

**ANALYSIS OF THE POSSIBILITY OF, AND CONSEQUENCES FROM, HYDROGEN DEFLAGRATION
AND DETONATION RESULTING FROM RADIOLYSIS-PRODUCED HYDROGEN IN AN IODINE-131
RADIOPHARMACEUTICAL SOLUTION FROM AN ACCIDENT SCENARIO WHEREBY THE
SOLUTION AND GASES, INCLUDING HYDROGEN, ARE DISTRIBUTED TO THE CLOSED AND
SEALED SHIPPING CAST INSERT VESSEL**

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Accident Scenario:

A sealed Schott vial having a volume of 26.3 mL containing 10 mL of aqueous basic I-131 radioisotope solution is sealed and contained in a shielding insert (HS-55x138-SS) with a PTFE liner having an air volume of 214.4 mL including the air contained in the Schott vial. This I-131 solution when sealed contains 100 Ci of I-131, which is allowed to decay in the sealed vial for 28 days during which time 0.008053 grams (0.003995 moles) of hydrogen gas is generated by radiolysis. At this time the Schott vial breaks and its entire liquid and gaseous contents are spilled into the shielding insert. Subsequent to this spill into the shielding insert vessel the hydrogen gas is ignited by a static spark having energy in excess of the hydrogen-gas minimum-ignition energy (0.02 mJ). The consequences of this accident are described below.

Background:

The conditions in the shielding insert vessel immediately prior to the ignition of the hydrogen gas are summarized in Table 1.

Table 1. Pre-Ignition Conditions for Loss of Containment of One I-131 Product Vial

Parameter	Description/Value
Temperature (T_o)	298 °K
Pressure (P_o)	1 atmosphere
Gas Volume	214.4 mL
Hydrogen Content	0.008053 grams (0.003995 moles)
Oxygen Content	0.05882 grams (0.001838 moles)
Nitrogen Content	0.19198 grams (0.0068515 moles)
Gas Effective Molecular Weight (pre-ignition)	28.115 g/mole (mixed gases)
Hydrogen Mole Fraction	0.31492
Oxygen Mole Fraction	0.14491
Nitrogen Mole Fraction	0.54016
Hydrogen Stoichiometric Mole Fraction	0.2953
Hydrogen Equivalence Ratio	1.0593
Hydrogen Mole Fraction (combustible range)	0.04 – 0.76
Hydrogen Mole Fraction (detonation range)	0.18 – 0.59

Combustion of hydrogen in air in a closed vessel generally results in a deflagration in which the hydrogen is oxidized at a subsonic velocity. On rare occasions, the combustion can be initiated as a detonation at a supersonic velocity; or the combustion can be initiated as a deflagration and then transition to a detonation. These three possibilities are analyzed below for the accident scenario described above.

Analysis:

The system in which the hydrogen accident scenario occurs is a closed, O-ring-sealed, smooth-wall, stainless steel vessel having a PTFE insert. The system is further described in Table 2.

Table 2. System Description for Loss of Containment of One I-131 Product Vial

Parameter	Description/Value
Vessel Diameter (with PTFE liner insert)	4.8 cm
Vessel Height (with PTFE liner insert)	12.4 cm
Vessel Volume	224.4 cm ³
Aqueous Volume	10 cm ³
Air Volume	214.4 cm ³
Hydrogen Mole Fraction	0.31492
Hydrogen Equivalence Ratio	1.0593
Hydrogen Minimum-Ignition-Energy	0.02 mJ
Typical Static-Spark Energy	10 mJ
Hydrogen Ignition Energy to Prompt Detonation	4.7 kJ
Auto Ignition Temperature Range (hydrogen)	400 °C ¹ - 585 °C ²
Adiabatic Explosion Flame Temperature (hydrogen) ³	2497 °K ⁴
Detonation Cell Size (λ) for Hydrogen at Equivalence Ratio \approx 1.0, $T_o = 298$ °K	1.5 cm ⁵
Gas Effective Molecular Weight [pre-ignition (M_o)]	28.115 g/mole (mixed gases: N ₂ , O ₂ , H ₂)
Gas Effective Molecular Weight [post-ignition (M_b)]	25.396 g/mole (mixed gasses: N ₂ , H ₂ , H ₂ O _v)
Peak Deflagration Pressure Range [during ignition (P_m)]	100.1 ⁶ – 136.3 ⁷ psig

1. *Sub-Scenario A: Hydrogen Deflagration:* In the unlikely event that a static spark could be originated in the high-humidity⁸ closed vessel or the auto-ignition temperature for hydrogen

¹ Zabetakis MG. Flammability characteristics of combustible gases and vapors. U.S. Bureau of Mines Bulletin 627, Washington D.C. (1965).

² HySafe, The International Association for Hydrogen Safety. Hydrogen Fundamentals, Table 1-1. http://www.hysafe.org/download/997/brhs_ch1_fundamentals-version%201_0_1.pdf (accessed March 30, 2016).

³ The adiabatic flame temperatures for the deflagration of hydrogen gas reported in the literature range from 2400 °K to 2497 °K. The maximum temperature is reported here.

⁴ Heidari A, Wen JX. Flame acceleration and transition from deflagration to detonation in hydrogen explosions. International Journal of Hydrogen Energy 2014;39:6184-6200.

⁵ NUREG/CR-4961 SAND87-7128 R3. A summary of hydrogen-detonation experiments. May 1989.

⁶ NFPA 68, Guide for venting of deflagrations, National Fire Protection Association (1988), Table C-1.

⁷ SFPE Handbook of Fire Protection Engineering (1988), Closed Vessel Deflagrations (calculated from the equation provided).

could be reached, a deflagration of the hydrogen gas would result until it is extinguished or the available oxygen is consumed. This deflagration could produce a maximum adiabatic⁹ flame temperature of 2497 °K and a peak deflagration pressure of 136.3 psig. This maximum pressure is calculated from following equation from the SFPE Handbook¹⁰.

$$\frac{P_m}{P_o} = \frac{M_o \cdot T_b}{M_b \cdot T_o}$$

where:

P_m = maximum pressure at completion of combustion

P_o = initial pressure prior to ignition

M_o = molecular weight of gas-air mixture

M_b = molecular weight of combustion products

T_b = burn gas temperature at end of combustion

T_o = initial temperature of gas-air mixture

The use of adiabatic flame temperatures is estimated to produce elevated pressure ratios on the average of 10%. In the instant case for hydrogen, the calculated pressure from the above equation of 136.3 psig compared to that tabulated in NFPA 68¹¹ of 100.1 psig represents a 36% higher value for the deflagration pressure.

2. *Sub-Scenario B: Hydrogen Prompt Detonation Initiated on Ignition:* This scenario is not considered to be possible based on the magnitude of the ignition-to-prompt-detonation energy for hydrogen (4.7 kJ), which exceeds the only minimally-plausible available energy input of 10 mJ from a static spark by a factor of 470,000. In NUREG/CR-4961¹², hydrogen explosions, originating in prompt detonation absent the presence of high explosives, are accorded “a very low probability”. Obviously, there are no high explosives in the closed vessel in which the radiopharmaceutical I-131 products, produced under rigorous cGMP protocols, are to be transported.
3. *Sub-Scenario C: Hydrogen Deflagration-to-Detonation Transition (DDT):* Under certain conditions it is possible for a hydrogen gas-air mixture that was initiated as a deflagration to transition to a detonation producing pressures that are approximately 2 times higher than the deflagration pressure. These conditions are described and discussed relative to the instant scenario.

⁸ Ten milliliters of water is also present in the closed vessel, which will produce an equilibrium water-vapor-pressure of 23.8 torr at 25 °C and 100% relative humidity in the closed vessel.

⁹ An adiabatic event presumes that no energy is transferred from the closed system to its surroundings, which is not thermodynamically possible but does result in a conservatively high estimation of the maximum deflagration pressure.

¹⁰ See footnote 7.

¹¹ See footnote 6.

¹² See footnote 5.

- a. For hydrogen gas-air mixtures to experience DDT, vessel diameter (D) must be less than the detonation cell width (λ)¹³; or $\lambda/D < 1$. Detonation sensitivity is inversely proportional to the detonation cell width, which varies over a u-shaped curve with its minimum width (1.5 cm at 298 °K) at the hydrogen-oxygen equivalence ratio = 1, (when the stoichiometric mole ratios are precisely balanced) or near to it. At the extremes (equivalence ratios of ≤ 0.4 –a fuel-lean mixture- to ≥ 5 –a fuel-rich mixture), the detonation cell width exceeds 1 meter. When a diluent, such as water vapor, is introduced to the hydrogen-air mixture, the detonation cell width increases. When the initial temperature (system energy) is increased the detonation cell width decreases.

Considering the instant scenario, the hydrogen-oxygen equivalence ratio is 1.0593 (ignoring for the moment the water vapor) and T_o is 298 °K. Under these conditions the hydrogen detonation cell width (λ) is 1.5 cm and $\lambda/D = 1.5 \text{ cm}/4.8 \text{ cm} = 0.3125$. At this λ/D value, DDT is possible if other conditions are favorable. However, under the scenario, 10 mL of aqueous solution is also contained in the vessel generating a water vapor diluent when the I-131 product solution vial fails. This could result in an expansion of the detonation cell width by a factor of 10 or more¹⁴ such that $\lambda/D > 1$, which would not support DDT. Whether or not the detonation cell width could support DDT under the scenario would depend on the timing of the introduction of the ignition energy (static spark). If it occurred coincident with the breakage of the I-131 product vial, and prior to water-vapor equilibration, the λ/D value could theoretically support DDT.

- b. For a hydrogen gas-air mixture to transition from deflagration to detonation (DDT), given a favorable detonation cell width, there must be turbulent flow in the combustion tube generally caused by pathway obstructions, expansions or contractions of the tube diameter, or bends in the tube. In the instant scenario, the combustion vessel approximates a smooth-wall tube without obstructions or bends and not inclined to generate the turbulent flow pattern requirement to propagate DDT.
- c. For hydrogen-DDT to occur in a pipe, a “run-up” distance of $L/D = 10$ to 60 is required between steady deflagration and the formation of a detonation wave; where L = pipe length and D = pipe diameter¹⁵. Under the instant scenario, L and D for the shipping vessel are 12.4 and 4.8 cm, respectively, or $L/D = 2.58$, which will not support hydrogen DDT.

¹³ The detonation cell size is discussed in NUREG/CR-6391 BNL-NUREG-52482. Detonation Cell Size Measurements in High-Temperature Hydrogen-Air-Steam Mixtures at the BNL High-Temperature Combustion Facility. November 1997.

¹⁴ Kaneshige M, Shepard JE. Detonation Database. Graduate Aeronautical Laboratories, California Institute of Technology, Pasadena, CA 91125. Explosion Dynamics Laboratory Report FM97-8. July 1997, revised September 1999.

¹⁵ National Fire Protection Association. Memorandum to NFPA Technical Committee on Explosion Protection Systems, September 2011. https://www.nfpa.org/Assets/files/AboutTheCodes/67/67_F2012_ROP_ballot.pdf (accessed March 30, 2016).

Conclusions:

1. It is highly improbable that a static spark could occur in the high-humidity shipping vessel environment resulting from the spillage of an I-131 product solution into the closed, sealed vessel.
2. Contrary to conclusion 1, if a static spark having an energy in excess of 0.02 mJ did occur in the closed shipping vessel with spilled liquid and gaseous contents, the equivalence ratio for hydrogen and oxygen is in the range that will support hydrogen deflagration in the vessel.
3. If hydrogen deflagration did occur, the maximum pressure reached in the closed vessel would be in the range of 100 to 136 psig.
4. The initiation of hydrogen combustion in the closed vessel by a static spark is 470,000 times less energetic than that required to initiate prompt hydrogen detonation. There are no high-explosives in the I-131 product vial or the closed shipping vessel or any other available ignition source with sufficient energy to initiate prompt hydrogen detonation.
5. The conditions for significant turbulent flow in a steady hydrogen deflagration in the smooth-wall closed vessel are not sufficient to produce deflagration-to-detonation transmission.
6. The "run-up" distance in the smooth-wall vessel is a minimum of 3.87 times shorter than that required to produce deflagration-to-detonation transmission.
7. Hydrogen detonation neither from prompt-initiation nor deflagration-to-detonation transmission can occur under the instant scenario.