SUITABILITY OF CF_3I TO REPLACE HALON 1301 AS THE INERTING AGENT IN WING FUEL TANKS ON THE F-16 AIRCRAFT

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ABSTRACT

At the request of the Under Secretary of Defense (Acquisition, Technology and Logistics), the Director of Defense Research and Engineering convened an Independent Review Panel (IRP) to assess the four critical technical issues and comment on how they might affect implementation of CF_3I as a viable substitute for halon 1301 in the F-16 inerting application.

The four technical areas identified as critical to the assessment were: materials compatibility, low temperature performance, human toxicology, and atmospheric chemistry. The questions to be answered were: was the research conducted scientifically, is there sufficient information on CF_3I to decide whether it is an acceptable alternative to halon 1301 for wing tank inertion on the F-16, and if not, what additional Science and Technology research is required?

The conclusions of the IRP were as follows:

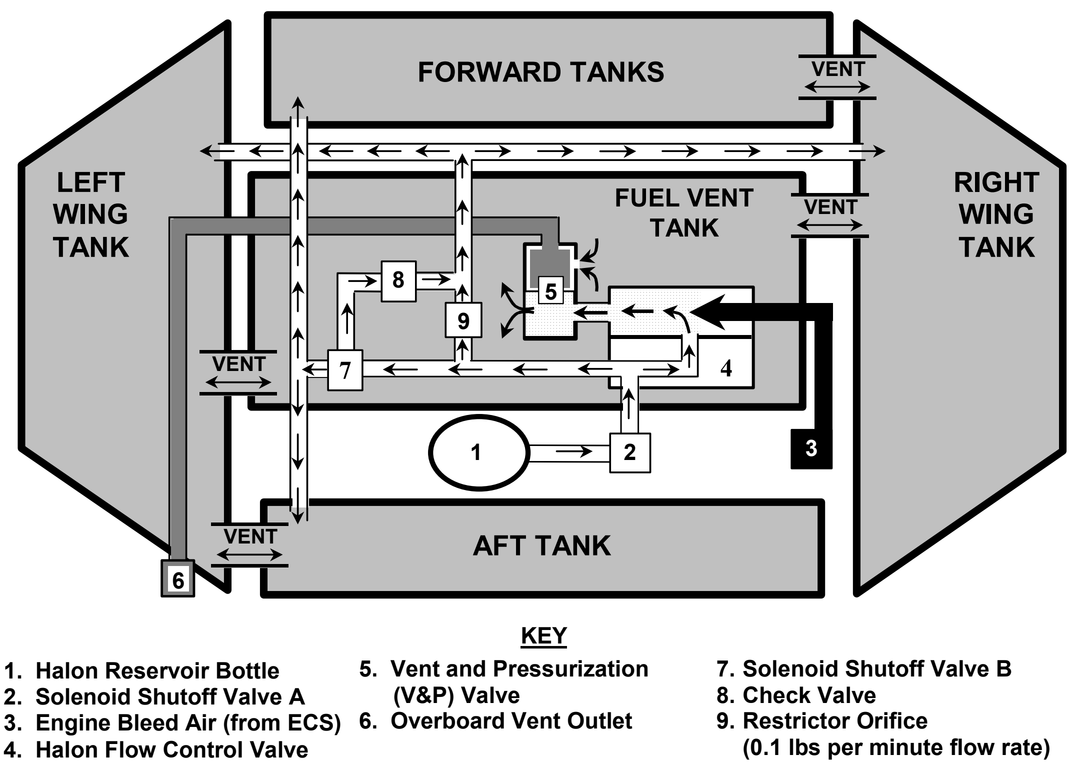
- CF_3I is more chemically reactive than halon 1301. After further qualification testing, it may be possible to specify materials that could be used in service with CF_3I.
- CF_3I is inadequate as a replacement for halon 1301 in the existing F-16 system due to its higher boiling point and resultant reduced delivery pressure at low temperatures.
- CF_3I is more toxic than halon 1301. It would be unwise to replace a chemical with a more toxic one. More rigorous toxicity testing of CF_3I would provide a more quantitative estimate of its toxicity in realistic exposure scenarios.
- Ozone depletion from F-16 application of CF_3I could be as small as one eighth that of halon 1301 (at lower altitudes) or as large as one and two-thirds times as damaging as halon 1301 (at higher altitudes). In any case, CF_3I use onboard an F-16 would be a Class I substance if significant amounts are released above 20,000 ft, and the U.S. Clean Air Act bans use of Class I substances.

HALON 1301 USE IN THE F-16

The Air Force currently uses halon 1301 (CF_3Br) to inert the wing tanks of its front line F-16 fighter aircraft while the aircraft is in a combat zone or other area known to be hostile, i.e., when the pilot believes there is the potential for hostile action that might cause ignition of fuel in the fuel tanks should a direct hit be taken. There are 1,400 aircraft in the F-16 fleet (not including those sold to foreign governments), and the Air Force continues to discharge at least 5,000 kg (10,000 lb) of halon 1301 into the atmosphere each year. This figure could rise 10- to 20-fold if there were a major regional conflict.

A schematic of the F-16 fuel tank inerting system is shown in Figure 1. The wing fuel tanks are inerted by halon 1301 vapor from a single, non-heated storage bottle. Once activated by the pilot, there is a 20 s burst that releases about half the agent. The control valve then resets to provide a 45 min continuous bleed of agent (ca. 1 lb/min) against ambient atmospheric pressure. This action maintains an inerting concentration of agent in the ullage space above the liquid fuel in the tank. During this bleeding phase, there is a continuous purge of the fuel tank head space to the outside atmosphere. The agent left in the bottle is vented as the aircraft climbs after its missions, usually towards refueling at *ca*. 10 km (30,000 ft). A sizable fraction of the total load could be released during this operation.

Figure 1. Components of the F-16 Fuel Tank Inerting System



There is no one standard flight profile that can be used to specify exactly when, where, and at what altitude inerting of the wing tanks will occur. Air Force data indicate that the F-16 can operate between ground level and 20 km (*ca*. 60,000 ft), and inerting of wing tanks normally occurs between 6 km (*ca.* 20,000 ft) and 14 km (*ca.* 45,000 ft).

PROJECT BACKGROUND

The Air Force will eliminate present halon 1301 usage on the F-16 through the phased replacement of the F-16 aircraft by the Joint Strike Fighter (JSF), which does not use halon 1301. These new production aircraft will use alternatives such as HFC-125 or an On Board Inert Gas

Generating System (OBIGGS). The JSF will reach Air Force initial operating capacity in 2011, and the F-16 will completely retire from the Air Force inventory by 2024.

To be responsive in the interim period, the Air Force has evaluated several halon 1301 alternatives. To be effective in the F-16, such an alternative would have to be a true “drop-in” replacement due to the time necessary to accomplish any retrofit engineering on the F-16 fleet prior to the complete phase-in of the JSF.

CF_3I was one of these potential alternatives. However, after completing an evaluation of CF_3I in 1999, the Air Force decided not to use it based on unresolved material compatibility, poor low temperature performance (condensation) and distribution, higher toxicity than halon 1301, and potentially harmful atmospheric chemistry.[1] There was also a concern regarding extensive modifications required to the F-16 fuel tank inerting system.

The decision was controversial, and in 2002 The Director of Defense Research and Engineering requested that an independent Review Panel of distinguished scientists and technical experts independently review the four critical technical areas of interest:

1. **Materials Compatibility:** The IRP should review test results for CF_3I compatibility with metals, gasket materials, and lubricants to ascertain whether sufficient data are available to determine if CF_3I is compatible with the F-16 airframe materials. If this is not the case, then the IRP should identify the critical failure points and what additional testing needs to be performed.
2. **Low Temperature Performance:** An effective fire suppressant in a fuel tank inerting mode must maintain sufficient vapor pressure to inert adequately against a munition-ignited fire. The boiling point of the suppressant relative to the temperature of the surroundings can significantly affect the performance of the compound. The IRP should review test data to determine whether the higher boiling point of CF_3I relative to CF_3Br would result in diminished fire inerting capability.
3. **Human Toxicology:** Toxicological testing and analysis should consider risks of human exposure to CF_3I under normal operating conditions and maintenance procedures. Previous testing and analysis should be reviewed for their sufficiency to enable the safety of personnel in appropriate exposure scenarios.
4. **Atmospheric Chemistry:** Halon 1301 has a significant ODP due to its chemical stability in the troposphere and its photolysis in the stratosphere. CF_3I has different behavior in both the troposphere and stratosphere that is in need of review to determine its impact on the ozone layer as a function of the altitude at which the compound is released.

In each area, they were to answer the following three questions:

- Was the prior research conducted scientifically to produce the resulting data?
- Is there sufficient information on CF_3I to decide whether it is an acceptable alternative to halon 1301 for wing-tank inert use on the F-16?
- If not, what additional S&T research is required?

The following were the participants in the study:

Review Director
Mr. Robert Boyd, Office of the Director of Defense, Research and Engineering (DDR&E)

Moderator for Materials Compatibility/Low Temperature Performance
Mr. William Leach, Fire Protection Team Leader, Naval Air Warfare Center

Materials Compatibility Panel Members
Dr. Richard Ricker, Materials Science and Engineering Laboratory, National Institute of Standards and Technology
Dr. Steven Lawrence, Chemistry Division, U.S. Naval Research Laboratory

Low Temperature Performance Panel Members
Dr. Jiann (John) Yang, Fire Research Division, National Institute of Standards and Technology
Dr. Marino di Marzo, FireProtection Engineering Department, University of Maryland

Moderator for Human Toxicology and Atmospheric Chemistry
Dr. Richard Gann, Fire Research Division, National Institute of Standards and Technology, and Technical Program Manager, Next Generation Fire Suppression Technology Program

Human Toxicology Panel Members
Dr. Edgar Kimmel, Toxicology Detachment, Wright-Patterson Air Force Base
Dr. Steven Packham, State of Utah Department of Environmental Quality

Atmospheric Chemistry Panel Members
Dr. Susan Solomon, Aeronomy Laboratory, National Oceanic and Atmospheric Administration
Dr. Malcolm Ko, Atmospheric and Environmental Research Inc.
Dr. Donald Wuebbles, Department of Atmospheric Sciences, University of Illinois

Other Technical Resources:
Mr. David Sassaman, F-16 Fuels System Engineer, Lockheed Martin Aeronautics Company
Mr. Sherman Forbes, Office of the Secretary of the Air Force
Major Robert Torrick, Occupational Requirements Directorate, U.S. Air Force
Dr. Leslie Chaney, U.S. Army Center for Health Promotion and Preventive Medicine

The IRP meeting was organized and hosted by HydroGeoLogic, Inc. on August 21 and 22, 2002. The report was issued in September 2002.[2] The following sections relate the sub-panel assessments of the extensive reading materials and their experience, and analyses performed for this project.

MATERIALS COMPATIBILITY

When selecting or changing a material used in a critical application such as an aircraft, the candidate material is required to demonstrate that it can survive the service conditions including the whole range of loads, temperatures and chemical compositions of the operations, service, and storage environments. Years of operating experience have not revealed any major incompatibility problems between halon 1301 and the more than 2,000 different metal and polymer components are found in the F-16 inerting system.

Materials compatibility tests with CF_3I have to date have been in the laboratory only, with no systems qualification testing. The laboratory work indicates potential compatibility problems. Data from a series of tests at the National Institute of Standards and Technology (NIST)[3, 4] (Table 1) showed that CF_3I exhibited higher corrosion rates for all materials tested than halon 1301. One case of stress corrosion cracking (SCC) was evidenced. Both NIST and Lockheed Martin[5] found significant interactions of CF_3I with elastomers, possibly due in part to impurities in the CF_3I. As a consequence of these studies, both the Air Force Research Laboratory[6] and Lockheed Martin[5] have recommended that further materials compatibility testing be conducted.

Table 1. Comparison of Corrosion Rate Data[7]

Material	Halon 1301	Std. Error	Cf$_3$i	Std. Error	Ratio
	g/m^{2}d		g/m^{2}d		CF_3I/CF_3Br
Nit 40	0.00042	0.00012	0.0014	0.0003	3.5
AA6061-T6	0.01262	0.0074	0.0396	0.18881	3.1
304 Stainless	0.00060	0.00016	0.0040	0.00055	6.8
Ti 15-3-3-3	0.00051	0.00007	0.0025	0.00048	5.0
AISI 4130	0.02791	0.01395	0.55297	0.06940	19.8

The panelists concurred and also noted that there remained issues of knowing the levels of impurities that are tolerable (necessary for specifying the procurement), the effect of dynamic service conditions.

The answers to the questions were:

1. *Was the research conducted scientifically?* Yes. The relevant work from NIST was planned carefully, conducted properly, and documented thoroughly. The Lockheed Martin compatibility testing also appears to have been conducted in an appropriate manner, given the limited scope that defined it. Neither study was designed to emulate fully the conditions of the F-16 fuel tanks.

2. *Is there sufficient information on CF_3I to decide whether it is an acceptable alternative to halon 1301 for wing tank inert use on the F-16?* No, nor is there sufficient information to reject it from further consideration. The NIST work was not specifically directed toward fuel line materials in an F-16, although many of the materials and environments studied are relevant. The Lockheed Martin study was too brief and too narrowly defined to make an informed decision regarding CF_3I qualification. Moreover, pass/fail criteria have not been established for this application, so the performance of halon 1301 becomes the only benchmark. CF_3I proved more aggressive than halon 1301 in many of the comparison tests of these studies, and hence caution should be exercised when proceeding to qualify this agent for such a critical application as this.

3. *If not, what additional S&T research is required?* Carefully designed flight qualification tests followed by monitored (limited) service with engineering performance evaluations should be conducted with CF_3I before converting agents. The cause of the observed SCC in Ti alloy should be investigated to ensure that this will not occur with alloys that are in the fuel system. The origin of the reaction with Cu should be investigated to determine why it occurred and why other alloys should not be susceptible to this or similar reactions.

LOW TEMPERATURE PERFORMANCE

Halon 1301 has a very low boiling point, and thus a relatively high vapor pressure at the low ambient temperatures found at the operational altitudes of the F-16 aircraft. When activated, halon 1301 transfers from the storage bottle to the wing tanks under its own vapor pressure to provide the necessary concentration to inert the fuel in the tank. The main issue associated with low temperature performance of CF_3I is its higher boiling point and resulting reduced vapor pressure relative to halon 1301. Further, a recent study[8] of cold discharge of CF_3I in an engine nacelle *(not wing tank)* showed that some pooling occurred.

At the minimum temperature prescribed by the F-16 operational envelope, *ca.* -62 °C (-80 °F), the vapor pressure of CF_3I is 13.9 kPa.[9] As the airplane altitude increases, the fuel tank pressure decreases. At 30 km (*ca*. 60,000 ft), the highest altitude at which the five suppressant would be released, the atmospheric pressure is 7.1 kPa. This is the minimum possible value of the atmospheric pressure within the operating envelope. The V&P valve (Figure 1) keeps the fuel tank at 17 kPa to 25 kPa above the atmospheric pressure in a combat situation. This means the fuel tank pressure is at least 24 kPa. Therefore, CF_3I cannot flow out of the bottle since it is at a lower pressure than the fuel tank (7.1 kPa *vs*. 24 kPa). A similar analysis for an operating temperature of -40 °C (-40 °F) shows that the agent would be viable between 30 km and 12 km (38,800 ft), but not lower.

Under these conditions, one also has to consider the possible mass flux of agent. The agent must flow at a rate sufficient to flush the tanks and to achieve the desired inerting concentration. Halon 1301 is delivered at 0.4 kg/s (085 lb/s) to achieve this objective. The critical discharge mass flux for a vapor varies linearly with the agent vapor pressure and with the square root of the molecular weight. At -40 °C, CF_3I will flow at about one fourth the rate of halon 1301 in the same system. At this reduced flux the agent would not be able to displace fuel vapor and air in the tank. One could resize the system to achieve similar flow. However, that would require increasing the flow area of some of the system components fourfold.

To achieve a performance similar to that of halon 1301, the simplest approach would be to increase the storage bottle pressure by maintaining it at a higher temperature. For CF_3I to supply the burst of 0.4 kg/s the bottle temperature needs to be *ca*. –22 °C (-8 °F), requiring about 4 kW. The piping system feeding the agent to the fuel tanks also would have to be heated appropriately. During this delivery of the agent into the colder fuel tank, two competing phenomena are occurring: most of the agent would condense in a mist due to the drop in temperature, while the remaining vapor contributes to the total pressure according to its molar fraction. The fine droplets in the mist may vaporize as they mix with the gases in the fuel tank but this process is not fast at low temperature.[8] Should the droplets hit the liquid fuel, it is likely that liquid CF_3I

will become segregated at the bottom of the fuel tank and some of the agent will not be available for inerting the tanks. This removal of some of the agent introduces a significant level of uncertainty as to the performance of the system over the required 45 min.

The answers to the questions were:

1. *Was the research conducted scientifically?* Yes.

2. *Is there sufficient information on CF_3I to decide whether it is an acceptable alternative to halon 1301 for wing tank inert use on the F-16?* Yes.

HUMAN TOXICOLOGY

In all cases of toxic risk assessment, risk is directly proportional to toxic potency. There is very low risk to life from inhalation of the suppressant during the actual inerting of F-16 wing tanks using either halon 1301 or CF_3I. However, system maintenance and repair, routine recharging of vented tanks, storage, and material transport occasions must be considered. Here, historically there is very little risk attendant with use of the current system that employs halon 1301. There are no comparable precedents to evaluate potential risk scenarios involving CF_3I. The system reliability factors for CF_3I remain unknown, especially if implementation of CF_3I involves a significant engineering retrofit. Therefore, the actual health risks that might be associated with implementing use of CF_3I cannot be estimated or quantified. It is possible to estimate the *relative* risk of halon 1301 *vs*. CF_3I based on toxic potency.

For these compounds, the toxic potency has been equated to the lowest observable adverse effect level (LOAEL) for cardiac sensitization. This is measured using an experimental protocol in which dogs are administered epinephrine in conjunction with agent exposure, simulating a physiologic condition of stress. The LOAEL values reported for halon 1301 and CF_3I are 7.5 volume % and 0.4 volume %, respectively. The design concentration for halon 1301 is cited as 5.0 volume %, which is below the LOAEL; the design concentration for CF_3I is 7.0 volume %, which is almost 20 times greater than its LOAEL. It is difficult to advocate the use of an agent when the concentration shown to elicit a lethal toxic effect is lower than the concentration required for the agent's intended use.

There are questions about the validity of the LOAEL values. The epinephrine challenge used in the protocol is about 10 times greater than endogenous epinephrine release rates in humans under stress. In addition, the LOAEL for CF_3I was set relying on responses observed in only two animals, one each in two experimental groups lading to a question of statistical accuracy.[10] An additional issue regarding CF_3I cardiac sensitization involves the anecdotal report of two human volunteers repeatedly breathing this material.[11] A physiologically based–pharmacokinetic model using estimates of applicable breathing parameters was used to simulate the blood levels of CF_3I in these individuals. These simulations estimated peak blood levels 100 times larger than peak blood levels associated with exposures used to set the LOAEL for this material, indicating that concentrations higher than the measured LOAEL might be safe for people. However, the inhaled concentrations of CF_3I were not verified, no scientific method was used to measure an effect, and factors related to possible tolerance from repeated trials were not demonstrated nor considered.

In the absence of data for characterizing actual risk, a hypothetical scenario can illustrate the relative precautions for storing and handling of CF_3I vs. halon 1301. Consider the situation in which the failure of a single container of either agent would result in an untenable environment, *i.e.*, the concentration would exceed the LOAEL. In a 3 m x 3 m x 2.4 m (10 ft x 10 ft x 8 ft) room, one could store halon 1301 in containers holding 8 kg (*ca.* 18 lb) of the chemical, but CF_3I would need to be stored in bottles holding no more than 0.5 kg (*ca.* 1 lb) to maintain the same level of safety.

The answers to the questions were:

1. *Was the research conducted scientifically?* Most of the research appeared to be well done and the analysis of the data was appropriate. However, a single determination of CF_3I cardiac sensitization is not sufficient. In the case of the human inhalation simulation there are no hard data to verify the concentration of the material inhaled and the "study" was not conducted under controlled scientific conditions.

2. *Is there sufficient information on CF_3I to decide whether it is an acceptable alternative to halon 1301 for wing tank inert use on the F-16?* Yes. Current information is sufficient to make a reliable scientific comparison between halon 1301 and CF_3I on the basis of toxic potency.

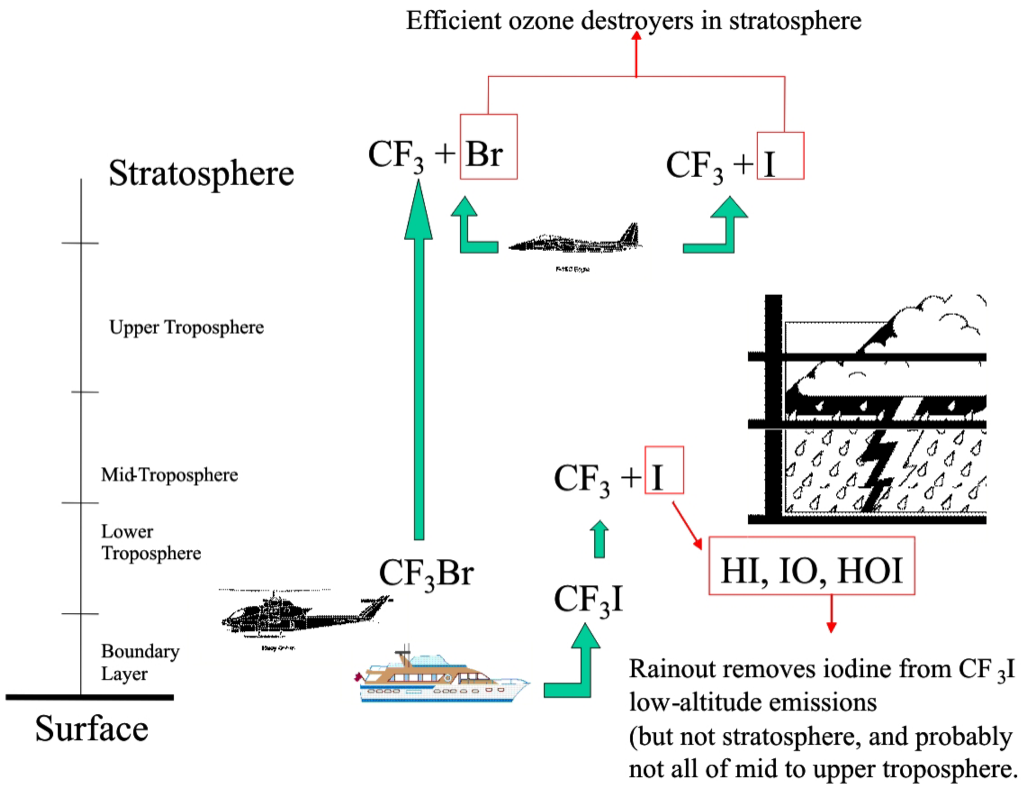
ATMOSPHERIC CHEMISTRY

Early studies examining the potential effects of CF_3I on stratospheric ozone assuming emissions at the Earth's surface studies resulted in extremely small ozone depletion potential (ODP) estimates for CF_3I due to surface emissions: <0.008[12] and 0.006.[13] A new analysis conducted for this project determined a value of 0.012. In contrast, the ODP for halon 1301 (CF_3Br) is about 12. The use of any chemical with an ODP greater than 0.2 is to be controlled under the current U.S. Clean Air Act, and the U.S. Environmental Protection Agency gives careful consideration to controls on chemicals with ODP values as small as 0.05.

The small ODP values for CF_3I result from its very short atmospheric lifetime, approximately 4 days in the latest model studies. CF_3I will quickly decompose by absorption of sunlight, and the iodine released will be removed in the lower troposphere through rainout. Only a tiny fraction can reach the stratosphere to destroy ozone. CF_3Br, on the other hand, absorbs sunlight much less effectively, and has an atmospheric lifetime of about 60 years. CF_3Br therefore reaches the stratosphere even if emitted at the surface. Once in the stratosphere, most of the reactive Br atoms are released directly into the ozone layer where they can affect ozone.

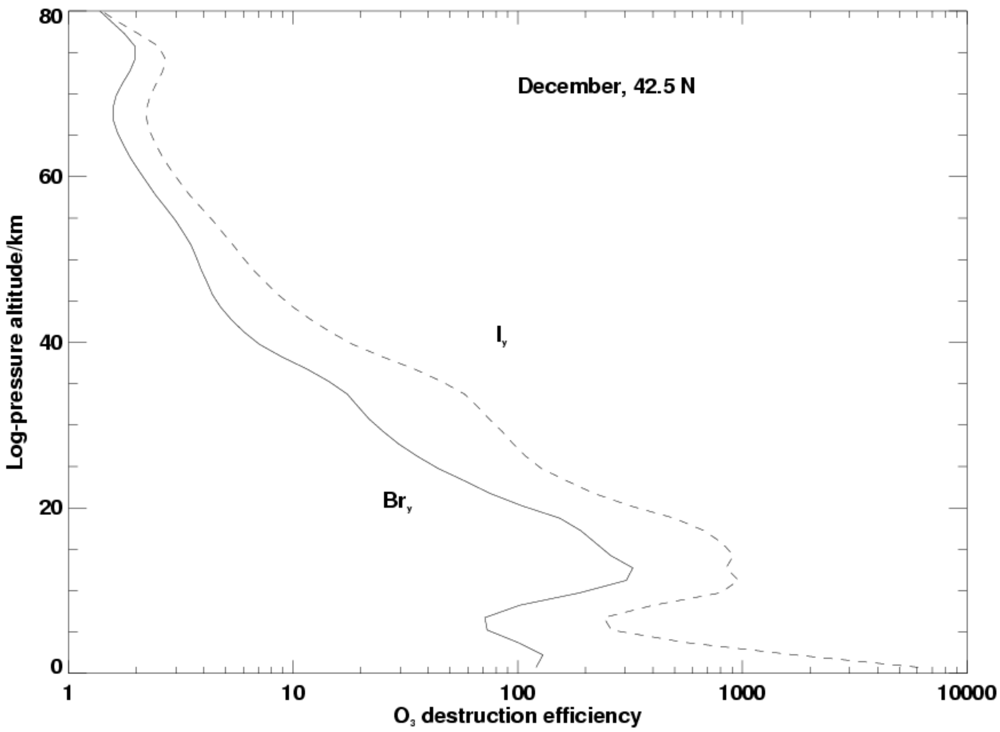
Almost all of the emissions of CF_3Br (and thus CF_3I if used as a replacement) from its use as an inerting agent in F-16s occur above 6 km (20,000 feet) altitude up to a peak altitude of 14 km (*ca.* 45,000 feet). Released at these altitudes, some or all of the reactive iodine is available above the altitude where it can be rained out, and will all be available to react with ozone. It is estimated that about 0.1 mole % is transported to the stratosphere from surface release, with the fraction increasing up to about 10 mole % for releases in the upper troposphere, and 100 mole % for direct release in the stratosphere. Because of its long lifetime, the fraction of CF_3Br reaching the stratosphere is essentially independent of whether it is released near the ground or directly into the stratosphere. This is shown pictorially in Figure 2. Short-lived molecules like CF_3I could have a larger short-term impact in the ozone layer even if the cumulative effect is smaller,[14] but the stratosphere would be cleansed of the emitted iodine soon after any discontinuing use of CF_3I as an inerting agent.

Figure 2. Halogen Transport to the Stratosphere from Use of Fire Suppression Agents



Once in the stratosphere, iodine atoms are 3 to 6 times as potent as Br atoms at destroying ozone. (See Figure 3.) Including transport effects, the panelists estimated CF_3I release from F-16 aircraft as being between 13 % and 167 % as damaging to the ozone layer as equivalent usage of CF_3Br. The variance results from the range of possible values for the ozone destruction efficiency of I relative to Br, the fraction of agent released by the aircraft directly into the stratosphere, and the fraction of agent reaching the stratosphere from lower altitude release. Reduction in the uncertainties associated with these estimates would require further analyses using numerical models of global atmospheric chemistry and physics. Three-dimensional modeling studies would be required to fully assess the effects of emissions from the aircraft. The above numbers imply a steady-state ODP for CF_3I in the F-16 application of 0.82 to 10.9. Compounds with an ODP above 0.2 are Class I ODSs under the United States Clean Air Act.

Figure 3. Relative Ozone Destruction Efficiency at Mid-Latitudes[15]



The answers to the questions were:

1. *Was the research conducted scientifically?* Yes.

2. *Is there sufficient information on CF_3I to decide whether it is an acceptable alternative to halon 1301 for wing tank inert use on the F-16?* Yes. The information provided suggests that release of CF_3I at the stated flight conditions could cause greater ozone depletion than halon 1301, particularly for flights/CF_3I release at higher latitudes.

3. *If not, what additional S&T research is required?* Additional understanding of the actual location of the emission (altitude and latitude) coupled with additional modeling would narrow the uncertainties associated with the estimates and help better assess if CF_3I is less harmful to the ozone layer compared to halon 1301 in specific cases.

INDEPENDENT REVIEW PANEL CONCLUSIONS

MATERIALS COMPATIBILITY

- The information provided does not indicate that qualification testing or trials can be dispensed with on the basis of similarity of CF_3I to CF_3Br.

- CF_3I is more chemically reactive than halon 1301, which could lead to metal corrosion or elastomer failure. CF_3I should not be accepted for inerting application on the basis that it corrodes like materials faster than halon 1301.

- More quality/service testing is required on the materials compatibility of CF_3I before it could be recommended as a replacement for halon 1301. After further service testing, it would be possible to specify materials that could be used in service with CF_3I.

LOW TEMPERATURE PERFORMANCE

- CF_3I is inadequate as a replacement agent for halon in the existing F-16 system due to the reduced delivery pressure of the CF_3I at low temperatures.

- Modifications of the system to increase the CF_3I delivery pressure may rely on heating the storage bottle and the connecting piping. This approach is somewhat piecemeal since condensation at the injection point in the fuel tank may remove a portion of the agent, thus reducing the overall inerting performance.

- If the agent storage bottle and distribution lines were heated, uncertainty remains in regard to condensation of the CF_3I in the fuel tank, which would compromise (or even totally negate) its inerting ability. More testing is necessary before a retrofitted system could be designed.

- It is possible to calculate and experimentally evaluate the impact of condensation in the fuel tank. However, the inherent variations in the operation of the F-16 aircraft (i.e., its altitude excursions) introduce a significant level of uncertainty in the performance of the CF_3I inerting system.

HUMAN TOXICOLOGY

- CF_3I is more toxic than halon 1301. More rigorous toxicity testing of CF_3I would provide a more quantitative estimate of its toxicity in realistic exposure scenarios.

- CF_3I is a more potent cardiac sensitizer than halon 1301. This is illustrated by fact that given a comparable exposure duration, the exposure concentration causing ventricular fibrillation is 18.75 times greater for halon 1301 than CF_3I.

- CF_3I presents a greater health risk than halon 1301. Current data are insufficient to estimate health risks associated with implementing use of CF_3I.

ATMOSPHERIC CHEMISTRY

- The ODP of CF_3I is highly dependent upon the altitude and latitude at which it is released. It was calculated that CF_3I usage onboard an F-16 aircraft could be between 13% and 167% as damaging to the ozone layer as usage of halon 1301. In other words, ozone depletion from F-16 application of CF_3I could be as small as one eighth that of halon 1301 (at lower altitudes) or as large as one and two-thirds times as damaging as halon 1301 (at higher altitudes). However, even for conservative choices, CF3I use onboard an F-16 would be a class I substance if significant amounts are released above 20,000 ft, and the US Clean Air Act bans use of class I substances.

- ODP is a measure of the cumulative effects (time integrated) on ozone from emission of an ODS. The effect from emitted halon 1301 is spread over several decades while that from CF_3I will last only several years. Thus, even for the case when the cumulative effects from CF_3I is one eighth of that from halon 1301, the immediate short term effect on ozone will still be comparable.

- These updated calculations indicate that there is not a clear-cut environmental advantage of CF_3I over halon 1301. Since this is the reason for proposing the change, CF_3I is not an acceptable alternative unless the results of more detailed modeling indicate a contrary position.

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