium and Tritiated Water

The body does not readily absorb H₂, HT, HD, D₂, DT, or T₂ from inhaled gases or through the skin. If inhaled in elemental form, almost all tritium in the gas is exhaled. Only a very small fraction is retained in the lungs.

Tritium in the form of water (HTO, DTO, and T_2O) is absorbed through the skin and in the lungs from inhaled gases. Tritium in water form is readily retained in the body and remains with a biological half-life of approximately 10 days. Due to the body's ready adsorption of tritium in the form of tritiated water, exposure to tritiated water in air is on the order of 10,000 times more hazardous than exposure to gaseous tritium (HT, DT, and T_2).

The Derived Air Concentration (DAC) for tritium is the airborne concentration that, if inhaled over a one-year period, would produce approximately a 5-rem dose to the "average" worker. The DAC is derived by the formula:

DAC	=	ALI/2400 DAC = derive	ed air concentration (µCi/ml)			
ALI	=	annual limit on intake (Ci)				
2400	=	breathing volume for the average worker over 1 year in m ³				
	=	.02 m³/min x 60 min/hr x 40 hr/wk x 50 wk/yr				

The DACs for elemental tritium and tritiated water^{1,2} are listed in Table 2-1.

¹ U.S. Environmental Protection Agency's Federal Guidance Report No. 11, Table 1 *Limiting Values of Radionuclide Intake and Air Concentration and Dose Conversion Factors for Inhalation, Submersion, and Ingestion*, September 1988

² 10 CFR Part 835, Appendix A

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	μCi/ml	Bq/m ³
HT	2E-01	9E9
HTO	2E-05	7E05

1) Table 2-1: Derived air concentrations for tritium and tritiated water

2.4.2 Special Tritium Compounds

Special tritium compounds (STCs) are defined as any compound, except for H₂O and H₂, that contains tritium, either intentionally (e.g., by synthesis) or inadvertently (e.g., by contamination mechanisms). Examples of STCs are metal tritides and organically bound tritium.

Special tritium compounds differ from the more common forms of tritium (elemental tritium and tritium oxide) in a variety of characteristics, including particle sizes, chemical behavior, and biological properties when ingested, absorbed, or inhaled into the human body. The physical properties of special tritium compounds may make their detection, characterization, and subsequent assessments of hazards and exposure effects (i.e., individual dose assessments) difficult. As a result of these unique behaviors, specific guidance has been developed (see Appendix E) to facilitate the development and implementation of appropriate protective programs.

Although the DOE radiological protection community has been aware of STCs for many years, to date their impact has been limited by the design features that are incorporated into DOE facilities that handle significant quantities of tritium. These design features include various forms of material containment and control, such as gloveboxes and high-efficiency particulate air (HEPA)-filtered ventilation systems that effectively prevent significant releases of STCs to occupied areas of the workplace or the environment. Recently, sensitivity to STC contamination has been increased as a result of recent DOE activities involving decontamination and decommissioning of older facilities. These activities may compromise the effectiveness of the installed design features and allow releases of STC contamination to the surrounding areas. Such releases may cause exposures to individuals in the area and releases of STCs to the environment, both on- and off-site. In light of such experiences, DOE suggests that individuals setting up programs for radiological control of STCs contact sites that either work, with or have worked, with tritium to learn of their experiences with STCs.

Appendix E (formerly DOE-HDBK-1184-2004) has been prepared by DOE to assist its employees and contractors in developing and implementing radiation protection programs that will provide adequate protection against the hazards presented by special tritium compounds.

2.5 Preferred Forms

Most tritium in the DOE complex exists as a gas, in the form of tritiated water, or as a metal tritide. The preferred form of tritium is dependent upon its use in a process, length of storage, or its classification as a waste.

2.5.1 Characterization of Tritium Forms

2.5.1.a Gaseous Tritium

The use, transfer, storage, and shipment of gaseous tritium at or near atmospheric pressure have been safely used for over fifty years in the DOE complex. Gaseous tritium at or near atmospheric pressure occupies 22.414 L/mole at 0°C, and approximately 24.2 L/mole at room temperature, and requires approved packages for shipment in either Type A or B quantities. If the containers are not properly designed or if they are damaged, the gas can leak from the container into the environment.

Gaseous tritium at ambient pressure is easily handled by most gas handling systems and is a good source for general-purpose use. At low pressure and temperature, the tritium does not penetrate deeply into the container wall. Helium and tritium embrittlement of the container wall is not a significant issue at low pressures even after several years of exposure. As tritium decays, the pressure in the container increase (see Figure 2-2) due to the generation of the monatomic gas ³He. This pressure increase, at most, would only be double the initial pressure. This factor has to accounted for during the initial design of the vessel so it does not become an issue later.

Gaseous tritium at high pressure takes up less space but is more difficult to contain in part due to the potential for tritium and helium embrittlement of the vessel materials. This embrittlement increases the probability of a tritium leak or catastrophic container failure. Unloading high-pressure gas requires specifically designed systems and experienced, skilled operators.

2.5.1.b Metal Tritides

Metal tritides reduce the overall volume of the stored tritium, but some of the finely divided metals used are pyrophoric. Some metals form low-melting-point alloys with the materials used in the construction of the metal tritide containers. Others require extremely high temperatures in order to recover tritium from the material. Depending on the individual design, the pressure in some vessels, containing tritium as a metal hydride, may increase by more than a factor of two during the life of the vessel. This can become problematic for shipping and disposal. Tritium as a hydride occupies very little volume but the decay helium-3, in some hydrides, will pressurize any open volume in the vessel. If the vessel is designed with little expansion volume then the helium-3 pressure can be significantly more than twice the loading pressure.

2.5.1.c Tritiated Water

Tritium in the form of T₂O may be difficult to store for long periods in part due to its corrosive properties. Experiments with T_2O indicate that pure T_2O is corrosive and as the percentage of T2O in the subject water increases so does its corrosivity. This corrosiveness is likely due to tritium oxide generating free radicals (OH⁻) from radiolytic decomposition of water in addition to extra energy from beta decay impinging on surrounding molecules. Additionally, pure T_2O , like distilled H_2O , will dissolve many materials. No data currently exist that quantify the degree of corrosiveness; therefore, there is no basis to definitively state that the U.S. Environmental Protection Agency (EPA) threshold of corrosivity (i.e., a characteristic of hazardous waste), defined in Title 40 of the Code of Federal Regulations (CFR), Section 261.22, is not exceeded. The author believes, however, that only a high-purity product, and not waste, would have a reasonable chance of exceeding this threshold. Pursuant to the RCRA regulations, it is the responsibility of the waste generator to determine if that waste is subject to the hazardous waste requirements [40 CFR 262.11]. A broader discussion of the relationship between tritiated water and hazardous wastes is contained in Section 3.1.3. Note that for transportation purposes, DOT has specific defining criteria for corrosive materials that is different from that of the EPA; see 49 CFR 173.136-137. Dilute tritiated water recovered from tritium removal systems, although not at the EPA threshold has still proven to be somewhat corrosive, due in part to the other constituents. In a severe case, storage of tritiated water recovered from tritium removal systems in liquid form at concentrations as low as a few curies per milliliter has corroded through the weld area of stainless steel vessels after only a few days of exposure. In this specific example, it is probable that the extreme corrosive nature of this dilute tritiated water was due, in large measure, to chlorine contamination of the catalyst in the tritium removal system. This corrosion is evidently inhibited by absorption of the tritiated water on clay or in molecular sieve material.

Figure 2-3 provides a comparison of the various concentrations of tritiated water found throughout the nuclear industry.

2.5.2 Identity of Common Forms

Tritium is usually supplied in gaseous or uranium tritide form. Other forms are also available but are not in common use for bulk shipment.

2.5.2.a Gas

In gaseous form, tritium is usually supplied at a purity of 90 to 95 percent tritium (99 percent in research applications) with deuterium and protium as the primary impurities.



3) Figure 2-3: Comparison of aqueous tritium levels found in the nuclear industry

2.5.2.b Metal Tritides

The use of metal tritide storage beds is one of the most convenient ways of handling tritium. The metal tritide beds have different operating parameters and characteristics, and there are advantages and disadvantages in use of the different materials.

2.5.2.b (1) Uranium

Uranium is currently the most useful material for general-purpose tritium storage beds. The equation form for the dissociation pressure of uranium tritide, deuteride, and hydride for the pressure in millimeters of mercury is, $P_{mm} = 10^{(-A/T +B)}$, where A and B are parameters listed in Table 2-3. Washington Savannah River Company (WSRC) has determined that in the hydride transport vessel (HTV), for a uranium-to-tritium ratio of 1:2.9 in the HTV vessel, the equation is

 $P_{atm} = 10^{(-4038.2/T + 6.074)}$

At room temperature, tritium in the presence of uranium powder forms uranium tritide. The tritium partial pressure in the bed is very low. As a result, at room temperature the bed acts as a vacuum pump that getters all of the hydrogen isotopes. The impurity gases that may be present, such as ³He, N₂, O₂, or Ar, either remain in the overpressure gas in the bed or react with uranium to form stable compounds. Inert gases, such as Ar, will remain in the overpressure gas, and can be removed by pumping off with a vacuum pump after the pressure has stabilized; however, ³He cannot be pumped off without first heating the bed. N₂ and O₂ will react chemically with the uranium to form stable uranium compounds in the bed, and, therefore, cannot be pumped off at all.

As the temperature of the bed is increased, the tritium partial pressure increases as a function of temperature. Depending upon the U:T ratio, it can reach a pressure of around 500 pounds per square inch absolute (psia) at 600°C. The tritium may be transferred into and out of manifolds, containers, etc., by heating the bed and then cooling it to room temperature. The general form of the equation for the dissociation pressure, P, in millimeters of mercury (mm) for uranium hydride, deuteride, and tritide is:

$$log Pmm = -A/T + B$$

or
$$Pmm = 10 - (A/T(K)) + B$$

where
$$T = temperature (K)$$

The values for A and B for hydrogen, deuterium, and tritium, determined by several different investigators, are listed in the following paragraphs, and the results are shown in Table 2-2 and plotted in Figure 2-4. Figure 2-5 is a plot of the general characteristics of uranium hydride, deuteride, and tritide.

					Temperature
					(°C) required to
		Temperature			generate a
Metal		Range (°C)	Α		pressure of
Tritide	Reference	Investigated	(/Kelvin)	В	1 atmosphere
UH₃	Spedding, et al.	260 to 430	4500	9.28	430
	Destriau & Seriot	243 to 412	4255	9.08	415
	Wicke & Otto	200 to 430	4450	9.20	434
	Mogard & Cabane	500 to 650	4480	9.20	435
	Libowitz & Gibb	450 to 650	4410	9.14	432
UD ₃	Spedding, et al.	unspecified	4500	9.43	414
	Destriau & Seriot	unspecified	4401	9.01	445
	Wicke & Otto	unspecified	4500	9.40	417
UT ₃	Flotow & Abraham	unspecified	4471	9.461	408
	WSRC	unspecified	4038.2	6.074	unspecified

2) Table 2-2: Dissociation pressure equation parameters for uranium hydride, deuteride, and tritide



4) Figure 2-4: Dissociation pressure for uranium, hydride, deuteride, and tritide


5) Figure 2-5: Plot of a good fit curve for the dissociation pressure of uranium hydride, deuteride, and

Each time the tritium is cycled into the system manifolds, it picks up impurity gases. These impurities collect in the bed overpressure gas and may be pumped off to remove them after each heating/cooling cycle. Active impurity gases, such as oxygen and nitrogen, are irreversibly removed by reaction with the uranium.

Disadvantages to using uranium tritide beds are: 1) uranium powder is pyrophoric; 2) the generation of significant tritium pressure requires a high temperature that results in permeation of tritium through the vessel wall; and 3) the capacity is also permanently reduced by exposure to active impurity gases.

2.5.2.b (2) Palladium

Palladium is a metallic element of Group 8 in the Periodic Table. The symbol for palladium is Pd, the atomic number is 46, the atomic weight is 106.42, and the melting point is 1554.9°C.

At room temperature, palladium absorbs up to 900 times its own volume in hydrogen. It diffuses easily through heated palladium; this is one means of purifying the gas. Finely divided Pd is a good catalyst, and is used for hydrogenation and dehydrogenation reactions.

Palladium powder is currently the second most-used material for general-purpose tritium storage beds. Palladium can be obtained in powdered form and loaded directly into the container used for the metal tritide bed. Palladium was used extensively at both Lawrence Livermore National Laboratory (LLNL) and Sandia National Laboratories–Livermore (SNLL) in the tritium storage beds.

When the tritium is exposed to the powder, it dissolves in the palladium powder with a maximum Pd:T ratio of approximately 0.7. Palladium powder is not pyrophoric, but it has a higher tritium partial pressure than uranium at room temperature.

At room temperature, tritium, deuterium, and protium dissolve in the palladium powder and the tritium partial pressure in the gas over the powder is approximately 50 torr. The overpressure increases as a function of temperature. As the temperature of the palladium is increased by heating the bed, the tritium partial pressure increases as a function of the temperature and reaches a pressure of around 750 psia at 350°C. The general form of the equation for the dissociation pressure, P, in millimeters of mercury (mm) for palladium hydride, deuteride, and tritide is:

log Pmm = (-A/T + B)or Pmm = 10 (-A/T + B)

where

T = temperature(K)

The values for A and B for hydrogen and deuterium determined by different investigators are given in Table 2-3, and the equations developed by the different experimenters over the temperature range they investigated are plotted in Figure 2-6.

Metal Tritide	Reference	Temperature Range (°C) Investigated	A	В
PdH _x	Gillespe & Hall	0 to 180	1835.4	7.3278
	Gillespe & Hall	200 to 300	1877.82	7.483
	Ratchford & Castellan	unspecified	2028.2	7.9776
	Wicke & Nernst	-78 to 175	2039	7.65
PdDx	Gillespe & Downs	to 300	1696.11	7.5138
	Wicke & Nernst	unspecified	1940	8.00

3) Table 2-3: Dissociation pressure equation parameters for palladium hydride and deuteride

The ³He generated as a result of decay of the tritium absorbed in the palladium is trapped in the palladium and is not released until the bed is heated or until the T:³He ratio reaches a particular value. ³He generated as a result of decay in the overpressure gas is not absorbed in the palladium and remains in the overpressure gas. Most impurities do not react with, and are not gettered by, the palladium powder. These impurities accumulate in the overpressure gas as the bed is used to support operations.



6) Figure 2-6: Dissociation pressure of palladium hydride and deuteride The generation of significant pressure at low temperature (750 psia at 350°C) is the primary advantage of palladium. The primary disadvantage of palladium is the high partial pressure of tritium over the powder at room temperature (50 torr at room temperature).

2.5.2.b (3) Titanium

Titanium is a metallic element in Group 4 of the Periodic Table. The symbol is Ti, the atomic number is 22, the atomic weight is 47.90, and the melting point is 1660°C. It is a low-cost metal, and can absorb and store tritium in a compact solid form at a tritium pressure of approximately 1E⁻⁷ torr.

Titanium hydride, TiH₂, in powder form, is a black metallic dust that is less prone to spontaneous ignition in air than the parent metal. Finely divided titanium hydride is reported to ignite at 440°C and its dust is an explosion hazard, which dissociates above 288°C. Titanium hydride is used in powder metallurgy, hydrogen production, foamed metals, glass solder, and refractories, and as a gas getter in the electronics industry. Titanium tritide in solid or massive form is stable in air for extended periods of time. Titanium tritide is considered an insoluable STC and must be completely contained. Titanium retains the decay helium up to a concentration of 0.3 He atom per Ti atom. SRS³, Ontario Power Generation (formerly Ontario Hydro)⁴⁵⁶⁷⁸, and Korea Hydro and Nuclear Power Company Limited (KHNP) have selected titanium as their long-term storage medium. The SRS titanium beds have an expected useful life of about 10 years, while the Ontario Power Generation and KHNP beds are expected to be in operation for over 20 years. The Canadians are not space-restricted, and therefore do not load their beds to the degree that SRS does. Additionally, longer times to maximum helium retention ratio (0.3 He:Ti) can be achieved by diluting the tritium concentration with deuterium or protium.

2.5.2.b (4) Zirconium

Zirconium is a metallic element of Group 4 in the Periodic Table. The symbol for zirconium is Zr, the atomic number is 40, and the atomic weight is 91.22. Zirconium is flammable as a powder and melts at 1850°C. Zirconium is a hard, lustrous, grayish metal that is strong and ductile, and is used in alloys, pyrotechnics, welding fluxes, and explosives.

Zirconium hydride ZrH₂ is a flammable gray-black powder and is used in powder metallurgy, nuclear moderators, and as a reducing agent. Finely divided zirconium hydride suspended in air will ignite at 430°C. Zirconium hydride contains about twice as many hydrogen atoms per unit of volume as liquid hydrogen. Massive zirconium hydride is stable in air for extended periods of time at

³ Heung, L.K., *Titanium for Long Term Tritium Storage*, WSRC-TR-94-0596, December 1994.

⁴ Drolet, T.S., Wong, K.Y., and Dinner, P.J., *Canadian Experience with Tritium – The Basis of a New Fusion Project*, <u>Nuclear Technology/Fusion</u>, Vol. 5, January 1984.

⁵ Kherani, N.P., and Shmayda, W.T., *Bulk Getters for Tritium Storage*, Ontario Hydro Research Division.

⁶ Shmayda, W.T. and Kherani, N.P., *On the Unloading of Titanium Getter Beds*, Ontario Hydro Research Division, Report No. 85-118-K, October 2, 1985.

⁷ Kherani, N.P., and Shmayda, W.T., *Titanium Sponge for Immobilization Tritium Containers*, Ontario Hydro Research Division, Report No. M85-120-K, December 19, 1985.

⁸ Noga, J.O., Investigations of Titanium and Zirconium Hydrides to Determine Suitability of Recoverable Tritium Immobilization for the Pickering Tritium Removal System, Ontario Hydro Research Division, Report No. 81-368-K, November 12, 1981.

temperatures below 600°C. Additionally, SRNL has conducted research on the effect of over pressurization of hydrogen on Zircaloy-4⁹. Note that zirconium tritide is considered an insoluble STC and must be completely contained.

Certain DOE radioactive zirconium fines (which are destined for disposal) are managed as D001 mixed ignitable wastes. These radioactive zirconium fines are pyrophoric under 40 CFR 261.21(a)(2); i.e., they are capable of causing fire through friction. If zirconium used for tritium storage beds is destined for disposal (i.e., constitutes a waste), the Resource Conservation and Recovery Act (RCRA) hazardous waste characteristic of ignitability must be analyzed, per 40.CFR.261.21. A broader discussion of RCRA hazardous waste is contained in Section 3.1.3.

2.5.2.b (5) Societá Apparecchi Elettrici e Scientifici (SAES) Getters

During the late 1990s, investigations were conducted concerning the use of SAES getters to remove tritium from tritium-contaminated gaseous waste streams. These investigations have concentrated on getters that cracked the gases containing tritium and removed the resulting free tritium from the gas stream. The primary advantage of these getter systems is that tritium is not converted by the tritium removal system to the more radiotoxic tritiated water. Additionally, the tritium can be recovered in gaseous form from the getter, purified, and reused.

The materials tested include those manufactured in the form of pressed pellets that can be used in low-pressure, drop-packed bed reactors designed for the size required by the application flow rate and lifetime requirements. The basic strategy implemented in prototype systems was to crack the molecules on a hot getter and remove the nontritiated reactive impurities that interfere with the performance of the hydrogen gettering alloys. Following purification, the gas is passed through a hydrogen gettering bed to remove the hydrogen isotopes from the gas stream. This philosophy worked well, and has gained acceptance for use in inerted gloveboxes.

⁹ Morgan, Jr., G.A. and Korinko, P.S. *The Adsorption of Hydrogen on Low Pressure Hydride Materials* Conference Proceedings, Material Science and Technology 2011, October 16-20, 2011.

2.5.2.b (6) LaNi₅-Based Alloys

The use of lanthanum-nickel hydrides has been a continuing topic of interest; promising results for hydrogen storage have been reported¹⁰. Promising results were also reported in the literature in 1988¹¹. Earlier research at Mound, however, in the 1970s and early 1980s indicated that lanthanum-nickel-based alloys were not appropriate for tritium service due, in part, to disproportionation. When cycled, the LaNi₅ had a tendency to separate to form the parent metals (La or Ni) or different alloys. The disproportionation tended to change the pressure, concentration, and temperature properties of the metal/alloy mix and increase the quantity of tritium bound in the heel that was not easily recoverable. However, research at Savannah River National Lab (SRNL) has shown that "Substitution of aluminum for a portion of the nickel in LaNi₅ was found to lower the hydrogen plateau pressure and allow LaNiAI alloys to be tailored to specific storage applications." SRNL found that the substitution of aluminum in LaNi₅ had the added benefit of stabilizing the alloy against disproportionation. Decay of absorbed tritium to ³He does cause an "aging" effect, which limits the useful life of LaNiAI alloy as a tritium storage material to less than about 10 years¹². Subsequently, SRNL determined that LaNiAl. 75 (LaNi_{4.25}Al_{0.75}) is a type F rather than a type S dissolution, thereby allowing relaxation of radiological controls in use for this hydride¹³. See Appendix E for further discussion of radiological controls associated with STCs.

2.5.2.c Absorbed Water

Molecular sieve material is used in tritium removal systems for removal of water contaminated with tritium. Systems such as tritium removal systems, effluent recovery systems, and cleanup systems remove tritium from a gas by oxidizing and/or cracking the tritium-containing components. The free tritium then combines with oxygen in the gas stream to form tritiated water. The gas stream is then cooled to room temperature, and the water contained in the gas stream, including the tritiated water, is removed by a molecular sieve trap.

A molecular sieve depending on type and size/mesh, can hold up to 25% water by weight., and the sieve may be regenerated to remove the water so it can be reused. Tritiated water absorbed on

¹⁰ LaNi₅ Intermetallic Hydride, extracted from State-of-the-Art Review of Hydrogen Storage in Reversible Metal Hydrides for Military Fuel Cell Applications, Gary Sandrock, Ph.D., for the Department of the Navy, Office of Naval Research, N00014-97-M-0001, July 24, 1997.

¹¹ Hydrogen Isotope Sorption Properties of LaNi₃Mn₂ Alloy as a Candidate for the Tritium Storage Material, T. Ide et al., Sumitomo Heavy Industries, Ltd. and H. Yoshida et al., Japan Atomic Research Institute, published in *Fusion Technology*, September 1988.

¹² Kirk Shanahan, et al., *Tritium Aging Effects in LaNi*_{4.25}*Al*_{0.75}, WSRC-MS-2002-00564, Rev. 1, November 12, 2002.

¹³ Farfán, E.B, LaBone, T.R., Staack, G.C., Cheng, Y-S., Zhou, Y., and Varallo, T.P. *Determination of In Vitro Lung Solubility and Intake-to-Dose Conversion Factor for Tritiated Lanthanum Nickel Aluminum Alloy*. <u>Health Physics</u>, 103(3):249-254; 2012.

molecular sieve is not corrosive and may be stored in this way for long periods without damage to the container wall.

Water contaminated with HTO is also stored on clay. The common method of solidification of tritium-contaminated wastewater for disposal is to solidify the water on clay so that it can be classified as solid waste. Clay will hold approximately 60 percent water by volume. Waste disposal sites generally require the use of 100 percent more clay than required to solidify the water, and, as a result, the water is generally limited to 30 percent of the volume of the clay for waste solidification purposes. Water absorbed on clay is not corrosive and may be stored for long periods without damage to the container wall.

2.5.3 Summary

2.5.3.a Best for Storage Conditions

The decision on storage media is a function of the storage length and frequency of unloadings. Media range from gas (short timeframe, many movements) to titanium (long timeframe, few or no movements) with other media (e.g., uranium) in between. Although the preferred form for storage is a metal tritide and the least desirable form is a liquid, there are always exceptions to this rule. Factors to be considered include:

Solid (Metal Tritides): Unless already in solid form, tritium is not readily available as a solid metal tritide and requires conversion before storage. Metal tritides can store large quantities of tritium without occupying large volumes, but the storage containers are more complex than gaseous storage containers. Depending upon the metallic tritide chosen for storage, there are both advantages and disadvantages. Titanium tritide is very stable, even when exposed to air, but it is more difficult to recover tritium from the titanium than from other metals. Stored as uranium tritide, the tritium can be easily and quickly recovered and provides for the removal of most impurities that might accumulate during storage. However, uranium powder is also pyrophoric, and starts releasing ³He after a few months.

Liquid (T₂O): Tritium is not readily available in water form and requires conversion before storage. Tritium is on the order of approximately 10,000 times more hazardous in oxide form than in elemental form. It takes very little space, but is difficult to store due in part to the potential corrosivity of the water. The tritiated liquid can be solidified on clay, molecular sieves, or polymers prior to disposal. In either case, the final decision is a function of the quantity of tritium and the tritium concentration of the water to be stored.

Gas (T₂): Tritium is readily available in gaseous form. A great deal of experience exists on the design of gaseous tritium storage systems. As a gas it takes up more volume than as a liquid or solid, but can be more easily released to the environment if the tritium container is breached. Gas also presents flammability vulnerability.

2.5.3.b Best for Operations/Process

Solid (Metal Tritides): When used as a gas in research where tritium is issued and returned as a gas, there are advantages to the use of hydride beds for storage. The heating/cooling cycle used to store and recover tritium from the bed results in routine removal of the ³He and other impurities from the tritium supply. It can be reused in other processes at reasonably high purity. Additionally, storage as a metal tritide allows the bed to be used as a pressure generator and, in some cases, eliminates the need for mechanical pumps.

Liquid (T₂O): Unless the process itself uses tritium in the form of water, there are no advantages to storage of tritium in liquid form for operations.

Gas (T₂): Tritium is primarily used in gaseous form, purified in gaseous form, assayed in gaseous form, and is more useful in this form than any other form. As a result, storage in gaseous form for operations is appropriate.

2.5.3.c Best for Disposal Conditions

Disposing of tritium in the form of a liquid waste or gaseous waste is difficult. Generally speaking, waste tritium is converted to solid form so that the material can be disposed of as a solid low-level (radioactive) waste, assuming there is no RCRA hazardous component.

Solid (Metal Tritide): It is possible to dispose of gaseous tritium by converting it to a solid metal tritide. However, the disposal sites require that the metal tritide not be pyrophoric. If it is in particulate form, the metal tritide must be contained to meet disposal site requirements.

Liquid (T₂O): If the waste is in gaseous form, the tritium is normally removed from the gas mixture and reused. If the concentration of tritium in the waste gas is too low to make recovery of the tritium economically worthwhile, the waste gas is sent to an effluent processing system, where the tritium is removed before the gases are released to the environment. Most current effluent processing systems remove tritium from the waste gas by converting it to water. The water is then solidified on molecular sieve, clay, mixtures of clay and cement, or Stergo[®] superabsorbent (discussed in Section 8.1.4.b (2)), and is then packaged as solid waste and shipped to the disposal site. Noted that tritium contaminated water on molecular sieve will develop increasing pressure over time due to the radiolysis of the water by tritium decay. Depending on the initial pressure, the water loading on the sieve and the tritium concentration in the water, the overpressure can exceed 1.5 atmosphers within months. LANL is developing a path forward concerning transportation and disposal associated with this issue on molecular sieve.

Gas (T_2) : Waste disposal sites generally will not accept packages containing pressurized gases or those in which a potential exists for generating 1.5 atmospheres (absolute) of pressure over time.

3.0 BASIC TRITIUM REGULATORY INFORMATION

Due to its more hazardous profile, most of the regulatory interest in tritium is concerned with the oxide form. Figure 2-3 pictorially illustrates various concentrations and regulatory setpoints. The radiological materials inventory for tritium accounting purposes may not coincide with the radiological materials inventory for documented safety analysis (DSA) purposes, which may not coincide with the radiological materials inventory for Environmental Impact Statement (EIS) purposes. This is due to prescribed allowances for excluding various portions of the inventory, as discussed in Sections 3.1 and 3.3. DOE regulations concerning tritium (along with other radionuclides) can be found in 10 CFR Part 830, which contains associated Quality Assurance (QA) Program requirements to be met.

3.1 Tritium Accountability and Environmental Considerations

3.1.1 Radiological Materials Inventory

The Atomic Energy Act of 1954, as amended (AEA) describes three categories of materials: byproduct, source, and special nuclear material (SNM). DOE O 474.2, Admin Chg. 3, *Nuclear Material Control and Accountability describe two categories of accountable nuclear material*: SNM and Other. Tritium is listed in Attachment 2, Table B in the Order, as an "other" category of accountable nuclear material that must be controlled and accounted for financial and nuclear materials management purposes and protected in a graded manner consistent with its strategic and monetary importance. Since tritium is not listed in Table A of DOE O 474.2, Attachment 2, it is not managed as SNM, and Table C, Graded Safeguards Table is not used to determine categorization and attractiveness levels. The reportable quantity of tritium is one gram. The quantity of tritium in accountable items must be reported to the hundredth of a gram (when at or above the reportable quantity level) for NMMSS input. Personnel should always check the latest revision to the Order to verify the current limits. Tritium contained in water (H₂O or D₂O) that is used as a moderator in a nuclear reactor is not an accountable nuclear material.

Material management at DOE facilities is different than Nuclear Material Management. DOE O 410.2, *Management of Nuclear Materials*, provide requirements for managing nuclear materials. Disposition of nuclear material can control how tritium can be released. If it falls below accountable levels it can be treated as waste, otherwise it must be dispositioned according to DOE O 410.2T. The Office of Nuclear Materials has issued an integration guidance document, *Nuclear Material Disposition Process Guidance*, issued September 2013,¹⁴ for use in this topical area. See section 8.2.3 for further discussion.

Quantities of tritium contained in waste may be part of the facility accountable nuclear materials inventory until it is removed from the facility to a waste accumulation area for storage or to a waste packaging area for packaging.

DOE requires tritium facilities with more than a reportable quantity of tritium (1-gram) establish material control and accountability systems to provide accurate nuclear materials inventory information, DOE Order 410.2. Transactions exceeding the reporting quantity for tritium (1-gram) must be reported to NMMSS, per DOE O 474.2. The facility tritium inventory and scrap levels of tritium must be minimized consistent with the operational needs and safeguards practices of the facility. A well-designed facility materials control and accountability system includes, in part, the following:

¹⁴ Nuclear Materials Guidance document phase 1 for implementing DOE Order 410.2, *Nuclear Material Management*, Office of Nuclear Materials Integration, NNSA. September 2013.

- Accounting system database;
- Account structure;
- Records and reports;
- Physical inventories
- Periodic physical inventories;
- Special inventories;
- Inventory verification/confirmation measurements;
- Measurements and measurement control;
- Organization;
- Selection and qualification of measurement methods;
- Training and qualification of measurement personnel;
- Measurement systems;
- Measurement control;
- Material transfers;
- External transfers;
- Internal transfers;
- Material control indicators;
- Shipper/receiver difference assessment;
- Inventory difference evaluation;
- Evaluation of other inventory adjustments;
- Documentation and reporting forms;
- Procedures and requirements.

3.1.2 Limits for Tritium in Drinking Water and the Environment

The current National Primary Drinking Water Regulation (NPDWR) for beta- and photon-emitting radionuclides is 4 millirem (mrem) per year. The maximum contaminant level (MCL) for tritium in drinking water systems, used to demonstrate compliance with the 4 mrem/year level regulatory criterion as determined by the EPA (40 CFR Part 141) is 20,000 pCi/L (740 Bq/L). Assuming that one drank 2 L per day, using the ICRP 30-based Derived Concentration Guides (DCGs), a concentration of 80,000 pCi/L (2,960 Bq/L) would produce a dose of 4 mrem per year. Other international standards are based on 10 percent of the public dose limits as recommended by ICRP 60 and ICRP 103; however, implementation varies by nation. Example drinking water values include: the World Health Organization, based on ICRP 60 of 270,000 pCi/L (10,000 Bq/L) and the Canada Nuclear Safety Commission of 189,000 pCi/L (7,000 Bq/L). The European Commission (EC) has a 2,700 pCi/L (100 Bq/L) screening value for tritium to determine if more detailed evaluations are necessary and to determine if tritium in combination with other radionuclides may exceed the 0.1 mSv/year (10 mrem/y) recommended dose criterion.

The EPA MCL of 20,000 pCi/L for tritium was promulgated in 1976 based on radiological risk estimates from the Biological Effects of Ionizing Radiation I report (BEIR I), dose factors from

Handbook 69, *Maximum Permissible Concentrations of Radionuclides in Air and Water for Occupational Exposure*, published by the National Bureau of Standards in 1959 and amended in 1963, and various assumptions regarding drinking water exposures. In 1991, as part of an effort to update and revise the drinking water standards contained in 40 CFR Part 141, the EPA evaluated potential doses from 20,000 pCi/L using Federal Guidance Report No. 11 dose factors based on ICRP 30, and determined that it would result in a 69,000 pCi/L limit; however, based on its policy for implementing the Safe Drinking Water Act Amendments of 1996, the EPA left unmodified the 20,000 pCi/L limit, over DOE objections.

NRC requirements (not applicable to DOE facilities) for their licensees include compliance with NRC public dose limits by calculating total effective dose equivalent to the individual likely to receive the highest dose and demonstrate that it does not exceed public dose limits or demonstrate that annual average concentration of effluents at the boundary of the unrestricted area does not exceed values in 10 CFR Part 20, Appendix B, Table II. The values for liquid effluents are based on an assumed ingestion of 2 L/day over the year and a dose constraint of 50 mrem/ year. DOE O 458.1, Radiation Protection of the Public and the Environment, similarly requires DOE contractors to monitor releases and calculate potential doses to members of the public to demonstrate that DOE activities are being managed so that public dose is as far below the 100 mrem in a year primary dose limit as is practical. DOE Technical Standard DOE-STD-1196-2011, Derived Concentration Technical Standard, contains a table of Derived Concentration Standards (DCSs) (which replaced DCGs), which are concentrations of radionuclides in water that would cause a 100 mrem in a year dose if an individual drinks 730 L (2 L/ day). The tritium DCS is 0.0019 µCi/ ml (approximately 2.000,000 pCi/ L); however, unlike NRC, DOE does not permit the use of concentration guidelines as a means of compliance. Dose estimates are necessary to demonstrate compliance and the DCSs are provided as a tool to assist in that evaluation. Although it is expected that discharges would be significantly less than DCS values, exceeding the DCS does not necessarily violate DOE O 458.1 if dose calculations demonstrate that public doses, as a result of all pathways, are as low as reasonably achievable (ALARA) below the primary dose limit (this includes all sources and pathways, and a 25 mrem/yr constraint, which is usually applied to single sources). DOE O 458.1 also requires that DOE facilities manage discharges so as not to cause public drinking water systems downstream to exceed the drinking water maximum contamination limits in 40 CFR Part 141, National Primary Drinking Water Regulations.

Neither DOE (DOE O 458.1) nor NRC (10 CFR Part 20, Subpart E) requirements for cleanup or clearance of real property have specific concentrations or dose limits for tritium in groundwater. Tritium must be considered along with all other radionuclides and pathways when demonstrating that the dose to the public will be as far below 25 mrem/ year as is reasonably achievable, per DOE O 458.1. However, DOE's requirement that DOE activities not cause existing public drinking water systems to otherwise exceed drinking water standards also applies to cleanup and clearance.

Although rarely a health concern, the detection of tritium in groundwater is of interest to many, and is sometimes a contentious issue both within and outside the DOE complex. For example, the identification of an onsite groundwater tritiated plume at Brookhaven National Laboratory

43 ENGINEERING-PDH.COM | NUC-132 | contributed to the decision to close the High Flux Beam Reactor (the source of the tritium in the plume), even though the plume did not present a significant public risk and the spent fuel pool had a stainless steel liner installed to prevent future leakage. Environment, Safety and Health Safety Advisory 2006-04, *Stakeholder Sensitivity to Tritium Releases*¹⁵, describes issues encountered at commercial nuclear power plants and non-RCRA-regulated landfills that have found tritium in their leachate (e.g., the Pennsylvania Department of Environmental Protection has identified tritium in the leachate of most of its landfills). Both NRC and the Nuclear Energy Institute are sensitive to tritium groundwater issues, as are the States. Effective monitoring programs and good outreach and communication programs are key to preventing and mitigating actual and perceived problems with tritium control. The accumulation and storage of tritiated water awaiting the disposition decision at Fukushima highlights the public's apprehension and interest with radioactivity in general and even tritium specifically.

3.1.3 RCRA Applicability

Under the implementing regulations of RCRA, specifically at 40 CFR 261.4(a)(4), source, SNM, and byproduct material, as defined by the AEA, is excluded from the definition of solid waste, and thus from the RCRA hazardous waste management requirements. The AEA definition of byproduct material includes "any radioactive material (except special nuclear material) yielded in or made radioactive by exposure to the radiation incident to the process of producing or utilizing special nuclear material." Tritium produced in a U.S. reactor meets the definition of byproduct material; therefore, the waste streams derived from U.S. reactor-produced tritium are excluded from RCRA regulation (provided such waste streams do not also contain a RCRA hazardous waste component in addition to the byproduct material component).

Accelerator-produced tritium, on the other hand, did not qualify for this exclusion, since the tritium is produced by a linear accelerator, and does not involve the production or utilization of SNM or the extraction or concentration of source material. However, the AEA was amended by the Energy Policy Act of 2005 (EPACT 2005), which amended the definition of byproduct material to include "any material that has been made radioactive by use of a particle accelerator, and is produced, extracted, or converted after extraction, before, on or after the date of enactment of [EPACT 2005] for use for a commercial, medical, or research activity." Therefore, accelerator-produced tritium used for weapons production does not qualify for the RCRA material exclusion, while other uses for the accelerator-produced tritium do meet the RCRA exclusion. Additionally, tritium produced in the original Canada Deuterium Uranium (CANDU) design, employing natural uranium as fuel, may not, meet the definition of byproduct material; therefore, it is prudent to assume that it also does not qualify for RCRA exclusion.

¹⁵ DOE/EH-0699, DOE Environment, Safety and Health Advisory 2006-4, *Stakeholder Sensitivity to Tritium Releases*, July 2006.

Thus, for U.S. reactor-generated or accelerator non-weapons production tritium waste to be considered hazardous waste, the waste stream also would have to contain a RCRA-listed or non-tritium-derived characteristic hazardous waste component. The waste stream from CANDUs and weapons-related accelerator tritium would not automatically be excluded from RCRA; however, unless such tritium wastes exhibit one of the characteristics of RCRA hazardous waste (ignitability, corrosivity, reactivity, or toxicity [40 CFR Part 261, Sections 21 through 261.24]) or contain a RCRA-listed hazardous waste, the waste streams would not need to be managed as RCRA hazardous or mixed waste. Pursuant to the RCRA regulations, it is the responsibility of the waste generator to determine if that waste is subject to the hazardous waste requirements [40 CFR 262.11]. Categories of characteristic hazardous waste (and associated properties) that appear to have some potential to apply to certain accelerator-produced tritium wastes are as follows:

- Ignitability [40 CFR 261.21] Ignitable wastes are solid wastes that exhibit any of the following properties: liquids with a flashpoint of less than 60°C (140°F); solids that are capable of causing fires through friction, absorption of moisture, or spontaneous chemical changes; ignitable compressed gases, as defined in 49 CFR 173.300; or oxidizers, as defined in 49 CFR 173.151.
- Corrosivity [40 CFR 261.22] Corrosive wastes are solid wastes that exhibit any of the following properties: an aqueous material with pH ≤2 or ≥12.5; or a liquid that corrodes steel at a rate greater than ¼ inch per year at a temperature of 55°C (130°F).
- Reactivity [40 CFR 261.23] Reactive wastes are solid wastes that exhibit any of the following properties: (1) they are normally unstable and readily undergo violent change without detonating; (2) they react violently with water; (3) they form potentially explosive mixtures with water; (4) when mixed with water, they generate toxic gases, vapors, or fumes in a quantity sufficient to present a danger to human health or the environment; (5) they are a cyanide- or sulfide-bearing waste which, when exposed to pH conditions between 2 and 12.5, can generate toxic gases, vapors, or fumes in a quantity sufficient to present a danger to human health or the environment; (6) they are capable of detonation or explosive reaction if subjected to a strong initiating source or if heated under confinement; (7) they are readily capable of detonation or explosive decomposition or reaction at standard temperature and pressure; (8) they are a forbidden explosive, as defined in 49 CFR 173.54, a Class A explosive, as defined in 49 CFR 173.58.

The discussion in Section 2.5.1.c provides only a qualitative argument for the determination that for tritiated waste, the characteristics of corrosivity typically are not generally exhibited as little data exists in this area. Moreover, little data are currently available to confirm whether or not the vapor space of some tritium containers (e.g., tritium oxide adsorbed on molecular sieves) would exhibit the hazardous characteristic of ignitability or reactivity over time due to radiolytic decay. As explained above, reactor-generated or accelerator non-weapons-production tritium waste streams that do not contain a hazardous waste component may be excluded from the RCRA hazardous waste

regulations pursuant to 40 CFR 261.4(a)(4). This may be the case even if sufficient quantities of both hydrogen and oxygen are present to exhibit characteristics of ignitability or reactivity. This is based on a regulatory policy that EPA has applied in certain cases whereby residuals derived from the management of exempt or excluded waste retain the exemption or exclusion.¹⁶ ¹⁷ ¹⁸ ¹⁹ ²⁰. However, as indicated above, if a tritium waste (irrespective of its source) also contains a distinct hazardous waste component, the waste stream should be managed as a radioactive mixed waste under the AEA and RCRA.

The application of RCRA to certain tritium waste streams may be subject to regulatory interpretation and enforcement discretion. With this in mind, it is recommended that determinations as to whether or not certain tritium wastes constitute RCRA hazardous waste be discussed and validated with the appropriate regulatory agency (e.g., the EPA Region or RCRA-authorized State agency). Section 8.2.2 provides a flow diagram and expanded discussion on this issue in addition to the definitions and options for tritium recovery and disposal.

The RCRA characteristics are vital for purposes of disposal, but DOT has specific and (often) distinct defining criteria for the purposes of transportation. See 49 CFR Part 173, Subpart D, *Definitions, Classification, Packing Group Assignments and Exceptions for Hazardous Materials Other Than Class 1 and Class 7*.

3.1.4 CERCLA Applicability

Under the CERCLA, cleanups are required to attain applicable or relevant and appropriate (ARAR) standards. With respect to contaminated aquifers, CERCLA designates MCLs (20,000 for tritium) established under the SDWA as the "relevant and appropriate" standard for the restoration of contaminated ground waters that serve as a current or potential future drinking water source. However, in situations where multiple contaminants are present and have the potential for additive effects, the cleanup goal may be set lower than the MCL. In general, discharges to surface water bodies require compliance with AWQC, although if the surface water body be used as a drinking water source, the MCL may be applied to such discharges. If RCRA hazardous listed or characteristic wastes be present, project managers will need to determine which RCRA requirements will apply as discussed in section 3.1.3.

3.2 Tritium Safeguards and Security

¹⁶ Preamble of the First Third Land Disposal Restrictions Final Rule, 53 FR 31149, August 17, 1988.

¹⁷ Memorandum, Environmental Protection Agency, Marcia E. Williams and Christina Kaneen to Robert L. Duprey, *Applicability of Bevill Amendment to the American Natural Gas Coal Gasification Facility*, September 1987.

¹⁸ Letter, Marcia E. Williams, EPA, to G. N. Weinreich, ANG Coal Gasification Co., June 16, 1986.

¹⁹ Memorandum, Environmental Protection Agency, John H. Skinner to Harry Seraydarian, *Clarification of Mining Waste Exclusion*, May 16, 1985.

²⁰ RCRA Superfund Hotline Report, February 1985.

Tritium is a nuclear material of strategic importance and must be safeguarded from theft or diversion. The current DOE safeguards and security directives do not explicitly grade or categorize tritium as predecessor directives had.

3.3 Tritium Facility Safety Analysis and Regulatory Quantity Limits

A documented safety analysis is required by 10 CFR Part 830, *Nuclear Safety Management*, for all Hazard Category 1, 2, and 3 nuclear facilities. Irrespective of these requirements, the good practices associated with the implementation of Integrated Safety Management (ISM) principles necessitate that hazards be identified and controlled, which is a major step in the safety analysis process.

3.3.1 Safety Analysis

Safety analyses address various accident scenarios. Some typical examples of accident categories include fire, explosion, tritium leaks, cooling water breaks, and failure of detritiation system components.

3.3.1.a Facility Requirements

There are a few fundamental assumptions normally made when performing safety analyses on tritium facilities, which, if not satisfied, require more detailed analyses or development of corrective actions. These include:

- The integrity of the primary container should be ensured for all normal operations, anticipated operational occurrences, and for the design basis accidents (DBAs) it is required to withstand.
- If the facility structure is not part of the secondary barrier, its failure as a result of severe natural phenomena or other postulated DBAs should not prevent the primary container or the secondary containment or confinement system from performing their necessary safety functions.
- When secondary containers (secondaries) are used, a tritium effluent removal system to handle tritium leakage from primary containers is recommended by this Standard, but not required.

3.3.1.b Radiological Materials Inventory

Attachment 1 to DOE-STD-1027-92, Change Notice 1, *Hazard Categorization and Accident Analysis Techniques for Compliance with DOE Order 5480.23,* Nuclear Safety Analysis Reports, states,

Additionally, material contained in [Department of Transportation (DOT)] Type B shipping containers (with or without overpack) may be excluded from summation of a facility's radioactive inventory if the Certificates of Compliance are kept current and the materials stored

are authorized by the Certificate. However, Type B containers [see Section 6.1] without an overpack should have heat protection provided by the facility's fire suppression system. Further discussion expands this clarification as follows:

The Material at Risk (MAR) is the bounding quantity of hazardous material that is available to be acted on by a postulated accident. MAR values used in hazard and accident analysis shall be consistent with the values noted in hazard identification/evaluation, and shall be bounding with respect to each accident being evaluated. While DOE-STD-1027-92 excludes material in Department of Transportation Type B qualified containers from consideration for the purposes of hazard classification, the existence of such material shall be acknowledged in the DSA and excluded from the source term for a particular event scenario only if the containers can be shown to perform their safety functions under the accident conditions. If the containers are not currently qualified (qualifications expire on a fixed schedule), then their contents must be included in the summation of facility inventory and be included in accident analyses, irrespective of accident conditions. If, however, the container is currently certified, then a comparison of the conditions resulting from transportation and facility accidents is performed. For example, consider a currently certified Type B container that has been qualified to withstand fire and crush loads (i.e., Type B Hypothetical Accident Crush Test loads) associated with a transportation accident. If these transportation accident conditions are more severe than the associated credible facility accident conditions (e.g., fire and seismic crush loads), than the inventory in these containers can be excluded from source terms for those associated accident scenarios (irrespective of fire suppression system coverage). If the facility fire conditions exceed the transportation fire conditions, the inventory is included. Note that credit for safety-class or safety-significant fire suppression affects the selection of the credible facility fire scenario, and therefore, the fire conditions for comparison with the transportation fire conditions.

If the transportation accident conditions are less severe than the facility accident conditions, then the contents are included in the accident scenarios. For example, if the seismic crush loads exceed the transportation crush loads, the contents cannot be excluded from the facility seismic accident scenarios. They could, however, still be excluded from the facility fire scenarios if the transportation fire conditions bound the facility fire conditions.

DOE-STD-1027-92, Change Notice 1 does not provide explicit exemption criteria for other than Type B containers. General guidance for other than Type B containers would be to include the tritium in the facility inventory. Specific guidance concerning the degree and amount of residual tritium inventory to include in safety analyses based on facility-specific configurations, can be obtained from AU.

The Hazard Category of a nuclear facility is based on threshold quantities of radiological material inventory. Gram quantities are rounded values based on the calculated number of curies. ²¹ The definitions for each Hazard Category are as follows:

- Hazard Category I (generally limited to nuclear reactors): Regardless of the quantity of tritium in the inventory, a facility that handles only tritium is not classified, by tritium quantity alone, as a Hazard Category I. The Program Secretarial Officer (PSO) may designate a tritium facility as Category I if the potential for significant offsite consequences exists.
- Hazard Category II: To be classified as a Category II nuclear facility, the facility tritium inventory must be > 30 grams.
- Hazard Category III: To be classified as a Category III nuclear facility, the facility tritium inventory must be > 1.6 and < 30 grams.
- Less than Hazard Category III: (formally called Radiological) Facilities that have less than 1.6 grams of tritium in the facility radiological material inventory.). [10 CFR Part 830]
- Some DOE sites have adopted a lower threshold limit for less than Haz Cat III Nuclear Facilities at the RQ level for the associated radionuclide, under which the facility would be considered non-radiological. This approach has also been endorsed in the past by various DOE Program Offices at HQ.²² Using this approach for tritium facilities for which the RQ value is 100 Ci, any facility possessing less than this would be considered non-nuclear or non-radiological. This approach, however, is contrary to the legal definition as stated in the Atomic Energy Act and DOE Standard 1027 in which there is no lower threshold identified to become a non-radiological facility for a facility that contains radiological inventory and users are cautioned not to treat tritium facilities with less than 100 Ci as non-nuclear. Unlike the existence of processes for downgrading Haz Cat II and III Nuclear Facilities there are none for a Haz Cat III Nuclear Facility to non-nuclear.

3.3.1.c Material Release Assumptions

Once the total inventory available for release is known, the appropriate source term can be calculated. The components of the source term, as described in DOE-HDBK-3010-94, *Airborne Release Fraction/Rates and Respirable Fractions for Nonreactor Nuclear Facilities*, are material at risk, damage ratio, airborne release fraction, respirable fraction, and leak path factor. The factors for airborne release and respirable fractions are normally assumed to be 1.0 for elemental tritium and oxide. The other factors are facility-specific. For DSA fire scenarios, the fraction of the release

²¹ DOE-STD-1027-92, Change Notice 1, *Hazard Categorization and Accident Analysis Techniques for Compliance with DOE Order 5480.23,* Nuclear Safety Analysis Reports, September 1997.

²² *Implementation Guidance for Authorization Basis*, DOE Office of Defense Programs, Revision 1, August 21, 1995.

assumed to be oxide is normally 100 percent. Typical scenarios to review for inclusion in safety analyses are area fires (single and multiple Fire Control Areas (FCAs)), full facility fire, leaks or spills, hydrogen explosions, and Natural Phenomena Hazards (NPH) events (the design basis earthquake (DBE) may have a seismic-induced fire, which usually results in the bounding accident). DOE-STD-3009-94, Change Notice 3, *Preparation Guide for U.S. DOE Nonreactor Nuclear Facility Safety Analysis*, provides detailed guidance for performing accident analyses.

Several dose methodologies have been used for safety analyses throughout the DOE complex. However, with the implementation of DOE G 414.1-4, *Safety Software Guide for Use with 10 CFR Part 830, Subpart A,* Quality Assurance Requirements, *and DOE O 414.1C,* Quality Assurance, some computer modeling methodologies are designated as toolbox codes for safety analysis, while others are not. Safety analysts should check the current DOE Safety Software Control Registry before using a specific program for safety analysis calculations.

The value associated with dry deposition velocity for tritium oxide used in safety basis calculations has been the subject of Defense Nuclear Facilities Safety Board (DNFSB) and SRS discussions since 2011. The DNFSB, in the Staff Issue Report of March 17, 2011²³, indicated that use of the value of 0.5 cm/s was non-conservative. Analyses by SRNL²⁴ to address this and other safety basis calculations concluded that 1) the Pasquill stability classification for regulatory application of SRS is based on measurements of the standard deviation of the vertical component of wind direction fluctuations, collected from the 61m level of the SRS meteorological towers and processed in full accordance with EPA-454/R-99-005, *Meteorological Monitoring Guidance for Regulatory Modeling Applications*²⁵; and that 2) meteorological databases used as input for MACCS2 calculations should contain hourly data for five consecutive annual periods from the most recently available 10 years.

Although it is likely that the realistic deposition velocity is approximately in the range of 0.1 cm/s, there is not currently data to support this supposition. Current toolbox codes do not model reemission and as such SRS research into re-emission has been proposed. The results of this research may allow credit for a portion of the re-emission to the canopy as oppose to assuming 100% reemission to the atmosphere, which will affect the value chosen for deposition velocity. Several models have been proposed for washout, which is difficult to model; however research is continuing in this area. A paper presented at the 10th International Conference on Tritium Science and

²³ August 19, 2011, letter from P. Winokur, DNFSB, to T. D'Agostino, NNSA Administrator, transmitted the March 17, 2011, Staff Issue Report *Review of Safety Basis, Tritium Facilities, Savannah River Site*.

²⁴ C.H. Hunter. SRNL-STI-2012-00055, A Recommended Pasquill-Gifford Stability Classification Method for Safety Basis Atmospheric Dispersion Modeling at SRS. Rev. 0, March 2012.

²⁵ U.S. Environmental Protection Agency. EPA-454/R-99-005, *Meteorological Monitoring Guidance for Regulatory Modeling Applications*, February 2000.

Technology (TRITIUM 2013) examined the relationship between exchange rate and washout coefficient²⁶.

The values for parameters (e.g., relative concentration, deposition velocity) selected for use in dose consequence analyses would ideally be site-specific. In the absence of the data to quantify reemission 0.00 cm/sec should be the default value to be used for deposition velocity.

Another program used primarily for modeling prior to environmental release, the Tritium Migration Analysis Program (TMAP)²⁷ was developed by EG&G Idaho, Inc., to dynamically analyze tritium transport in fusion reactor facilities. TMAP solves conservation equations for any number of gaseous species in a system composed of solid structures or walls, and related gas filled enclosures by including the phenomena of surface molecular dissociation and atomic recombination, bulk diffusion with the possibility of trapping by material defects produced by neutron damage, chemical reactions within enclosures, and convective flow between enclosures. In TMAP, the movement of hydrogen species across structure surfaces is not only governed by molecular surface kinetics but by solution laws, such as Sieverts' or Henry's laws, or inhibited from crossing the surface. Movement in solids (may be a layered composites) is modeled by one-dimensional Fick's law of diffusion equations. The thermal response of these structures is obtained from the solution of one dimensional heat conduction equations that account for applied heat or boundary temperature loadings conditions. The code was specifically developed to predict the inventories of tritium in and release from fusion reactor systems that experience both plasma driven permeation at very high implanted fluxes (10^{24} ions/m²-s) and pressure driven permeation at very low tritium pressures (< 10 Pa). However, it is evident that TMAP has application to a much wider variety of problems, including modeling experiment facilities developed to measure tritium material transport properties.

TMAP4 can be obtained from the Department of Energy's (DOE's) Energy Science and Technology Software Center (ESTSC).

Several Federal environmental laws (e.g., Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), and the Clean Water Act (CWA)) require that releases of hazardous substances above reportable quantities (for tritium, this is 100 curies in 24 hours) be reported to the National Response Center. In many cases, the curie levels are back-calculated from offsite dose receptor requirements. DOE O 231.1A, DOE M 231.1-2, DOE O 151.1C, and DOE G 151.1-4 make distinctions between "normal" or "routine" releases and "abnormal" or "accidental" releases, and suggest reporting abnormal or accidental releases, even if they are below Federally permitted levels.

²⁶ A.V. Golubev et al. *The Field Experiments on the HTO Washout from the Atmosphere*. Presented at the 10th International Conference on Tritium Science and Technology (TRITIUM 2013), Nice, France.

²⁷ G. R. Longhurst, D. F. Holland, J. L. Jones, B. J. Merrill, TMAP4 User's Manual, EGG-FSP-10315, Idaho National Engineering Laboratory, July 1992

3.3.2 Integrated Safety Management

All tritium-related operations and activities, including design, construction, system acceptance and turnover, operations, shutdown, deactivation, should follow commitments identified in DOE ISM directives of the 450.4 series, which were an outgrowth from the Defense Nuclear Facilities Safety Board (DNFSB) Recommendation 95-2 Implementation Plan. The objective of ISMS, as articulated in 48 CFR § 970.5223-1, *Integration of Environment, Safety, and Health into Work Planning and Execution*, is that, in performing work for DOE, the Contractor shall perform work safely, in a manner that ensures adequate protection for employees, the public, and the environment, and shall be accountable for the safe performance of work. The Contractor shall exercise a degree of care commensurate with the work and the associated hazards. The Contractor shall ensure that management of environment, safety and health (ES&H) functions and activities becomes an integral but visible part of the Contractor's work planning and execution processes.

This clause goes on to address ISMS in more detail. The commitments for ISM follow the seven Guiding Principles:

- 1. Line Management Responsibility for Safety;
- 2. Clearly Defined Roles and Responsibilities;
- 3. Personnel Competence Commensurate with Responsibilities;
- 4. Balanced Priorities;
- 5. Identification of Safety Standards and Requirements;
- 6. Hazard Controls Tailored to the Work Being Performed;
- 7. Operations Authorization.

The process for planning and conducting pre-work hazards analysis for all work operations at tritium facilities should be consistent with the Guiding Principles listed above and should follow a structured approach commensurate with the risks and hazards involved. Several methods for enhanced work planning and related work planning strategies used throughout the DOE complex follow five steps:

- 1) Define the Scope of Work;
- 2) Analyze the Hazards;
- 3) Develop and Implement Hazard Controls;
- 4) Perform Work within Controls; and
- 5) Provide Feedback and Continuous Improvement.

This sequence is one of many ways to ensure a structured approach in work planning with a focus on worker safety and reduced environmental risks.

3.3.3 Facility Segmentation

Facility segmentation is discussed in DOE-STD-1027-92. Activities conducted in the same facility may be separated into different areas for analysis purposes, but only if independence (in accident space) can be shown. Potential areas for segmentation include:

- Receiving area;
- Receiving storage area;
- Shipping area;
- Shipping storage area;
- Tritium unpackaging, handling, and packaging operations;
- Low-level waste accumulation area;
- Low-level waste packaging area; and
- Packaged low-level waste storage area.

The independence of the segments, however, is not easily demonstrated. Common piping and heating, ventilation, and air conditioning (HVAC) cannot exist to use this segmentation process. Additionally, common-cause initiating events (e.g., fire, seismic) affect multiple segments, thereby placing an additional burden of proof on the analyst to demonstrate independence. A successful segmentation analysis, however, would not affect the applicability of Price-Anderson enforcement of the Nuclear Safety Rules to the facility.

3.4 Radiological Material Quantity Limits

3.4.1 Tritium Shipping, Radioactive Material Inventory, Quantity Limits

Once an item has met the DOE and DOT requirements for shipment (e.g., properly packaged, radioactively surveyed, properly marked, properly completed shipping papers), the item inside the approved shipping package can be shipped to a new location.

During shipment, the item inside the approved shipping package is expected to be subject to the normal activities associated with its movement from one location to another; for example, loading and unloading the package from vehicles, transport to a shipping area, storage in the shipping area prior to transport, loading and unloading the package onto trucks/trains/airplanes, and storage in the receiving area after arrival at the new destination.

The packaging required by DOT regulations is designed to protect the workers, the public, and the environment from the radioactive material during normal package handling, transport, and shipping/receiving storage.

The applicable requirements for various quantities of tritium for transportation and storage are roughly as follows:

- Limited Quantity (< 21.6 Ci for gas; see Table 7-1 for solids, liquids, and applicable 49 CFR Part 173 requirements): Limited quantities of tritium can be packaged and shipped in strong, tight containers (paper boxes, paint cans) with proper markings.
- Type A Quantity (21.6 to < 1080 Ci): Type A quantities of tritium use DOT Specification 7A containers, properly marked and surveyed prior to shipment. A number of different packages are available from small cans, 55- and 85-gallon drums, 4 x 4 x 7-foot steel boxes, up to and including oversized, specially designed containers. These containers are relatively inexpensive.
- Type B Quantity (≥ 1080 Ci): Type B quantities of tritium must be shipped in a certified Type B package. There is only a limited number of these Type B packages available for tritium shipment (e.g., BTSP, UC-609), and special routing (i.e., prescribed routes employing highway route control such as using major highways or bypassing cities) is required.
- Type B-Quantity, Low-Level Radioactive Waste: For the purposes of storage at the waste site, Type B-quantity solid waste can be stored in Type A containers.

At the waste generation location, items containing greater than 1080 Ci of tritium are normally stored in Type A containers. Type A containers containing over 1080 Ci must then be placed into Type B containers for shipping to DOE waste sites. At the DOE waste site, the Type A containers can

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be removed from the Type B package and stored in the Type A package. This allows the expensive Type B package to be returned to the shipper and reused for another Type B shipment. A radiological materials inventory must still meet the requirements as discussed in Section 3.3.1.b. Additionally, 10 CFR Part 835 contains labeling requirements.

3.4.2 Tritium Receiving Area, Shipping Area, Quantity Limits

There are no limits (other than local administrative limits) on the inventory of approved containers that can be stored in a properly marked shipping area, receiving area, shipping storage area, and receiving storage area. There are, however, site-wide limits that may be imposed in the EIS that could restrict the total inventory quantities.

These areas must be inside an area posted as a Controlled Area, per 10 CFR Part 835. The Controlled Area encloses an area posted as a Radioactive Materials Area (RMA). The Controlled Area and the RMA can be the same area. The RMA must be periodically surveyed and appropriately marked to indicate the nuclear hazard associated with the area. These areas may have more than one incoming or outgoing certified package containing Type A or B packages waiting for transport.

3.5 Tritium Unpackaging, Handling, and Packaging Areas, Quantity Limits

The tritium is removed from the specification package/certified package in unpackaging, handling, and packaging areas, and, as such, these areas if not emcompassed by the nuclear facility will be designated as a nuclear facility (Hazard Cat 2, 3 or less than 3), depending upon the quantity of tritium in the inventory.

3.6 Tritium Waste Collection and Waste Packaging Area, Quantity Limits

The waste collection/packaging area will have, in process, the collection and packaging of low-level waste. The waste collection/packaging area should likewise be reviewed for designation as a nuclear facility as defined by the quantity of tritium.

3.7 Tritium Radworker Training

Subpart J of 10 CFR Part 835, *Occupational Radiation Protection*, requires that individuals complete radiation safety training commensurate with the hazards in the area and the required controls. DOE-STD-1098-2008, *Radiological Control* lists Appendix F of this Standard, "Radiological Training for Tritium Facilities," as a reference to be considered in addition to DOE's core training material for radiological workers at tritium facilities. This Appendix provides a recommended implementation process for conducting the radiation safety training at tritium facilities as required by 10 CFR Part 835 and as recommended in DOE-STD-1098-2008.

3.8 Tritium Focus Group (TFG)

The TFG comprises both DOE Federal and contractor personnel associated with tritium operations. It was formed in 1991, in response to the Secretary of Energy's Task Group on tritium operations, and has expanded in scope and stature since that time. Its charter is contained in Appendix H.

APPENDIX A: USEFUL NUMERICAL VALUES

A.1 General Data

- 1 becquerel (Bq) = 1 disintegration/second = 2.7 x 10⁻¹¹ Ci
- 1 Ci = 3.7×10^{10} disintegrations/second = 3.7×10^{10} Bq = 37 GBq
- Avogadro's Number = 6.023 x 10²³ molecules/mole
- STP conditions: 760 Torr, and 0°C (1 atm and 273K)
- 1 mole of ideal gas at STP = 22.414 L at 0° C, and approximately 24.2 L/mole at room temperature
- 1 Sievert (Sv) = 83.8 roentgens = 100 rem
- A1 quantity-special form
- A2 quantity –other than special form or normal form

A.2 General Tritium Data

- Tritium decays to ³He + beta + neutrino
- Half-life of tritium (Scientific purposes) = 12.323 ± 0.004 years (4500.88 ± 1.46 days) Half-life of tritium (Accountability purposes) = 12.33 +/- 0.06 years (DOE M 474.1-2, Figure IV-2)
- Tritium decay factor = 0.99984601/day
- Maximum beta energy of decay (E max.) = 18.6 keV
- Mean beta energy of decay (E mean) = 5.69 keV
- Volume of 1 Ci of tritium (T₂) at STP = 0.386 mL
- Tritium (T₂) gas = 9619 Ci/g
- T₂ gas contains 58023 Ci/mole
- 2.589 Ci/cm³ of T_2 at STP
- Diameter of a tritium atom (approximate) = 1.1 Angstroms
- Dissociation energy, T₂ to 2T = 4.59 eV
- Ionization energy, T to T+ + e- = 13.55 eV
- Atomic weight = 3.01605
- Gram molecular weight of tritium = 6.0321 g
- Grams tritium/liter at STP = 0.269122 g/L
- Liters/gram of tritium at STP = 3.71579 L/g
- Boiling point of tritium at 1 atmosphere = 25.0 K
- T₂ gas, at 1 atmosphere pressure and 25°C = 2.372 Ci/cm³
- Tritiated water, T₂O = 3200 Ci/cm³

A.3 Regulatory Quantities

- Type B Quantity = > 1080 Ci
- Type A Quantity = > 0.11 to <1080 Ci depending on form
- Limited Quantity = < 21.6 Ci of tritium in gaseous form
 - < 1.1 Ci of tritium in solid form
 - < 1 Ci of tritium at a concentration of > 1 Ci/L liquid
 - < 100 Ci at a concentration of > 0.1 to < 1 Ci/L liquid
 - < 1000 Ci at a concentration of < 0.1 Ci/L liquid
- A2 Quantity = 40 TBq (1080Ci)
- Limited Quantity Excepted Package Requirement for tritium
 - Radiation level < 0.005 mSv/hr (0.5 mrem/hr)
 - Quantity of radioactive material < limit in 49 CFR 173.425
 - Package meets general design requirements for radioactive material packaging from 49 CFR 173.410
 - Nonfixed/ removable contamination on the external surface of the package is < limit in 49 CFR 173.443 (0.41 Bq of tritium/cm² or 22 disintegrations/min (dpm)/cm² for tritium)
 - Outside of inner or outer packaging is marked "Radioactive"
- Low Specific Activity (LSA) A quantity of Class 7 (radioactive) material with limited specific activity
 - LSA-I
 - Earth, concrete, rubble or other debris = 4 x 10⁵ TBq of tritium/g (0.001 Ci of tritium/g, 1 Ci of tritium/kg or 2.2 lb/Ci of tritium)
 - LSA-II
 - Tritium-Contaminated Water up to: 0.8 TBq of tritium/L (20.0 Ci/L)
 - Solids and Gases up to 0.004 TBq of tritium/g (0.1 Ci/g, 100 Ci/kg)
 - Liquids 4 x 10⁴ TBq of tritium/g (0.01 Ci/g, 10 Ci/kg)
 - LSA-III
 - Solids, consolidated wastes, or activated material that meet 49 CFR 173.468 water leach test; and
 - Uniformly distributed in a collection of solid objects or uniformly distributed in solid compact binding agent; i.e., concrete, bitumen, ceramic, etc.
 - Relatively insoluble or intrinsically contained in relatively insoluble material such that, under loss of packaging and placed in water for seven days, would not exceed 4 TBq of tritium (110 Ci of tritium)
 - The average specific activity of the solid does not exceed 0.08 TBq of tritium/g (2.16 Ci/g)
- SCO (Surface Contaminated Object) Non-radioactive solid objects with Class 7 (radioactive) materials distributed on the surfaces
 - SCO-I
 - Nonfixed contamination on accessible surface averaged over 300 cm² is < 4 Bq of tritium/cm² (10⁴ μCi/cm²)

- Fixed contamination on the accessible surface averaged over 300 cm² is < 4 x 10⁴ Bq of tritium/cm² (1 μCi/cm²)
- Nonfixed plus fixed contamination on the inaccessible surface averaged over 300 cm² is < 8 x 10⁵ Bq of tritium/cm² (20 μCi/cm²)
- SCO-II
 - Solid object on which limit for SCO-I is exceeded and meets the following:
 - Nonfixed contamination of accessible surface averaged over 300 cm² is < 400 Bq of tritium/cm² (10⁻² µCi/cm²).
 - Fixed contamination of accessible surface averaged over 300 cm² is < 8 x 10⁵ Bq of tritium/cm² (20 μCi/cm²).
 - Nonfixed plus fixed contamination of accessible surface averaged over 300 cm² is < 8 x 10⁵ Bq of tritium/cm² (20 μCi/cm²).
- Type A Packages limited to 40 TBq of tritium (< 1080 Ci) per package
- Type B Packages for quantities > 40 TBq of tritium (> 1080 Ci) per package
- Graded Safeguards Program
 - Category III: Weapons or test components, containing reportable quantities > 50 g T_2 with isotopic fraction T_2 > 20 percent
 - Category IV: All other reportable quantities
- •
- Facility Categories
 - Hazard Category 1: Category A reactors and facilities designated by PSO.
 - Hazard Category 2: > 30 g of tritium
 - Hazard Category 3: > 1.6 but < 30 g of tritium
 - Radiological Facility:< 1.6 g of tritium

A.4 Tritium Dose and Exposure Data

- Biological half-life = 8 to 12 days (oxide); biological half-life of tritides is currently being researched
- Derived Air Concentration (DAC)
 - DAC for HTO = $20 \,\mu\text{Ci/m}^3$ = $2 \,\times 10^{-5} \,\mu\text{Ci/mL}$ = $7 \,\times 10^5 \,\text{Bq/m}^3$
 - DAC for HT = 200,000 μ Ci/m³ = 2 x 10⁻¹ μ Ci/mL = 9 x 10⁹ Bq/m³
 - DACs for STCs see Appendix E
- Dose Conversion Factor (DCF)
 - DCF = 0.067 mrem/ μ Ci (inhalation)
 - DCF = 0.1 mrem/ μ Ci (inhalation plus 50 percent allowance for skin absorption)
- Annual Limit on Intake (ALI)
 - ALI for HTO = 80,000 μCi
 - An initial exposure equilibrium urine count of 1 μCi/L equates to approximately a 3-mrem dose.
 - A urine count of 50 μ Ci/L for a year equates to approximately a 5,000-mrem dose.

- Breathing 20 μCi/m³ HTO in air for 8 hours/day, 50 week/year will result in a dose of approximately 5,000 mrem
- Tritiated water is approximately 10,000 times more hazardous than tritium gas because of rapid uptake mechanisms.
- Tritium Beta Particles
 - Range in Air = 4.5 to 6 mm
 - Range in Water = 0.0005 cm
 - Range in Tissue = 0.0007 cm
 - Radiation, 1 mCi in man (70 kg) = 0.0044 rem/day
 - Maximum Penetration = 0.6 mg/cm³

A.5 Tritium Container Data

- SRS Hydride Transport Vessel (HTV)
 - Reusable container for transporting up to 18 grams of tritium
 - Shipped in UC-609/BTSP
 - Dual port, flow through capable
 - One female, one male port, Cajon[®] SS-4-VCR
 - Tritium stored as uranium tritide
 - Contains 493 g depleted uranium
 - Stoichiometry Maximum 1:2.9
 - Weight 9.3 lbs.
 - Height 9.995 in
 - Diameter 4.6 in
 - Volume 690 cm³
 - Maximum normal operating temperature = 450°C
 - Pressure Limit at Maximum normal operating temperature = 2.9 psia
 - Tritium vapor pressure as a function of temperature at U:T = 1:2.9
 - Dissociation Equations
 - Log $P_{atm} = -4038.2/T + 6.074$, $P_{atm} = 10^{-4038.2/T + 6.074}$
 - Log P_{psia} = -4038.2/T + 7.2413, P_{psia} = 10^{-4038.2/T+7.2413}
 - Maximum specified tritium leak rate in std cc = $<1.26 \times 10^{-7}$ std cc/s.
- SRS Product Vessel (PV)
 - Reusable container for transporting 10 g of tritium in gas form
 - Shipped in UC-609/BTSP
 - Volume 21 L
 - Maximum pressure 1,200 torr
 - Height 30.5 in
 - Diameter 9.875 in
 - Weight 44 lb
 - Single valve, Nupro[®] SS-4-HS-TW

- Male Nut, Cajon[®] SS-4-VCR-4
- Female Cap Cajon[®] SS-4-VCR-CP
- Maximum helium leak rate = 1×10^{-7} STP cc/s He with 8.5 psig helium internal pressure by belljar method
- SRS Hydride Storage Vessel (HSV)
 - Container for storing up to 1600 STP liters of hydrogen isotopes
 - Capable of being shipped in UC-609/BTSP
 - Dual port, flow through capable
 - One female, one male port, Cajon[®] SS-4-VCR
 - Tritium stored as titanium tritide
 - Contains 4400 g titanium (Ergenics HY-STOR 106)
 - Weight 45 lb
 - Height 16.3 in
 - Diameter 6.6 in
 - Maximum normal operations temperature = 760°C
 - Pressure Range at normal operating temperature = 192 psig to Full Vacuum
 - Pressure Limit at 120°C = 1000 psig
 - Maximum helium leak rate = 1×10^{-7} STP cc/s He with 30 psig helium internal pressure by belljar method
- SRS Bulk Tritium Shipping Package (BTSP)
 - Type B(M) Reusable Shipping Package
 - Authorized Content; Up to 150 grams of Tritium as a gas, solid or adsorbed tritiated water
 - Vapor on molecular sieve materials.
 - Package Gross Weight 650 lb
 - Maximum Content Weight 120 lb
 - Packaging Overpack
 - Height 50.5 in
 - Diameter 24.5 in
 - Containment Vessel (CV)
 - Height 37.5 in
 - Diameter 15 in
 - Available Volume 2,943 in3
 - 30.625 in high x 10 in ID
 - CV Weight ~153 lbs
 - CV Design Pressure Limit at 400°F @ 500 psig
 - SRS LP-50 (No longer certified for shipping).
 - Container for storing tritium in gas form
 - Volume 50 L
 - Aluminum shell for contamination control and valve protection

- Maximum initial pressure at loading 1,200 torr
- Height 28.3 in
- Diameter 13.2 in
- Product Container Weight 32 lb
- Aluminum Shell Weight 43 lb
- Full Package Weight including drum 260 lb
- Single valve, Hoke Model 4213X2 packless valve
- Male Nut, Cajon[®] SS-4-VCR-4
- Female Cap Cajon[®] SS-4-VCR-1-BL
- Maximum helium leak rate = 7×10^{-8} STP cc/s He with 22.7 psia helium internal pressure by belljar method
- Mound AL-M1-5
 - Up to 100,000 Ci absorbed on molecular sieve, silica gel or commercial clay
 - Used for storage and shipment of absorbed tritiated water.
 - Cylindrical vessel 6 5/8 in O.D. by 23 7/8 height
 - 316 Stainless Steel
 - Cap which is screwed onto threaded center post of container containing two self-sealing quick disconnect fittings used for connection to tritium monitors to check for tritium leak from container
 - Cap has two functions; physical protection of valves, fittings and pressure transducer at top of container and also secondary containment. The cap is sealed with four O rings; one face seal at the bottom circumference of the cover, another near the top of the center post and two sealing the quick disconnect fittings in their wells at the top of the cap.
 - Organic compounds should be limited to 1% or less of the water content of the container.
 - Halogen compounds are to be avoided

A.6 Other Data

- Calorimeter Factor
 - 3.0657 +/- 0.009 g of tritium per Watt
 - 0.3240 +/- 0.0009 Watts/g of tritium
- ANSI N14.5-87 Leakage Test
 - < 1 x 10⁻⁷ cm³/s [/]He

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APPENDIX B: DEFINITIONS

Actual Activity – The total quantity of radioactive material within a particulate; Sometimes referred to as true activity

Airborne radioactivity area: Any area where the measured concentration of airborne radioactivity, above natural background, exceeds or is likely to exceed the derived air concentration (DAC) values listed in Appendix A or Appendix C of 10 CFR Part 835, or where an individual present in the area without respiratory protection could receive an intake exceeding 12 DAC-hrs in a week (10 CFR Part 835).

As low as reasonably achievable (ALARA): A phrase (acronym) used to describe an approach to radiation protection to control or manage exposures (both individual and collective to the work force and the general public) and releases of radioactive material to the environment as low as social, technical, economic, practical, and public policy considerations permit (DOE 5400.5 Chg 2).

Below regulatory concern : A definable amount of low-level waste that can be deregulated with minimal risk to the public (DOE O 435.1 Chg. 1)

Best available technology for radioactive effluent control (BAT): The preferred technology for a particular activity, selected from among others after taking into account factors related to technology, economics, public policy, and other parameters. As used in this Order, the BAT is not a specific level of treatment, but is the conclusion of a selection process in which several alternatives are evaluated (DOE O 435.1).

Biokinetic Model: A mathematical model that describes in quantitative terms the retention and transport of a material in the body. The biokinetic model used in ICRP 78 is recommended to evaluate intakes of STCs.

Breathing Zone Air Sampler (BZA): An air sampler that draws air from the area close enough to the nose so the sample can be considered representative of the air a person breathes (ANSI Z88.2-1992). An example of a breathing zone air sampler is a lapel monitor.

Buffer zone: The smallest region beyond the disposal unit that is required as controlled space for monitoring and for taking mitigative measures, as may be required (DOE O 435.1 Chg 1).

Byproduct material: (1) any radioactive material (except special nuclear material) yielded in or made radioactive by exposure to the radiation incident to the process of producing or utilizing

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(1) any radioactive material (except special nuclear material) yielded in or made radioactive by exposure to the radiation incident to the process of producing or utilizing special nuclear material;

(2) the tailings or wastes produced by the extraction or concentration of uranium or thorium from any ore processed primarily for its source material content;

(3) (A) any discrete source of radium-226 that is produced, extracted, or converted after extraction, before, on, or after the date of enactment of this paragraph for use for a commercial, medical, or research activity; or

- (B) any material that
 - (i) has been made radioactive by use of a particle accelerator; and
 - (ii) is produced, extracted, or converted after extraction, before, on, or after the date of enactment of this paragraph for use for a commercial, medical, or research activity; and

(4) any discrete source of naturally occurring radioactive material, other than source material, that –

- (A) the Commission, in consultation with the Administrator of the Environmental Protection Agency, the Secretary of Energy, the Secretary of Homeland Security, and the head of any other appropriate Federal agency, determines would pose a threat similar to the threat posed by a discrete source of radium-226 to the public health and safety or the common defense and security; and
- (B) before, on, or after the date of enactment of this paragraph is extracted or converted after extraction for use in commercial, medical, or research activity.

Certified waste: Waste that has been confirmed to comply with disposal site waste acceptance criteria (e.g., the Waste Isolation Pilot Plant-Waste Acceptance Criteria for transuranic waste, the DOE/NVO-325 criteria) under an approved certification program (DOE O 435.1 Chg 1)

Confinement system: Any equipment, structure, or system, which limits the release and/or dispersion of a hazardous/radioactive material within a facility. Examples are fume hoods, air locks, ventilation systems, and may include containment and recovery systems. Confinement systems may consist of multiple techniques and barriers depending upon the quantity of tritium involved and the consequences of an uncontrolled release (U.S. DOE Tritium Focus Group).

A collection of barriers that can satisfy a specified leak criterion contingent upon operation of its ancillary (active) system. Examples of confinement systems include: a glovebox and its associated cleanup system, and a room with its associated cleanup system. Note that in the context of this definition, a glovebox with an associated glovebox cleanup system is a confinement system. A glovebox structure itself is a containment system if, and only if, the specified leak criterion can be met by the structure itself (DOE-HDBK-1129-99).

An area having structures or systems from which releases of hazardous materials are controlled. Primary confinement systems are process enclosures (gloveboxes, conveyors, transfer boxes, and other spaces normally containing hazardous materials). Secondary confinement areas surround one or more primary confinement systems (operating area compartments) (DOE O 435.1 Chg 1).

Containment system: Any equipment, structure, or systems that serve as an integral and essentially leak tight barrier against the uncontrolled release of hazardous/radioactive material to the environment and other areas within the facility. Examples include process piping, sealed containers, tanks, gloveboxes, and any other closed loop system, which holds the material for possible recovery of tritium (U.S. DOE Tritium Focus Group).

A collection of passive barriers that can satisfy a specified leak criterion without operation of any ancillary equipment. An example of a containment system is a series of piping and vessels enclosing tritium gas operations. An example of a simple double containment system is a container within another container with each container acting as a separate and independent containment system; more intricate double containment systems have the capability to monitor the volume between the containers for leak detection of the inner container (DOE-HDBK-1129-99).

The assembly of components of the packaging intended to retain the radioactive material during transport (10 CFR Part 71).

Controlled Area: Any area to which access is managed by or for DOE to protect individuals from exposure to radiation and/or radioactive material (10 CFR Part 835).

Derived Air Concentration (DAC): For the radionuclides listed in Appendix A of 10 CFR Part 835, the airborne concentration that equals the Annual Limit on Intake (ALI) divided by the volume of air breathed by an average worker for a working year of 2,000 hours, assuming a breathing volume of 2,400 m³ (10 CFR Part 835).

Derived Concentration Guide (DCG): The concentration of a radio nuclide in air or water that, under conditions of continuous exposure for one year by one exposure mode (i.e., ingestion of water, submersion in air, or inhalation), would result in an effective dose equivalent of 100 mrem (1 mSv). DCGs do not consider decay products when the parent radionuclide is the cause of the exposure (DOE Order 5400.5 Chg 2).

DOE/DOT Type A, approved shipping package: For the purpose of this text, these are packages that can be used for the transport of Type A quantities of radioactive materials. The two typical packages used for solids are metal 55-gallon drums with full removable lids and metal boxes 4 feet wide by 4 feet high and 7 feet long with removable lids. DOT 7A packages may be fabricated in almost any size to fit special needs like packaging of gloveboxes.

Documented Safety Analysis (DSA): Documented safety analysis means a documented analysis of the extent to which a nuclear facility can be operated safely with respect to workers, the public, and the environment, including a description of the conditions, safe boundaries, and hazard controls that provide the basis for ensuring safety (10 CFR Part 830). Successor to the Safety Analysis.

Dose Assessment: Process of determining radiation dose and uncertainty included in the dose estimate, through the use of exposure scenarios, bioassay results, monitoring data, source term information and pathway analysis.

Dose Conversion Factor (DCF): Dose per unit intake.

Dosimetric Model: A mathematical model that prescribes how to use the biokinetic and radiation transport models to quantify the dose to specific organs and tissues and how to calculate effective dose. The dosimetric models for STC are described primarily in ICRP publications 67 and 71.

Facility segmentation: The concept of independent facility segments should be applied where facility features preclude bringing material together or causing harmful interaction from a common severe phenomenon. Therefore, the standard permits the concept of facility segmentation provided the hazardous material in one segment could not interact with hazardous materials in other segments. For example, independence of HVAC and piping must exist in order to demonstrate independence for facility segmentation purposes. This independence must be demonstrated and places the "burden of proof" on the analyst. Additionally, material contained in DOT Type B shipping containers (with or without overpack) may also be excluded from summation of a facility's radioactive inventory if the Certificates of Compliance are kept current and the materials stored are authorized by the Certificate. However, Type B containers without overpack should have heat protection provided by the facility's fire suppression system (DOE-STD-1027-92, Chg 1, Rev. 1).

Free liquids: Liquids that readily separate from the solid portion of a waste under ambient temperature and pressure (DOE O 435.1 Chg 1)

Gastrointestinal (GI) Tract Model: A mathematical representation of the behavior of radionuclides in the contents of the human gastrointestinal tract.

Hazard Category 1: A facility in which the hazard analysis shows the potential for significant off-site consequences. Category A reactors and facilities designated by PSO. Regardless of the quantity of tritium, a facility that handles only tritium is not a Hazard Category 1 facility unless it is designated so by the PSO (DOE-STD-1027-92, Chg 1, Rev. 1).

Hazard Category 2: A facility in which the hazard analysis shows the potential for significant on-site consequences. Facilities with the potential for nuclear criticality events or with sufficient quantities of hazardous material and energy, which would require on-site emergency planning activities. The

threshold tritium inventory for a tritium facility to be designated as a Hazard Category 2 facility is 30 grams or 300,000 Ci (DOE-STD-1027-92, Chg 1, Rev. 1)

Hazard Category 3: A facility in which the hazard analysis shows the potential for only significant localized consequences. Facilities included are those with quantities of hazardous radioactive materials that meet or exceed values in Table A.1 of DOE-STD-1027-97. The threshold for tritium is specified as 1.6 grams or 16,000 Ci (DOE-STD-1027-92, Chg 1, Rev. 1)

Hazardous materials: Those materials that are toxic, explosive, flammable, corrosive, or otherwise physically or biologically health-threatening (DOE-STD-3009)

Hazardous wastes: Those wastes that are designated hazardous by EPA regulations (40 CFR Part 261) (DOE O 435.1 Chg 1) The DOT Hazardous Material Regulations define hazardous materials and hazardous waste differently; see 49 CFR 171.8.

Insoluble Metal Tritide (IMT): A type of insoluble special tritium compound in which tritium has formed a chemical bond to a metal

Insoluble Special Tritium Compound: A special tritium compound, for which the tritium cannot be rapidly taken up by the systemic compartment of the body

Insoluble Tritiated Particle (ITP) – Any tritiated particle from which the tritium is not readily released in air or aqueous solutions during the time interval over which the sample is collected and initially analyzed. This time interval may vary significantly, typically ranging from minutes to days.

Leak-tight: A leakage rate, which, "in a practical sense, precludes any significant release of radioactive materials. This degree of containment is achieved by demonstration of a leakage rate that is \leq to 1 x 10⁻⁷ ref cm³/s of air, at an upstream pressure of 1 atmosphere (atm) absolute, and a downstream pressure of 0.01 atm abs, or less. Note: A leakage rate of 1 x 10⁻⁷ ref cm³/s is equal to 4.09E-12 gram-moles of dry air or helium, and is equivalent to a helium leakage rate, under the same conditions, of approximately 2 x 10⁻⁷ cm³/s." (ANSI N14.5-2014))

Less than Hazard Category 3 Nuclear Facilities (replaces the term Radiological Facilities):

Facilities that do not meet or exceed Category 3 threshold criteria specified in DOE STD-1027-92, Rev. 1, Table A.1, but still possess some amount of radioactive material are still Nuclear Facilities. The Category 3 threshold quantity of tritium is 16,000 curies. Less than Hazard Category 3 Nuclear Facilities are exempt from some requirements such as development and maintenance of DSAs but are not exempt from other safety requirements (e.g., 10 CFR Part 820 Subpart A, 10 CFR Part 835). Less than Hazard Category 3 Nuclear Facilities are those with an inventory of radiological materials below the levels as defined in DOE-STD-1027-92, Chg. 1, (currently 16,000 curies). There is no official or legal lower threshold limit to be become a non-nuclear facility for the Less than Hazard Category 3 nuclear facilities.
Low-level radioactive waste or Low-level waste: radioactive material that is not high-level radioactive waste, spent nuclear fuel, or AEA section 11.e.2 byproduct material. The phrase is defined in the (Low-Level Radioactive Waste Policy Amendments Act of 1985 and . DOE M 435.1-1)

Mixed waste: Waste containing both radioactive and hazardous waste components as defined by the Atomic Energy Act and the Resource Conservation and Recovery Act, respectively (DOE O 435.1-1)

Nonreactor nuclear facility: those facilities, activities or operations that involve, or will involve, radioactive and/or fissionable materials in such form and quantity that a nuclear or a nuclear explosive hazard potentially exists to workers, the public, or the environment, but does not include accelerators and their operations and does not includeactivities involving only incidental use and generation of radioactive materials or radiation such as check and calibration sources, use of radioactive sources in research and experimental and analytical laboratory activities, electron microscopes, and X-ray machines (10 CFR Part 830).

Nuclear facility: means a reactor or a nonreactor nuclear facility where an activity is conducted for or on behalf of DOE and includes any related area, structure, facility, or activity to the extent necessary to ensure proper implementation of the requirements established by this Part (10 CFR Part 830). DOE-STD-1027-92, Chg. 1 defines tritium inventory thresholds for nuclear facilities.

Observed Activity: The apparent quantity of radioactive material within a particulate as determined by liquid scintillation counting, without attempting to correct for beta particle self-absorption, bremsstrahlung, or the emissions from HT or HTO.

Organically Bound Tritium (OBT): A type of tritiated material in which the tritium has formed a chemical bond with an organic material – typically via a carbon-tritium bond.

Primary containment: The first barrier to an uncontrolled release of hazardous/radioactive material to the environment and/or other areas in the facility. The barrier may/may not serve for containment of the radioactive material (U.S. DOE Tritium Focus Group).

Protective Action Guides (PAGs): Projected numerical dose values established by EPA, DOE, or States for individuals in the population. These values may trigger protective actions that would reduce or avoid the projected dose.

Radioactive waste: Solid, liquid, or gaseous material that contains radionuclides regulated under the Atomic Energy Act of 1954, as amended, and of negligible economic value considering costs of recovery (DOE O 435.1 Chg. 1).

Radiological area: Any area within a controlled area which must be posted as a "radiation area," "high radiation area," "very high radiation area," "contamination area," "high contamination area," or "airborne radioactivity area" in accordance with (10 CFR 835.603)

Receiving and/or shipping area: An area or two different areas that have been designated as radioactive materials receiving and/or Shipping Areas and have been posted for the receipt and shipment of packaged radioactive materials.

Receiving and/or Shipping, Storage Area: An area or two different areas that have been designated as the Receiving and/or Shipping Area, Storage Area and have been posted for the storage of packaged incoming and outgoing shipments of radioactive materials.

Reference man: A hypothetical aggregation of human (male and female) physical and physiological characteristics arrived at by international consensus (ICRP Publication 23). These characteristics may be used by researchers and public health workers to standardize results of experiments and to relate biological insult from ionizing radiation to a common base. The "reference man" is assumed to inhale 8,400 cubic meters of air in a year and to ingest 950 liters of water in a year (International Commission on Radiological Protection (ICRP) Publication 89, "Basic Anatomical and Physiological Data for Use in Radiological Protection: Reference Values," September 2001).

Release of property: As used in DOE Order 5400.5 Chg. 2, it is the exercising of DOE's authority to release property from its control after confirming that residual radioactive material (over which DOE has authority) on the property has been determined to meet the guidelines for residual radioactive material in Chapter IV of DOE Order 5400.5 Chg. 2 or any other applicable radiological requirements. There may be instances in which DOE or other authority will impose restrictions on the management and/or use of the property if the residual radioactive material guidelines of Chapter IV of DOE Order 5400.5 Chg. 2 are not met or if other applicable Federal, state, or local requirements cause the imposition of such restrictions (DOE Order 5400.5 Chg. 2).

Safety analysis: A documented process that: Provides systematic identification of hazards within a given DOE operation, describes and analyzes the adequacy of the measures taken to eliminate, control, or mitigate identified hazards, and analyzes and evaluates potential accidents and their associated risks (DOE Standard 3009).

Safety-class structures, systems, and components (safety-class SSCs): the structures, systems, or components, including portions of process systems, whose preventive or mitigative function is necessary to limit radioactive hazardous material exposure to the public, as determined from safety analyses (10 CFR Part 830).

Safety-significant structures, systems, and components (safety-significant SSCs): the structures, systems, and components which are not designated as safety-class structures, systems, and

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Secondary containment: The second barrier to an uncontrolled release of hazardous or radioactive materials to the environment and/or other areas in the facility. The barrier may/may not serve for containment of the radioactive material (U.S. DOE Tritium Focus Group).

Self-Absorption Factor for Beta Particles (SAFβ): The fraction of beta particles emitted from within a particulate that escapes the particulate.

Self-Absorption Factor for Energy (SAFe): The fraction of energy emitted from within a particulate that escapes the particulate.

Soil column: An in-situ volume of soil through which liquid waste streams percolate from ponds, cribs, trenches, drain fields, or other areas or facilities used for the primary purpose of removing or retaining the suspended or dissolved radionuclides contained within the liquid process waste stream (DOE O 435.1).

Soluble Tritiated Particle: Any tritiated particle from which the tritium is readily released in air or aqueous solutions during the time interval over which the sample is collected and initially analyzed. This time interval may vary significantly, typically ranging from minutes to days.

Source material: (1) uranium, thorium, or any other material which is determined by the commission pursuant to the provisions of section 61 (42 USC 2091) to be source material; or (2) ores containing one or more of the foregoing materials in such concentration as the Commission now DOE and NRC may by regulation determine from time to time (Atomic Energy Act of 1954, 42 USC 2011 et seq.).

Special nuclear material: (1) plutonium, uranium enriched in the isotope 233 or in the isotope 235, and any other material which the Commission, pursuant to the provisions of section 51 (42 USC 2071) determines to be special nuclear material, but does not include source material; or (2) any material artificially enriched by any of the foregoing, but does not include source material (Atomic Energy Act of 1954, 42 USC 2011 et seq.).

Special Tritium Compound (STC): means any compound, except for H2O, that contains tritium, either intentionally (e.g., by synthesis) or inadvertently (e.g., by contamination mechanisms) (10 CFR Part 835).

Stochastic effects: means malignant and hereditary diseases for which the probability of an effect occurring, rather than its severity, is regarded as a function of dose without a threshold, for radiation protection purposes (10 CFR Part 835).

B-8 ENGINEERING-PDH.COM | NUC-132 | **Technical safety requirements (TSRs)**: the limits, controls, and related actions that establish the specific parameters and requisite actions for the safe operation of a nuclear facility and include, as appropriate for the work and the hazards identified in the documented safety analysis for the facility: Safety limits, operating limits, surveillance requirements, administrative and management controls, use and application provisions, and design features, as well as a bases appendix (10 CFR Part 830).

Tritiated Material: Any material containing at least an accountable amount of tritium

Tertiary containment: The third barrier to an uncontrolled release of hazardous or radioactive materials to the environment and/or other areas in the facility. The barrier may/may not serve for containment of the radioactive material (U.S. DOE Tritium Focus Group).

Treatment: Any method, technique, or process designed to change the physical or chemical character of waste to render it less hazardous, safer to transport, store or dispose of, or reduced in volume (DOE O 435.1 Chg. 1).

Uptake: For STCs, the process by which the tritium atoms in STCs are taken into the systemic compartment of the body. This process includes the uptake of tritium that has been dissociated from the host molecule as well as the uptake of an entire STC molecule

Waste container: A receptacle for waste, including any liner or shielding material that is intended to accompany the waste in disposal (DOE O 435.1 Chg 1)

Waste package: The waste, waste container, and any absorbent that are intended for disposal as a unit. In the case of surface contaminated, damaged, leaking, or breached waste packages, any overpack shall be considered the waste container, and the original container shall be considered part of the waste (DOE O 435.1 Chg. 1).

APPENDIX C: ASSAY METHODS

There are a number of different assay methods used at the DOE tritium facilities. Most facilities need assay equipment capable of measuring tritium in gaseous, solid, and liquid form.

- Gas Analysis: For assay of gaseous tritium, most facilities use some form of mass spectrometer ranging from quadrapole to large sophisticated light isotope drift tube systems. Gas analysis equipment; especially gas analysis equipment which will measure the low molecular weight gases like H₂, HD, HT, D₂, DT and T₂ accurately; is very expensive and requires a high degree of expertise to operate. These systems can cost from fifty to several hundred thousand dollars.
- Solid (Metal Tritide): Tritium stored in solid form such as a metal tritide must either be decomposed to return it to the gas form for analysis, or the heat output of the solid caused by the decay of tritium can be measured in a constant heat flow calorimeter. In order to use calorimetry to measure the tritium quantity, it must be known that the item being assayed does not contain any other radioactive component and that no chemical reactions are taking place in the container. Constant heat flow calorimeters vary in chamber size from a few cubic centimeters up to a few liters, and the item to be assayed must be small enough to fit inside the calorimeter chamber. The constant heat flow assay process is the most accurate assay method available if the chamber size and item to be assayed are well matched.
- Liquid (HTO, DTO, T₂O): Tritium at high concentrations in liquid form is generally measured using calorimetry. Low concentrations of tritium in liquid form are generally measured by using a scintillation counter. A sample of the liquid is mixed in a scintillation cocktail, and the quantity of tritium in the sample is measured.

C.1 Measurement Accuracy and Safeguards and Security

Past DOE directives required that tritium be accounted for to the hundredth of a gram and was a problem in that most of the equipment and the techniques used cannot accurately determine the tritium quantity to a hundredth of a gram once the quantity assayed exceeds about one half gram. Sophisticated equipment was justified mostly for special process needs. Even sophisticated equipment does not measure the quantity of tritium accurately to a hundredth of a gram once the quantity exceeds about five grams. The assay technique to be used in an operation or facility should be discussed with DOE safeguards and security to make sure that it will meet the DOE needs for the facility safeguards and security category and the activities performed in the facility. Current requirements for accountability have been raised to the gram level as discussed in Section 3.1.

C.2 Tritium Assay Analysis by PVT Mass Spectrometer

The most common method of assaying tritium in gaseous form, i.e., T_2 , HT, and DT, mixed with other gases such as Ar, $N_{2,}$, O_2 , and ³He, is referred to as "PVT mass spec." The total number of moles of gas, n, in a container is calculated using the equation

n = PV/zRT

where P = pressure in the container in torr

V = volume of the container in liters

z = compressibility factor (See Table C.1)

R = constant = 62.3631 (See below)

T = temperature (K)

In the formula, the container volume (V) is determined ahead of time by measurement using a volume measuring system, or, if no other means is available, it may be calculated from the physical dimension of the container. The gas pressure (P) and temperature (T) are determined by measurement with available instruments at the time of the mass spec sampling. R is a constant, which is a function of the units of pressure and volume used in the equation and is equal to 62.3631 for pressure in torr and volume in liters.

The compressibility factor (z) is a function of gas type, pressure, and temperature and is either determined from a compressibility table for tritium or estimated using a standard equation such as

z_(T2) = 1 + [(P (torr) x 0.000832)/1000]

This equation is for a temperature of 295 K.

Most operating facilities have established methods for determining the compressibility factor. For those facilities that do not already have these methods established, Table C-1, *Table of Tritium Compressibility Factors*, may be helpful.

As an example, for a container with a volume of 22.414 L at a pressure of 760 torr and a temperature of 273.15 K (Standard Temperature and Pressure (STP) conditions) the number of moles is calculated as follows:

N = PV/zRT = (760 x 22.414)/(1.000 x 62.3631 x 273.15) = 1.0000 mole

Note: z_(T2) at 273.15 K = 1.000.

The total moles of gas in the container at any time, t, is the sum of the moles of the individual gases present in the mixture at that time or in equation form:

 $PV/zRT = n_{(Moles Total)} = n_{(T2)} + n_{(HT)} + n_{(DT)} + n_{(CT4)} + n_{(qTw)} + n_{(He-3)} + n_{(N2)} + n_{(O2)} + n_{(Ar)} + n_{(etc.)}$

The $n_{(qTw)}$ represents a generic tritium-containing component. The "q" in, $n_{(qTw)}$, represents any other element which may be present, and the "w" represents the number of tritium atoms in the molecule. The $n_{(etc.)}$, represents any generic, non-radioactive, non-tritium component. From this equation, it follows that

 $PV/zRT = n_{(Moles Total)} = n_{(Total Moles of Tritium Containing Gases)} + n_{(Total Moles of Non-tritium Gases)}$

where

 $n_{\text{(Total Moles of Tritium Containing Gases)}} = n_{\text{(T2)}} + n_{\text{(HT)}} + n_{\text{(DT)}} + n_{\text{(CT4)}} + n_{(qTw)} + etc.$

and

 $n_{\text{(Total Moles of Non-Tritium Gases)}} = n_{\text{(He-3)}} + n_{\text{(N2)}} + n_{\text{(O2)}} + n_{\text{(Ar)}} + n_{\text{(etc.)}} + \text{etc.}$

The number of moles of tritium in the container is the sum of the number of moles of tritium in each tritium component. The number of moles of tritium in each tritium component is equal to the number of moles of the component multiplied by the moles of tritium per mole of component. The moles of tritium per mole of component, is defined as the ratio of the number of tritium atoms in the component chemical formula to the number of tritium atoms in T_2 , i.e., 2.

 $n_{(\text{Total Moles of Tritium})} = \underline{2}n_{(\text{T2})} + \underline{1}n_{(\text{HT})} + \underline{1}n_{(\text{DT})} + \underline{4}n(\text{CT}_4)/2 + \underline{w} n_{(\text{qTw})} + \text{etc.}$

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TABLE C-1: Table of tritium compressibility factors at 295 K

Р		Р						Р		Р	
(atm)	z(T2)	(atm)	z(T₂)	P (atm)	z(T₂)	P (atm)	z(T₂)	(atm)	z(T₂)	(atm)	z(T₂)
0.0	1.0000	3.0	1.0019	6.0	1.0038	9.0	1.0057	12.0	1.0076	15.0	1.0095
0.1	1.0001	3.1	1.0020	6.1	1.0039	9.1	1.0058	12.1	1.0077	15.1	1.0095
0.2	1.0001	3.2	1.0020	6.2	1.0039	9.2	1.0058	12.2	1.0077	15.2	1.0096
0.3	1.0002	3.3	1.0021	6.3	1.0040	9.3	1.0059	12.3	1.0078	15.3	1.0097
0.4	1.0003	3.4	1.0021	6.4	1.0040	9.4	1.0059	12.4	1.0078	15.4	1.0097
0.5	1.0003	3.5	1.0022	6.5	1.0041	9.5	1.0060	12.5	1.0079	15.5	1.0098
0.6	1.0004	3.6	1.0023	6.6	1.0042	9.6	1.0061	12.6	1.0080	15.6	1.0099
0.7	1.0004	3.7	1.0023	6.7	1.0042	9.7	1.0061	12.7	1.0080	15.7	1.0099
0.8	1.0005	3.8	1.0024	6.8	1.0043	9.8	1.0062	12.8	1.0081	15.8	1.0100
0.9	1.0006	3.9	1.0025	6.9	1.0044	9.9	1.0063	12.9	1.0082	15.9	1.0101
1.0	1.0006	4.0	1.0025	7.0	1.0044	10.0	1.0063	13.0	1.0082	16.0	1.0101
1.1	1.0007	4.1	1.0026	7.1	1.0045	10.1	1.0064	13.1	1.0083	16.1	1.0102
1.2	1.0008	4.2	1.0027	7.2	1.0046	10.2	1.0064	13.2	1.0083	16.2	1.0102
0.1	1.0001	4.3	1.0027	7.3	1.0046	10.3	1.0065	13.3	1.0084	16.3	1.0103
1.4	1.0009	4.4	1.0028	7.4	1.0047	10.4	1.0066	13.4	1.0085	16.4	1.0104
1.5	1.0009	4.5	1.0028	7.5	1.0047	10.5	1.0066	13.5	1.0085	16.5	1.0104
1.6	1.0010	4.6	1.0029	7.6	1.0048	10.6	1.0067	13.6	1.0086	16.6	1.0105
1.6	1.0010	4.7	1.0030	7.7	1.0049	10.7	1.0068	13.7	1.0087	16.7	1.0106
1.8	1.0011	4.8	1.0030	7.8	1.0049	10.8	1.0068	13.8	1.0087	16.8	1.0106
1.9	1.0012	4.9	1.0031	7.9	1.0050	10.9	1.0069	13.9	1.0088	16.9	1.0107
2.0	1.0013	5.0	1.0032	8.0	1.0051	11.0	1.0070	14.0	1.0089	17.0	1.0107
2.1	1.0013	5.1	1.0032	8.1	1.0051	11.1	1.0070	14.1	1.0089	17.1	1.0108
2.2	1.0014	5.2	1.0033	8.2	1.0052	11.2	1.0071	14.2	1.0090	17.2	1.0109
2.3	1.0015	5.3	1.0034	8.3	1.0052	11.3	1.0071	14.3	1.0090	17.3	1.0109
2.4	1.0015	5.4	1.0034	8.4	1.0053	11.4	1.0072	14.4	1.0091	17.4	1.0110
2.5	1.0016	5.5	1.0035	8.5	1.0054	11.5	1.0073	14.5	1.0092	17.5	1.0111
2.6	1.0016	5.6	1.0035	8.6	1.0054	11.6	1.0073	14.6	1.0092	17.6	1.0111
2.7	1.0017	5.7	1.0036	8.7	1.0055	11.7	1.0074	14.7	1.0093	17.7	1.0112
2.8	1.0018	5.8	1.0037	8.8	1.0056	11.8	1.0075	14.8	1.0094	17.8	1.0113
2.9	1.0018	5.9	1.0037	8.9	1.0056	11.9	1.0075	14.9	1.0094	17.9	1.0113
3.0	1.0019	6.0	1.0038	9.0	1.0057	12.0	1.0076	15.0	1.0095	18.0	1.0114

$Z_{(T2)} = 1 + \{[(P_{atm} \times 760) \times 0.000832]/1000\}$

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Table C-1: Table of Tritium Compressibility Factors at 295 K (continued)

Р		Р		Р		Р		Р			
(atm)	z(T₂)	(atm)	z(T₂)	(atm)	z(T₂)	(atm)	z(T₂)	(atm)	z(T ₂)	P (atm)	z(T2)
18.0	1.0114	21.0	1.0133	24.0	1.0152	27.0	1.0171	30.0	1.0190	33.0	1.0209
18.1	1.0114	21.1	1.0133	24.1	1.0152	27.1	1.0171	30.1	1.0190	33.1	1.0209
18.2	1.0115	21.2	1.0134	24.2	1.0153	27.2	1.0172	30.2	1.0191	33.2	1.0210
18.3	1.0116	21.3	1.0135	24.3	1.0154	27.3	1.0173	30.3	1.0192	33.3	1.0211
18.4	1.0116	21.4	1.0135	24.4	1.0154	27.4	1.0173	30.4	1.0192	33.4	1.0211
18.5	1.0117	21.5	1.0136	24.5	1.0155	27.5	1.0174	30.5	1.0193	33.5	1.0212
18.6	1.0118	21.6	1.0137	24.6	1.0156	27.6	1.0175	30.6	1.0193	33.6	1.0212
18.7	1.0118	21.7	1.0137	24.7	1.0156	27.7	1.0175	30.7	1.0194	33.7	1.0213
18.8	1.0119	21.8	1.0138	24.8	1.0157	27.8	1.0176	30.8	1.0195	33.8	1.0214
18.9	1.0120	21.9	1.0138	24.9	1.0157	27.9	1.0176	30.9	1.0195	33.9	1.0214
19.0	1.0120	22.0	1.0139	25.0	1.0158	28.0	1.0177	31.0	1.0196	34.0	1.0215
19.1	1.0121	22.1	1.0140	25.1	1.0159	28.1	1.0178	31.1	1.0197	34.1	1.0216
19.2	1.0121	22.2	1.0140	25.2	1.0159	28.2	1.0178	31.2	1.0197	34.2	1.0216
19.3	1.0122	22.3	1.0141	25.3	1.0160	28.3	1.0179	31.3	1.0198	34.3	1.0217
19.4	1.0123	22.4	1.0142	25.4	1.0161	28.4	1.0180	31.4	1.0199	34.4	1.0218
19.5	1.0123	22.5	1.0142	25.5	1.0161	28.5	1.0180	31.5	1.0199	34.5	1.0218
19.6	1.0124	22.6	1.0143	25.6	1.0162	28.6	1.0181	31.6	1.0200	34.6	1.0219
19.7	1.0125	22.7	1.0144	25.7	1.0163	28.7	1.0181	31.7	1.0200	34.7	1.0219
19.8	1.0125	22.8	1.0144	25.8	1.0163	28.8	1.0182	31.8	1.0201	34.8	1.0220
19.9	1.0126	22.9	1.0145	25.9	1.0164	28.9	1.0183	31.9	1.0202	34.9	1.0221
20.0	1.0126	23.0	1.0145	26.0	1.0164	29.0	1.0183	32.0	1.0202	35.0	1.0221
20.1	1.0127	23.1	1.0146	26.1	1.0165	29.1	1.0184	32.1	1.0203	35.1	1.0222
20.2	1.0128	23.2	1.0147	26.2	1.0166	29.2	1.0185	32.2	1.0204	35.2	1.0223
20.3	1.0128	23.3	1.0147	26.3	1.0166	29.3	1.0185	32.3	1.0204	35.3	1.0223
20.4	1.0129	23.4	1.0148	26.4	1.0167	29.4	1.0186	32.4	1.0205	35.4	1.0224
20.5	1.0130	23.5	1.0149	26.5	1.0168	29.5	1.0187	32.5	1.0206	35.5	1.0224
20.6	1.0130	23.6	1.0149	26.6	1.0168	29.6	1.0187	32.6	1.0206	35.6	1.0225
20.7	1.0131	23.7	1.0150	26.7	1.0169	29.7	1.0188	32.7	1.0207	35.7	1.0226
20.8	1.0132	23.8	1.0150	26.8	1.0169	29.8	1.0188	32.8	1.0207	35.8	1.0226
20.9	1.0132	23.9	1.0151	26.9	1.0170	29.9	1.0189	32.9	1.0208	35.9	1.0227
21.0	1.0133	24.0	1.0152	27.0	1.0171	30.0	1.0190	33.0	1.0209	36.0	1.0228

To determine the component in the gas and the number of moles of each component in the gas, a sample of the container gas is analyzed, and the mole percent of each gas is determined. This gas analysis results in a number for each component in the mixture, which represents the mole percent of each gas at the time of the analysis. The mole percent (m%) is calculated by

m% (component) = (Moles of a component/Moles Total) x 100

Therefore, the Mole Percent Total (m%(Total)) is

 $m\%_{(Total)} = 100 = m\%_{(T2)} + m\%_{(HT)} + m\%_{(DT)} + m\%_{(CT4)} + m\%_{(qTw)} + m\%_{(He-3)} + m\%_{(N2)} + m\%_{(O2)} + m\%_{(etc.)} + m\%_{(He-3)} + m\%_{(N2)} +$

The number of moles of each gas component in the container is calculated by

n (Moles of Component) = (m%(component) /100) x n(Total Moles)

The grams of each component can then be calculated using the formula

Grams of Component = $(m\%_{(component)}/100) \times (n_{(Total Moles)}) \times (Gram Molecular Weight of Component)$

The following is the process used to determine the number of moles and grams of tritium in the HT component in a container.

- 1. Calculate the total moles of material in the container.
- 2. Analyze the sample using a mass spectrometer to determine the mole percent of HT.
- 3. Calculate the number of moles of HT in the container.
- 4. Calculate the number of grams of HT in the container.
- 5. Multiply the moles of HT by $\frac{1}{2}$ to determine the moles of T₂ in the HT component.
- 6. Multiply the moles of HT by ½ and by the gram molecular weight of tritium to determine the grams of tritium in the HT component.

In steps 5 and 6, the $\frac{1}{2}$ is used because it is the ratio of the number of tritium atoms in HT to the number of tritium atoms in T₂ (HT/T₂ = 1/2).

The percent tritium in the container is the sum of the mole percent of each tritium component multiplied by the number of moles of tritium per mole of the tritium component. The moles of tritium per mole of component is equal to the ratio of the number of tritium atoms in the component chemical formula to the number of tritium atoms in T₂; i.e., 2. This can be expressed as the following formula:

```
m\%_{(Tritium Per Mole Total)} = \underline{2} m\%_{(T2)} + \underline{1} m\%_{(HT)} + \underline{1} m\%_{(DT)} + \underline{4} m\%_{(CT4)} + \underline{2w} m\%_{(qTw)} + etc.
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The moles of tritium in the container are the sum of the moles of tritium contained in each component in the container. This is calculated using the following equation, which is the ratio of the tritium atoms in the component chemical formula to the tritium atoms in T_2 ; i.e., 2. In the formula qT_w/T_2 this would be w/2, or in HT/T₂ this would be1/2.

 $\begin{aligned} \text{Moles of Tritium} &= \left[(m\%_{(T2)}/100) \times (T_2/T_2) \times n_{(\text{Moles Total})} \right] + \left[(m\%_{(\text{HT})}/100) \times (\text{HT}/T_2) \times n_{(\text{Moles Total})} \right] + \\ &= \left[(m\%_{(\text{DT})}/100) \times (\text{DT}/T_2) \times n_{(\text{Moles Total})} \right] + \left[(m\%_{(\text{CT4})}/100) \times (\text{CT}_4/T_2) \times n_{(\text{Moles Total})} \right] \\ &+ \left[(m\%_{(\text{qTw})}/100) \times (\text{qT}_{\text{w}}/T_2) \times n_{(\text{Moles Total})} \right] + \\ \end{aligned}$

where x/T_2 is the number of moles of tritium per mole of the tritium component.

Factoring out n_(Moles Total)/100 and rearranging, the equation becomes

 $(Moles of tritium x 100)/(n_{(Moles Total)}) = (m_{(T2)} + m_{(HT)} x 1/2 + m_{(DT)} x 1/2 + m_{(CT4)} x 2 + m_{(qTw)} x w/2 + etc.)$ = m_{(Tritium Per Mole Total)}

Rearranging the equation becomes

Moles of tritium = (n_(Moles Total) x m%_(Tritium Per Mole Total))/100

The amount of tritium in grams is obtained by multiplying the moles of tritium obtained in the last equation by the gram molecular weight of tritium (6.0321g).

As an example, the grams of tritium in a shipment of research grade tritium are determined using the following process.

An analysis of a shipment of research grade gaseous tritium shows the following:

Component	Percent
T ₂	99.704
D ₂	0.115
DT	0.079
HT	0.050
HD	0.023
³ He	0.016
Ar	0.012
N ₂	0.010
H ₂	0.005

The container pressure is 742 mm, temperature is 20°C, and volume is 49.348 liters. This gives a compressibility factor ($z_{(T2)}$) of 1.0006 and the constant, R, i+s 62.3631.

Calculating the percent tritium is as follows:

$$\begin{split} m\%_{(\text{Tritium Per Mole Total})} &= m\%_{(\text{T2})} + m\%_{(\text{HT})} \ge 1/2 + m\%_{(\text{DT})} \ge 1/2 \\ &= 99.704 + (0.050 \ge 1/2) + (0.079 \ge 1/2) \\ &= 99.704 + 0.025 + 0.0395 \\ &= 99.7685 \text{ percent} \end{split}$$

The number of moles of gas in the container is calculated by

 $n_{(Moles Total)}$ = PV/zRT = (742 x 49.348)/(1.0006 x 62.3631 x 293.15) = 2.002 moles total

The amount of tritium in grams is

Grams of tritium = $(n_{(Moles Total)} \times m_{(Tritium Per Mole Total)} \times 6.0321)/100$ = (2.002 x 6.0321 x 99.7685)/100 = 12.046 grams tritium

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The determination of the amount of tritium is only for the point in time that the sample was analyzed as a result of the decay of tritium. Over time, the number of moles of the gases containing tritium decreases. The pressure and number of moles of non-tritiated gases increase with time due to the ³He produced and the molecules formed by the atoms of other materials released when the tritium decays. Therefore, the mole percent and number of moles of gas in the container and in the sample change with time. Figure C-1 shows an example of the changing moles in a gas mixture.



FIGURE C-1. Change in mole percent with time in a mixture of 40% T₂, 40% ³He, and 20% Ar

The total number of moles in the container is known at the time of the sampling but not at the time of the analysis. If the gas analysis is performed on the same day as the sampling, then, since the half-life of tritium is 4500.88 days, the error caused by the decay is small (< 0.015 percent for 1 day, approximately 1 percent in 67 days). Some facilities are equipped to perform the sample analysis within a few minutes or on the same day as the sampling. Others facilities depend upon collecting a gas sample, on the sampling date, for analysis at a later date.

The following equations include three significant dates. The Sample Date is the day the gas sample for analysis is collected, and the pressure, volume, and temperature of the container are measured and recorded to determine the total moles of gas. The Analysis Date is the date the gas sample is analyzed to determine the mole percent of tritium per mole in the sample. The Book Value Date is a date on which the quantity of tritium in the container is known from a previous assay. Additionally,

it assumes a gaseous mixture at the start of 100% tritium and other stable gases; i.e., it does not contain HT, DT, HTO, or other radioactive or non-inert gases. The process steps are as follows:

- 1. Calculating the number of moles of gas in the container on the Sampling Date.
- 2. Determining the percent of tritium in the collected sample on the Analysis Date by gas analysis.
- 3. Using the two values in steps 1 and 2, the time period, in days, between the two dates and the half-life of tritium, calculating the number of grams of tritium in the container on the Sampling Date.

Once the quantity of tritium in the container on the Sampling Date is known, the quantity of tritium in the container for any other date, including the Book Value Date can be calculated.

The number of moles of gas in the container on the Sampling Date $(n_{(TotCSmplDa)})$ is the sum of the number of moles of the non-tritiated gases present in the container, which do not change with time due to decay, $(n_{(Non-tritium)})$, plus the number of moles of tritium in the container at the time of the sampling $(n_{(T2CSmplDa)})$. In equation form

 $PV/zRT = n_{(TotCSmpIDa)}$ = $n_{(Non-tritium)} + n_{(T2CSmpIDa)}$

Rearranging the equation it becomes

$$n_{(Non-tritium)} = n_{(TotCSmpIDa)} - n_{(T2CSmpIDa)}$$

{1}

The total number of moles of material in the container on the Analysis Date, $(n_{(TotCAnIDa)})$ is

 $n_{(TotCAnIDa)} = n_{(Non-tritium)} + n_{(T2CSmpIDa)} \times e^{((t \ln(0.5))/4500.88)} + 2 \times (n_{(T2CSmpIDa)} - n_{(T2CSmpIDa)} e^{((t \times \ln(0.5))/4500.88)} + 1 \times (n_{(T2CSmpIDa)} - n_{(T2CSmpIDa)} + 1 \times (n_{(T2CSmpIDa)} + 1 \times (n_{(T2CSmpIDa)} - n_{(T2CSmpIDa)} + 1 \times (n_{(T2CSmpIDa)} + 1 \times (n_{(T2CSmpIDa)} - n_{(T2CSmpIDa)} + 1 \times (n_{(T2CSmpIDa)} + 1 \times (n_{(T2CSmpIDa)}$

where $n_{(Non-tritium)} = sum of the moles of the other gases$ $(n_{(T2CSmpIDa)} (e^{((t \ln(0.5))/4500.88)}) = number of moles of T_2 decayed$ $2 x (n_{(T2CSmpIDa)} - n_{(T2CSmpIDa)} e^{((t \ln(0.5))/4500.88)}) = number of moles of ³He created$ t = time between the Sampling Date and Analysis Date in days

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Factoring, the equation becomes

 $n_{(TotCAnIDa)} = n_{(Non-tritium)} + n_{(T2CSmpIDa)} x (2 - e^{((t \times ln(0.5))/4500.88)})$ ^{2}

On the day the gas analysis is performed, the mole percent of tritium (m% $_{(T2MAnIDa)}$) is determined by gas analysis. The equation is

m% _(T2MAnlDa) is equal to the number of moles of tritium on the sampling date decayed to the analysis date; i.e., $(n_{(T2CSmplDa)} \times e^{((t \times ln(0.5))/4500.88)})$ divided by the number of moles in the sampled container on the analysis date; i.e., $(n_{(TotCAnlDa)})$ multiplied by 100 to convert it to percent.

 $m_{(T2MAnIDa)} = \{ (n_{(T2CSmpIDa)}e^{((txln(0.5))/4500.88)}) / n_{(TotCAnIDa)} \} x 100$

where $(n_{(T2CSmpIDa)} \times e^{((t \times ln(0.5))/4500.88)}) =$ number of decayed moles of T $(n_{(TotCAnIDa)}) =$ number of moles in the sample on the Analysis Date t = time between the Sampling Date and Analysis Date in days

Rearranging the equation, it becomes

$$n_{(TotCAnIDa)} = \{ (n_{(T2CSmpIDa)} e^{((t \times ln(0.5))/4500.88)}) / m_{(T2MAnIDa)} \} \times 100$$
(3)

Substituting Equation {1} into Equation {2}, we have

 $n_{(TotCAnIDa)} = n_{(TotCSmpIDa)} - n_{(T2CSmpIDa)} + n_{(T2CSmpIDa)} x (2 - e^{((t \times ln(0.5))/4500.88)})$

Rearranging the equation, it becomes

$$n_{(TotCAnIDa)} = n_{(TotCSmpIDa)} + n_{(T2CSmpIDa)} \times (1 - e^{((t \times ln(0.5))/4500.88)})$$
^{{4}

Substituting Equation {3} into Equation {4}, we have

100 $(n_{(T2CSmplDa)} e^{((t \times ln(0.5))/4500.88)}) / m_{(T2MAnlDa)} = n_{(TotCSmplDa)} + n_{(T2CSmplDa)} (1 - e^{((t \times ln(0.5))/4500.88)})$

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Multiplying through by m% (T2MAnIDa), it becomes

100 $(n_{(T2CSmpIDa)} e^{((t \times ln(0.5))/4500.88)}) = m_{(T2MAnIDa)} n_{(TotCSmpIDa)} + m_{(T2MAnIDa)} n_{(T2CSmpIDa)} (1 - e^{((t \times ln(0.5))/4500.88)})$

Rearranging and factoring, we have

 $n_{(T2CSmplDa)} = (n_{(TotCSmplDa)} \times m_{(T2MAnlDa)})/((e^{((t \times ln(0.5))/4500.88)} \times (100 + m_{(T2MAnlDa)})) - m_{(T2MAnlDa)}))$

The quantity of tritium in grams is then the number of moles of tritium on the Sampling Date, $n_{(T2CSmplDa)}$, multiplied by the gram molecular weight of tritium (6.03210 g) or

If a container has pure tritium mixed with other non-decaying and non-chemically reacting gases on the Book Value Date, sampled on the Sample Date and analyzed on the Analysis Date, then the gram of tritium in the container on the Sample Date can be calculated using the derived formula, the PV/zRT data and the m%_(T2MAnIDa) data measured on the Analysis Date.

Figure C-2 is a graph of the changes in the moles of material taking place in a container of pure T_2 versus time over a period of six tritium half-lives. The graph shows the moles of tritium decreasing from 1.0 and approaching 0.0, the ³He increasing from 0.0 and approaching 2.0, and the total moles increasing from 1.0 and approaching 2.0.



FIGURE C-2. Moles of T_2 and ³He versus time

Similar formulas can be derived for other two-component gases, such as HT mixed with other non-tritiated gases and DT mixed with other non-tritiated gases. See Figures C-3 to C-6 for other examples.



FIGURE C-3: Moles of DT, 3 He, and D₂ versus time



FIGURE C-4: Mole percent of T_2 , D_2 , DT, and ³He versus time



FIGURE C-5: 40% T₂, 40% ³He, and 20% Ar - Changes in mole percent of components versus time



FIGURE C-6: 40% DT, 40% ³He, and 20% Ar, Change in mole percent of each component versus time

C.3 Calorimetry Assay

Calorimetry is the quantitative measurement of heat. A calorimeter is an apparatus for measuring heat quantities generated in or emitted by materials in processes such as chemical reaction, changes of state, and formation of solutions. Heat is generally measured in calories or joules. A calorie is a unit of heat energy equal to the heat energy required to raise the temperature of a gram of water from 14.5 to 15.5°C, at a constant pressure of 1 atmosphere. A calorie is equal to 4.186 joules.

A calorimeter designed to be used in processes that continually generate heat (power sources) and measures power instead of heat is called a Constant Heat Flow (CHF) calorimeter. A CHF calorimeter measures the power (joules/second) of a source not the heat output (joules) of a source. The power is usually measured in Watts, which is a unit of power equal to 1 joule/second.

A radioactive material is a power source, which deposits the energy due to decay in the radioactive material itself and in the materials surrounding the radioactive material. The power generated by the decay of tritium has been measured and is equal to 0.3240 ± 0.0009 watts/gram of tritium.

C-17 ENGINEERING-PDH.COM | NUC-132 | Mound Laboratory has been the leader in the design, fabrication, calibration, and operation of CHF calorimeters for many years. Mound has specialized in the development of CHF calorimeters to be used in the measurement of radioactive material quantities by measuring their power output. CHF calorimeters are generally designed to meet the specific needs of the items to be assayed and are limited in application by the following:

- Physical size of the calorimeter measurement chamber,
- Wattage range of the measurement system,
- Precision and accuracy of the measurement for the size and wattage range of the item to be measured,
- Throughput or number of samples to be measured per day.

CHF calorimeters have been designed in many different configurations, such as over/under, and twin. Most CHF systems in use today use digital control systems operated by a stored program and are easy to operate. The steps in making a CHF measurement are generally as follows:

- Install a dummy mass in the calorimeter container, pack steel or copper wool around the dummy mass, and install it in the measurement chamber.
- Make a zero baseline run at a wattage level (W_{zbl}), which is at a wattage level greater than the unknown wattage level of the sample to be measured.
- During the baseline run, the digital control system establishes a calorimeter bridge voltage value for a known (W_{zbl}) wattage input.
- Remove the calorimeter container from the measurement chamber, remove the dummy sample from the container, and replace it with the sample to be measured, place it back in the measurement chamber, and make an unknown sample run.
- During the unknown sample run, the digital control system decreases the power in the calorimeter until the bridge voltage is the same as that measured in the zero baseline run.
- The power input to the calorimeter during this unknown sample run (W_{usr}) is measured.
- The power of the sample being measured (W_s) is calculated by subtracting the wattage value measured during the zero baseline run from the wattage measured during the unknown sample run to find the wattage of the sample. In equation form:

$$W_s = W_{zbl} - W_{usr}$$

The calorimeter factor for tritium used at most DOE sites for the purposes of reporting accountable quantities of tritium to DOE is 0.3240 +/- 0.0009 Watts/g of tritium.

CHF calorimetry can be used to measure tritium in solid form. CHF is the most accurate method available for the measurement of tritium quantities if the chamber size and wattage level of the item to be measured are well matched to the specifications of the CHF system being used. CHF systems, however

- Do not provide any information about the different gases present in a container (e.g., HT, DT, H₂, D₂, ³He),
- Only measure the quantity of tritium in the container,
- Are not currently available for items larger than 11 inches in diameter and 16 inches long, and
- Take several hours to complete a single measurement.

APPENDIX D: CONTAMINATION AND SURFACE ACTIVITY THRESHOLDS

D.1 Appendix D to Part 835 - Surface Radioactivity Values

The data presented in Appendix D are to be used in identifying contamination and high contamination areas as defined in Sec. 835.2(a), identifying the need for surface contamination monitoring and control in accordance with Sec. 835.404, identifying the need for radioactive material controls in accordance with Sec. 835.1101.

	Total (fixed +				
Removable	removable) {2},				
{2}, {4}	{3}				
1,000{7}	5,000				
20	500				
200	1,000				
1,000	5,000				
10,000	See footnote 6				
	Removable {2}, {4} 1,000{7} 20 200 1,000 10,000				

Surface Radioactivity Values {1} [In dpm/100 cm²]

{1} The values in this Appendix, with the exception noted in footnote 6, apply to radioactive contamination deposited on, but not incorporated into the interior of, the contaminated item. Where surface contamination by both alpha- and beta-gamma-emitting nuclides exists, the limits established for alpha- and beta-gamma-emitting nuclides apply independently.

{2} As used in this table, dpm (disintegrations per minute) means the rate of emission by radioactive material as determined by correcting the counts per minute observed by an appropriate detector for background, efficiency, and geometric factors associated with the instrumentation.

{3} The levels may be averaged over one square meter provided the maximum surface activity in any area of 100 cm^2 is less than three times the value specified. For purposes of averaging, any square meter of surface should be considered to be above the surface radioactivity value if (1) from measurements of a representative number of sections it is determined that the average contamination level exceeds the applicable value; or (2) it is determined that the sum of the activity of all isolated spots or particles in any 100 cm₂ area exceeds three times the applicable value.

{4} The amount of removable radioactive material per 100 cm2 of surface area should be determined by swiping the area with dry filter or soft absorbent paper, applying moderate pressure, and then assessing the amount of radioactive material on the swipe with an appropriate instrument of known efficiency. (Note—The use of dry material may not be appropriate for tritium.) When removable contamination on objects of surface area less than 100 cm² is determined, the activity per unit area should be based on the actual area, and the entire surface should be wiped. It is not necessary to use swiping

techniques to measure removable contamination levels if direct scan surveys indicate that the total residual surface contamination levels are within the limits for removable contamination.

{5} This category of radionuclides includes mixed fission products, including the Sr-90 which is present in them. It does not apply to Sr-90 which has been separated from the other fission products or mixtures where the Sr-90 has been enriched.

{6} Tritium contamination may diffuse into the volume or matrix of materials. Evaluation of surface contamination shall consider the extent to which such contamination may migrate to the surface in order to ensure the surface contamination value provided in this appendix is not exceeded. Once this contamination migrates to the surface, it may be removable, not fixed; therefore, a "Total" value does not apply. In certain cases, a "Total" value of 10,000 dpm/100 cm₂ may be applicable either to metals of the types from which insoluble special tritium compounds are formed, that have been exposed to tritium, or to bulk materials to which insoluble special tritium compound particles are fixed to a surface.

{7} These limits apply only to the alpha emitters within the respective decay series.

D.2 Response to Questions and Clarification of Requirements and Processes: DOE Order 5400.5 Chg.
2, Section II.5 and Chapter IV Implementation (Requirements Relating to Residual Radioactive Materials), DOE Office of Assistant Secretary for Environment, Safety and Health, dated November 17, 1995

TABLE 1 SURFACE ACTIVITY GUIDELINES	
Allowable Total Residual Surface Activity (dpm/100 cm	²) ⁴

Radionuclides ⁵	Average ^{6/7}	Maximum ^{9/8}	Removable ⁹
Group 1 – Transuranics, I-125, I-129, Ac-227, Ra-226, Ra-	100	300	20
228, Th-228, Th-230, Pa-231			
Group 2 – Th-natural, Sr-90, I-126, I-131, I-133,	1,000	3,000	200
Ra-223, Ra-224, U-232, Th-232			
Group 3 – U-natural, U-235, U-238, and associated decay	5,000	15,000	1,000
products, alpha emitters			
Group 4 – Beta-gamma emitters (radionuclides with decay	5,000	15,000	1,000
modes other than alpha emission or spontaneous ¹⁰ fission)			
except Sr-90 and others noted above ⁷			
Tritium (applicable to surface and subsurface) ¹¹	N/A	N/A	10,000

4 As used in this table, dpm (disintegrations per minute) means the rate of emission by radioactive material as determined by counts per minute measured by an appropriate detector for background, efficiency, and geometric factors associated with the instrumentation.

5 Where surface contamination by both alpha- and beta-gamma-emitting radionuclides exists, the limits established for alpha- and beta-gamma-emitting radionuclides should apply independently.

6 Measurements of average contamination should not be averaged over an area of more than 1 m². For objects of smaller surface area, the average should be derived for each such object.

- 7 The average and maximum dose rates associated with surface contamination resulting from beta-gamma emitters should not exceed 0.2 mrad/ h and 1.0 mrad/ h, respectively, at 1 cm.
- 8 The maximum contamination level applies to an area of not more than 100 cm².
- 9 The amount of removable material per 100 cm² of surface area should be determined by wiping an area of that size with dry filter or soft absorbent paper, applying moderate pressure, and measuring the amount of radioactive material on the wiping with an appropriate instrument of known efficiency. When removable contamination on objects of surface area less than 100 cm² is determined, the activity per unit area should be based on the actual area, and the entire surface should be wiped. It is not necessary to use wiping techniques to measure removable contamination levels if direct scan surveys indicate that the total residual surface contamination levels are within the limits for removable contamination.
- 10 This category of radionuclides includes mixed fission products, including the Sr-90 that is present in them. It does not apply to Sr-90 that has been separated from the other fission products or mixtures where the Sr-90 has been enriched.
- 11 Property recently exposed or decontaminated should have measurements (smears) at regular time intervals to ensure that there is not a build-up of contamination over time. Because tritium typically penetrates material it contacts, the surface guidelines in Group 4 are not applicable to tritium. The Department has reviewed the analysis conducted by the DOE Tritium Surface Contamination Limits Committee ("Recommended Tritium Surface Contamination Release Guides," February 1991), and has assessed potential doses associated with the release of property containing residual tritium. The Department recommends the use of the stated guideline as an interim value for removable tritium. Measurements demonstrating compliance of the removable fraction of tritium on surfaces with this guideline are acceptable to ensure that non-removable fractions and residual tritium in mass will not cause exposures that exceed DOE dose limits and constraints.