

***NIST Technical Note 1278***

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***Preliminary Screening Procedures  
and Criteria for Replacements  
for Halons 1211 and 1301***

***Richard G. Gann, John D. Barnes, Sanford Davis, Jonice S. Harris,  
Richard H. Harris, Jr., John T. Herron, Barbara C. Levin,  
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National Institute of Standards and Technology  
Gaithersburg, MD 20899

Sponsored by:  
U.S. Air Force Engineering Laboratory  
Air Force Engineering and Services Center  
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August 1990



**U.S. Department of Commerce**  
Robert A. Mosbacher, Secretary

National Institute of Standards and Technology  
John W. Lyons, Director

**U.S. Department of Commerce**  
National Institute of Standards and Technology  
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Gaithersburg, MD 20899

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## EXECUTIVE SUMMARY

The objective of this project is the identification of methods for rapidly and inexpensively screening a large number of chemicals for good performance with respect to each of the following properties:

- fire suppression efficiency,
- low residue level,
- low electrical conductivity,
- low metals corrosion,
- high materials compatibility,
- stability under long-term storage,
- low toxicity,
- stratospheric ozone depletion, and
- global warming.

The project also establishes the figures of merit by which the test results will be judged.

The signing of the Montreal Protocol in 1987 demonstrated an international consensus that a variety of fully halogenated organic chemicals (halocarbons) were damaging stratospheric ozone. The current halogenated fire suppressants, or halons, were among the chemicals whose production is restricted by the Protocol. The likelihood of major reductions or a total ban on their production by the turn of the century is driving a search for alternative chemicals.

No such search has been conducted since the late 1940s, when the U.S. Army conducted the study that led to today's predominant halogenated fire suppressants: halons 1301 ( $\text{CF}_3\text{Br}$ ) and 1211 ( $\text{CF}_2\text{ClBr}$ ). Halon 2402 ( $\text{C}_2\text{F}_4\text{Br}_2$ ) is in use to a lesser degree, as are halons 1001 and 1011.

This project corresponds to a first step in a government/industry program to identify and qualify candidate replacements for halons 1301 and 1211 that will satisfy the needs of the major users for existing applications. The strategy is to conduct a program of closely coordinated research, empirical testing, and analysis. These are to be performed by experts in the critical technical areas and are to be focussed tightly on the objective.

The National Institute of Standards and Technology (NIST) has assembled a team of specialists in each of the areas of testing. These experts have surveyed the existing methods in their fields and compiled descriptions of the protocols. Each procedure has been analyzed, considering at least the following factors:

- ease of operation for these types of chemicals,
- number of locations having the capability to perform the test,
- amount of chemical required, and
- relevance of the figure(s) of merit to this program.

In several cases, adaptations were needed to improve the fit to this application. In some cases, no standard methods existed and procedures were derived from the most appropriate current practice.

Each method then under consideration was examined. The test was performed for at least halons 1211 and 1301. Since it was likely that these compounds would perform similarly in the test, a third chemical that would behave differently was selected and tested. The results of these checks were analyzed for quality.

Screening tests are used to identify those chemicals worthy of further examination as alternative clean fire suppressants. Because the emphasis should be on accurate indication, rather than high precision, we have chosen to report the results of each test in a series of Performance Classes. We have related each Performance Class either to the performance of halons 1211 and 1301, or to some accepted criterion for practical use. In both cases, the scientific and fire suppression communities have a sensible basis for deciding whether to study a chemical further.

**The reader is reminded that these methods and performance classes have been developed for screening purposes only and should not be used for final acceptance of an agent without more extensive evaluation.**

If more extensive evaluation is appropriate, it can be performed at additional cost, requiring more time and materials. While some of the screening procedures can be adapted to this purpose, in many cases we urge the use of alternative methods.

Nine screening procedures have been defined for characterizing potential candidates for replacing halons, particularly 1211 and 1301, now in use for fire suppression applications. These screening procedures have shown that they are able to distinguish between gases and liquids of varying degrees of performance. The results of this study leads to the following statements.

- A battery of screening tests has been constructed to guide the search for alternatives to the current halogenated fire suppressants. Some are based on standard ASTM procedures, some involve modifications of standard tests, and some are extensions of nonstandard practices. These can be used to decide whether to pursue a particular chemical further.
- The full battery of tests requires about 4 moles of chemical and can be performed in about 8 days for less than \$15,000. Lower costs would result for concurrent testing of a large number of chemicals. Sequences of testing, potentially conserving resources, can be constructed, as described below.
- The tests are straightforward to conduct. Where a standard method has been modified or a non-standard method is recommended, operating procedures are described. Multiple laboratories are available for performing each of these tests, but few can perform them all.
- High purity of the samples of chemicals to be tested is critical.
- There are different uses for these tests, e.g., research or production. This report contains examples of testing sequences for each of these. A well-conceived plan is especially important for production testing.
- The interpretation of the data from this battery of screens requires the expertise of persons knowledgeable in each of the fields described. Weak performance in any given area may not be the basis for eliminating any material from further consideration.
- Classes of performance have been determined for ease of interpretation. These relate to the current values placed on halons 1211 and 1301.
- These tests should only be used to make decisions on proceeding to investigate a chemical further. In that further study, most of these tests would be superseded by different uses of the apparatus or by different methods altogether.

- Neither the methods nor the performance classes are appropriate for specification or regulation at this time.

The authors appreciate the sponsorship of this project by the Engineering & Services Laboratory, Air Force Engineering & Services Center, Capt. John M. Floden, Contract Monitor. Consultation with several other people and organizations has added to the quality of the work: Major E. Thomas Morehouse, U.S. Air Force; Dr. Robert Tapscott and staff from the New Mexico Engineering Research Institute; Dr. William Pitts, NIST Center for Fire Research, and Mr. Daniel Moore, Du Pont Company. Drs. Ronald Sheinson and Dan Driscoll of the Naval Research Laboratory provided advice and facilities for performance of some of the fire suppression measurements. The members of the Technical Committee of the Halon Alternatives Research Corporation, chaired by Ms. Denise Mauzerall, provide helpful review during the project. Finally, Ms. Paula Garrett applied her considerable word processing skills to making the many parts of this report into a single, readable entity.

**SECTION I**  
**INTRODUCTION AND BACKGROUND**

Richard G. Gann and Sanford Davis  
Fire Measurement and Research Division  
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## SECTION I

### INTRODUCTION AND BACKGROUND

#### A. OBJECTIVE

This project is a first step in a government/industry program to identify and qualify candidate replacements for halons 1301 and 1211 that will satisfy the needs of the major users for existing applications.

The objective of this project is the identification of methods for rapidly and inexpensively screening a large number of chemicals for good performance of each of the properties by which a candidate will be judged:

- fire suppression efficiency,
- low residue level,
- low electrical conductivity,
- low metals corrosion,
- high materials compatibility,
- stability under long-term storage,
- low toxicity,
- stratospheric ozone depletion, and
- global warming.

The objective also includes establishing the figures of merit by which the test results will be judged.

#### B. BACKGROUND

The Montreal Protocol, signed by 41 countries in September, 1987, demonstrated an international consensus that a variety of fully halogenated organic chemicals (halocarbons) were causing damage to stratospheric ozone. The signers agreed to a freeze in the production and consumption levels of the named chlorinated fluorocarbons (CFCs) and halogenated hydrocarbon fire extinguishing agents (halons) beginning in January, 1989.<sup>1</sup> Furthermore, the participating countries agreed that by mid-1989, CFCs 11, 12, 113, 114, and 115 would be reduced to 1986 levels; by mid-1993, be reduced to 80 percent of those levels; and by mid-1998, be reduced to 50 percent. Halons 1211, 1301, and 2402 would be frozen at 1986 levels by 1992. The United States, Canada, and some of the European and Nordic countries have also discussed removing those CFCs and halons from the marketplace by the year 2000. It is believed that the terms of this complete phase-out will be included in the next version of the Montreal Protocol, to be written at the meeting scheduled for June 1990. The Environmental Protection Agency (EPA) has also notified the public that they will propose that restrictions on methyl chloroform and carbon tetrachloride be included in the next version of the Protocol [1].

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<sup>1</sup> Elkins, C.L., Remarks prepared for delivery by Charles L. Elkins, Director, Office of Toxic Substances, U.S. Environmental Protection Agency, International Conference on CFC and Halon Alternatives, Washington, DC, October 10, 1989.

The chemicals in question are being released in many ways, e.g., leaking air conditioners, degreasing of metal parts, expanding of foam plastics, and fire suppression. Indeed, their usage permeates the world's societies while harming the world's environment. The Protocol signifies a worldwide intent to decrease and eventually ban their production. This is driving a search for alternative chemicals for fire suppression.

Although these halocarbons were once regarded as beneficial to society and safe for people, a growing base of scientific theory and evidence has established that these halocarbons are serious depleters of stratospheric ozone. Ozone ( $O_3$ ) is a gas that filters the sun's ultraviolet radiation and limits the amount of radiation that reaches the earth's surface. Once released near ground level, the relatively nonreactive halons remain in the troposphere, for decades, gradually, crossing the boundary into the stratosphere. While in the stratosphere, they are photodissociated by absorbing the unfiltered ultraviolet rays from the sun. The chlorine (Cl) and bromine (Br) atoms which are produced then enter a complex sequence of reactions, resulting in a catalytic reduction of the ozone in the stratosphere and, eventually, to an increased intensity of ultraviolet rays reaching the earth's surface. The potential harm from this includes an increase in skin cancer incidence, global warming, and interference in the many food chains.

Since prehistoric times, people have used water to put out fires. Suppressing fires of any considerable size required a lot of water, and the damage from the suppression was often comparable to that from the fire. Toward the end of the nineteenth century, it was discovered that carbon tetrachloride ( $CCl_4$ ) was far more efficient and left no residue. It thus was the first "clean" fire suppression agent. A variety of devices were developed to deliver the chemical. This included pumpers and "grenades," glass jars filled with carbon tetrachloride, which were thrown into the fire. The jar broke, the liquid evaporated, the fire went out quickly, and the only cleanup was from the now-limited fire damage. Methyl bromide ( $CH_3Br$ ) and chlorobromomethane ( $CH_2ClBr$ ) were also developed as clean fire suppressants. All of these, however, were soon recognized to have harmful effects on people, thus limiting their use.

In the late 1940s, the U.S. Army began to search for new, effective, safe, and clean suppressants [2], focussing their search on compounds similar to the three mentioned above (although other chemicals were included). They called these chemicals "halons," short for (fully saturated) halogenated hydrocarbons and devised a shorthand nomenclature as follows. The chemical compound would have a number directly related to its chemical composition:

halon abcde has the chemical formula  $C_aF_bCl_cBr_dI_e$ .

Terminal zeroes were dropped; any atoms not identified as halogens were assumed to be hydrogens. Thus, carbon tetrachloride was halon 104; methyl bromide was halon 1001; and chlorobromomethane was halon 1011.

The Army program checked out many variants of the then-existing halons - mostly with one or two carbon atoms and a mixture of halogen atoms attached. Their small-scale flame inhibition tests were followed by others' larger scale fire suppression tests [3] and toxicity tests [4]. As a result, several halons were developed for commercial use. Today, two dominate usage: halons 1301 ( $CF_3Br$ ) and 1211 ( $CF_2ClBr$ ). Halon 2402 ( $C_2F_4Br_2$ ) is in use to a lesser degree, as are halons 1001 and 1011.

Halons 1211 and 1301 have properties that have made them a frequent choice of the fire suppression system designer. They are very effective at putting out fires. They leave no residue to clean up after the fire has been extinguished. They are low in toxicity, can be stored safely and compactly for long times; are noncorrosive and electrically nonconductive. Thus, they can be used in sensitive areas, for instance, around electronic equipment or in places where water damage is unacceptable, such as libraries or museums. Moreover, because people do not have to evacuate immediately, they can stay behind and continue possibly critical operations. As the use of these agents spread, facilities were designed with other safeguards reduced,

all because of the effectiveness and safety of the halons. An estimated 250,000 halon systems are in operation, containing about 50,000 tons of halons 1211 and 1301 [5], a total investment of about 125 billion dollars.<sup>2</sup>

With the current halons now earmarked for phaseout, there is an urgent need to identify alternative chemicals, halons or others, that satisfy the most critical properties of the current halons:

- fire suppression efficiency,
- low residue level,
- low electrical conductivity,
- low metals corrosion,
- high materials compatibility,
- stability under long-term storage, and
- low toxicity (inhalation and contact) of the chemical and its combustion products.

In addition, the new chemicals must make low contributions toward:

- stratospheric ozone depletion and
- global warming.

In 1987, an effort, driven mainly by the Air Force, was begun to formulate a comprehensive plan to identify and qualify such new fire suppressants. By 1989, a group of industrial entities and Federal agencies assembled to complete this. For the reader's convenience, the resulting document is included as Appendix A. This plan is evolutionary, with the version shown being that of August 1, 1989.

The objective of the plan is to identify and qualify candidate replacements for halons 1301 and 1211 that will satisfy the needs of major users. The strategy is to conduct a program of closely coordinated research, empirical testing, and analysis.

This program will identify acceptable candidate chemicals. To the extent that the program identifies only choices of partially desirable chemicals, the trade-offs will be clearly presented so that policy officials may make informed decisions. All information on chemicals and their test results will be in the public domain to facilitate technology transfer interchange with industrial firms who are actively pursuing similar objectives. Breakthroughs from this program or theirs would appreciably shorten this time frame and reduce the resource needs. Conversely, new technological, environmental, or political constraints would necessitate further analysis and research.

The key accomplishment will be the establishment of a reliable predictive model for the effectiveness of real-scale fire suppression. This will be supported by accurate input data and tested on the current halons. The predictive capability will then be tested on other candidate chemicals.

The basis for this concept lies in the following assumptions:

- Because a number of the more obvious chemicals have already been tested and found wanting, a plan that is strictly testing is unlikely to succeed. This "from-the-ground-up" plan develops the systematic knowledge needed to identify new candidates.

---

<sup>2</sup> Communication from Daniel Moore, E.I. du Pont, to Sanford Davis regarding the estimated total domestic investment in halon fire suppression systems.

- The environmental demands on the agents will change during the course of the program. Under the Montreal Protocol, both technical and political forces are likely to revise the list of regulated chemicals and the acceptable values of ozone-depletion potential. Unacceptable values of other properties, such as toxicity and global warming potential, have not yet been established.
- A predictive capability for the performance of a chemical is needed. A massive trial-and-error study now may find suppressants that meet current environmental and toxicological concerns. However, as the multiple and evolving performance constraints tighten, a new empirical search would have to start all over and would have a seriously reduced chance of success. By contrast, the ability to predict performance allows identification of successive candidate agents promptly and at reasonable effort. It also eases difficult decisions among alternative, not-quite-perfect candidates.

The research plan begins with:

- The development of a set of quick, relatively inexpensive performance screening tests to identify chemicals and chemical families with true potentials as alternative suppressants;
- A broad search of fire suppression principles and chemical families;
- A survey to identify the fire types for which halons are currently deployed and the requirements of a "drop-in" replacement agent;
- Research to identify the chemical, physical, and fluid mechanical properties of chemicals that would be most effective, economical, and safe;
- Establishment of a systematic database to aid analysis of all pertinent information in support of the above; and
- Several projects to capture the state of the art in the scientific disciplines involved in modeling the suppression of flames.

These efforts will lead to the establishment of a reliable predictive capability for the effectiveness of fire suppression at full-scale and experience with the behavior of various types of chemicals under tests for the other needed properties. These results will, in turn, guide improvement in both the successive selection of compounds and the tests for obtaining performance data. As the selected chemicals become better and fewer, the scale of testing increases, culminating in full-scale toxicity and fire suppression tests. A schematic of this approach is shown in Figure A1. Figure A2 shows how the program elements fit together and provide the basis for their successors. Figure A3 depicts the time line for these elements.

The principal output of the first 4 years of the program will be appropriate test methods and criteria, compilation of information, and knowledge for designing or selecting potential replacement chemicals. Thus, the chemical industry will have ample opportunity to develop candidates before the total program embarks on substantial testing.

As the plan is constructed, one of the first steps in identifying possible replacements must be the identification of methods for rapidly and inexpensively screening a large number of chemicals for good performance of each of these properties. It is also critical to establish the figures of merit by which the test results will be judged.

## C. SCOPE

### 1. Structure of this Project

Under U.S. Air Force sponsorship, the National Institute of Standards and Technology (NIST) has undertaken to determine the most appropriate, currently available screening methods and a reasonable first approximation for rating of acceptable performance for each screen. This project also identifies laboratories having the capabilities for conducting the screening procedures described in this report and the approximate cost of this testing.

The Air Force or others could then use these screens to proceed rapidly with developing a first set of data to guide the search for further chemicals, to provide a basis for research into desirable physical and chemical properties of future suppressants, and to support the development of more rigorous screening methods, if needed.

The construction of this task considered significant constraints.

- First, the methods must be selected rapidly. The time frame for identifying halon replacements is short, and the start of other key projects will rely on these results.
- Second, the methods must be selected or tuned to require small quantities of the chemical. This is because many of the candidates to be tested will not be off-the-shelf, and long and expensive syntheses should be minimized.
- Third, the conventional figures of merit from these tests may not suffice for the current purpose. For instance, a current toxicity test device may be applicable, but lethality following a 30 minute exposure may not.

To complete the project, meeting the constraints, NIST has assembled a team of specialists in each of the areas of testing. These experts have surveyed the existing methods in their fields and compiled descriptions of the protocols. Each procedure has been analyzed, considering at least the following factors:

- ease of operation for this type of chemicals,
- number of locations able to perform the test,
- amount of chemical required, and
- relevance of the figure(s) of merit to this program.

Each specialist searched the published literature for data on compounds similar to the current halons to establish the appropriateness of the method(s) and estimate values for historically good performance. In many cases, adaptations were needed to improve the fit to this application. In some cases, no standard methods existed and best use was made of the most appropriate current practice.

Each method then under consideration was examined. The test was performed for at least halons 1211 and 1301. Since it was likely that these compounds would perform similarly in the test, a third chemical that would behave differently was selected and tested. The results of these checks were analyzed for quality.

These results led to the selection of methods, measures of merit, and criteria to recommend. In most cases, the criteria reference the data obtained for halons 1211 and 1301.

## **2. Screening Tests**

Screening tests are used to identify those relatively few chemicals worthy of further examination as alternative clean fire suppressants. Because of the large number of chemicals to be screened, the test battery must be rapid, inexpensive, and use little chemical. High precision is not needed. Rather, the emphasis must be on an accurate indication. This feature allows the time, cost, and amount of chemical to be kept low.

For this reason, we have chosen to report the results of each test in a series of performance classes. We have related each performance class either to the performance of halons 1211 and 1301, or to some accepted criterion for practical use. In both cases, the scientific and fire suppression communities have a sensible basis for evaluating the desirability of studying a chemical further.

**The reader is reminded that these methods and performance classes have been developed for screening purposes only and should not be used for final acceptance of an agent without considering more extensive evaluation.**

If more extensive evaluation is appropriate, it can be performed at additional cost, requiring more time and materials. While some of the screening procedures can be adapted to this purpose, in many cases we urge the use of alternative methods.

## **3. Structure of the Report**

This report is organized by the list of properties against which a new agent must be tested. For the reader's convenience, within each section is a self-contained presentation of current procedures in use, our analysis of the tests and selection of choice, our experience with the selected test(s), and our recommended screening procedures. All necessary figures, tables and references are included in each section. Full documentation of the tests is included as an appendix to each section, if appropriate.

In the course of presenting this material, certain commercial equipment, instruments, materials, or organizations are identified. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology nor does it imply that they are necessarily the best available for the purpose.

Section II describes a procedure for measuring the level of residuals which may remain after deployment of the agent.

Section III describes the technique for assessing the fire suppression efficiency of any candidate material.

Sections IV and V describe a series of measurements necessary as input data to calculations of the ozone depletion potential and the global warming potential.

Section VI provides a means for estimating the toxic potency of an agent towards humans exposed to the agent during its manufacture, after deployment at the time of system testing, or during a fire.

Section VII describes a predictive method for estimating the "life" of the agent during long-term storage.

Section VIII describes a combination of procedures for predicting the effect on metals by prolonged contact of the agent with the hardware used for storing and distributing the agent.

Section IX describes a procedure for determining the consequences of an agent coming into contact with electrical or electronic equipment.

Section X describes a procedure for determining what effect incidental contact of the agent will have on plastic materials in the environment; this screen does not address the question of prolonged contact, under pressure, with seals and gaskets in the hardware.

Section XI of the report continues with guidance on how best to use the screens for their various applications.

Section XII contains the conclusions.

#### **D. REFERENCES**

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Appendix A



**REPLACEMENT FIRE SUPPRESSANTS:  
A RESEARCH STRATEGY AND PLAN**

**Technical Committee**

**Halon  
Alternatives  
Research  
Consortium**

**August 1, 1989**

# REPLACEMENT FIRE SUPPRESSANTS: A RESEARCH STRATEGY AND PLAN

## I. BACKGROUND

Because of their role in depleting stratospheric ozone, production of the current halogenated fire suppressants will likely be small or phased out by the turn of the century. A consortium of concerned Federal agencies and industrial firms has formed to support a program to identify candidate replacement chemicals.

The Steering Committee of sponsors has commissioned its Technical Committee to prepare and guide a research plan that will find one or more agents to replace halons 1301 and 1211 that will satisfy the needs of major users for existing applications.

## II. THE PROBLEM

The search for new fire suppressant chemicals is not likely to be brief or easy. Successful candidates must perform appropriately in tests for a wide variety of properties:

- fire suppression efficiency,
- ozone depletion potential,
- greenhouse warming potential,
- suppressant residue level,
- electrical conductivity,
- metals corrosion,
- materials compatibility,
- stability under long-term storage, and
- toxicity (inhalation and contact) of the chemical and its combustion products.

In addition, there is a practical benefit to identifying chemicals that are "drop-in" replacements for the current suppressants. This requires similar state and fluid mechanical properties.

Satisfying this combination of demands will be distinctly more difficult than identifying, for instance, a new refrigerant, de-greaser, or aerosol propellant. It will require a high level of technical expertise, a strong commitment of resources, and a clear sense of direction to find suitable replacements.

Fortunately, the expertise, science, and technology to solve this problem exist. We have identified key personnel who have performed research in this field and others working in scientifically-related fields. They possess the background and talent needed to bring this program to fulfillment.

This program will identify acceptable candidate chemicals. To the extent that we only find choices of partially-desirable chemicals, the trade-offs will be clearly presented so that policy officials may make informed decisions. All information on chemicals and their test results will be in the public domain.

This plan is the consensus of the Technical Committee. It is intended to commence near the end of FY 1989. We will reach completion in 11 years at a cost of approximately \$25 M. Breakthroughs can appreciably shorten this time frame and reduce the resource needs. The Technical Committee is highly confident that this program will succeed in identifying and qualifying substitutes for the existing halons in a timely manner.

### III. RESEARCH STRATEGY

Our strategy is to conduct a program of closely-coordinated research, empirical testing, and analysis. These are to be performed by experts in the critical technical areas and focussed on the Consortium objective. The Technical Committee, supplemented by a technical manager, will assure the coherence of the program elements.

The principal output of the first four years of the program will be appropriate test methods and criteria, compilation of information, and knowledge for designing or selecting potential replacement chemicals. Thus, the chemical industry will have ample opportunity to develop their own candidates before the Consortium embarks on substantial testing.

A key intermediate accomplishment that will facilitate the development of alternative suppressants is a reliable predictive model for the effectiveness of fire suppression at full-scale. This will be supported by accurate input data and tested on the current halons. The predictive capability will then be tested on other candidate chemicals.

The basis for this concept lies in the following assumptions:

- **A number of the more obvious chemicals have already been tested and found wanting.** Thus, a plan that is strictly testing is unlikely to succeed. This "from the ground up" plan develops the systematic knowledge needed to identify new candidates efficiently.
- **The environmental demands on the agents will change during the course of the program.** Under the Montreal Protocol, both technical and political forces are likely to revise the list of regulated chemicals and the acceptable values of ozone depletion potential. Acceptable values of other properties, such as toxicity, are similarly subject to change.
- **It is therefore necessary to develop a predictive capability for the performance of a chemical.** A massive trial-and-error study now may find suppressants that meet current environmental and toxicological concerns. However, as the multiple and evolving performance constraints tighten, a new empirical search would have

to start all over and would have a seriously reduced chance of success. By contrast, the ability to predict performance allows us to identify successive candidate agents promptly and at reasonable effort. It also eases difficult decisions among alternative, not-quite-perfect candidates.

By the end of the seventh year, the possible alternative chemicals will be sufficiently few of high enough quality that manufacturers could proceed with their strategic planning. At the end of the eleventh year, the success of a small number of chemicals will have been fully documented.

#### IV. RESEARCH PLAN

The plan is meant to be a "living" document. As presented, it represents our best current thinking. As that thinking evolves and as new findings emerge, we expect to modify the plan. Breakthroughs will allow us to find more direct channels toward the conclusion; complications will necessitate further analysis and research.

The research plan begins with:

- A selection of trial chemicals and quick, relatively inexpensive performance screening tests to be run on them;
- A survey to identify the fire types for which halons are currently deployed;
- Research to identify the chemical, physical, and transport properties of chemicals that would be most effective, economical, and safe; and
- Establishment of a systematic database to aid analysis of all pertinent information in support of our objective.

These efforts will lead to the establishment of a reliable predictive capability for the effectiveness of fire suppression at full-scale and experience with the behavior of various types of chemicals under tests for the other needed properties. These results will, in turn, guide improvement in both the successive selection of compounds and the tests for obtaining performance data. As the selected chemicals become better and fewer, the scale of testing increases, culminating in full-scale toxicity and fire suppression tests. A schematic of this approach is shown in Figure A1.

The plan now consists of 27 elements, each a critical step towards a final choice of chemicals. Figure A2 shows how these elements fit together and provide the basis for their successors. Figure A3 depicts the time line for these elements.

The funding levels for the elements are estimates for a solid effort. Enhanced funding would substantially promote our likelihood of success, and might speed that success by increasing the chance of a breakthrough.

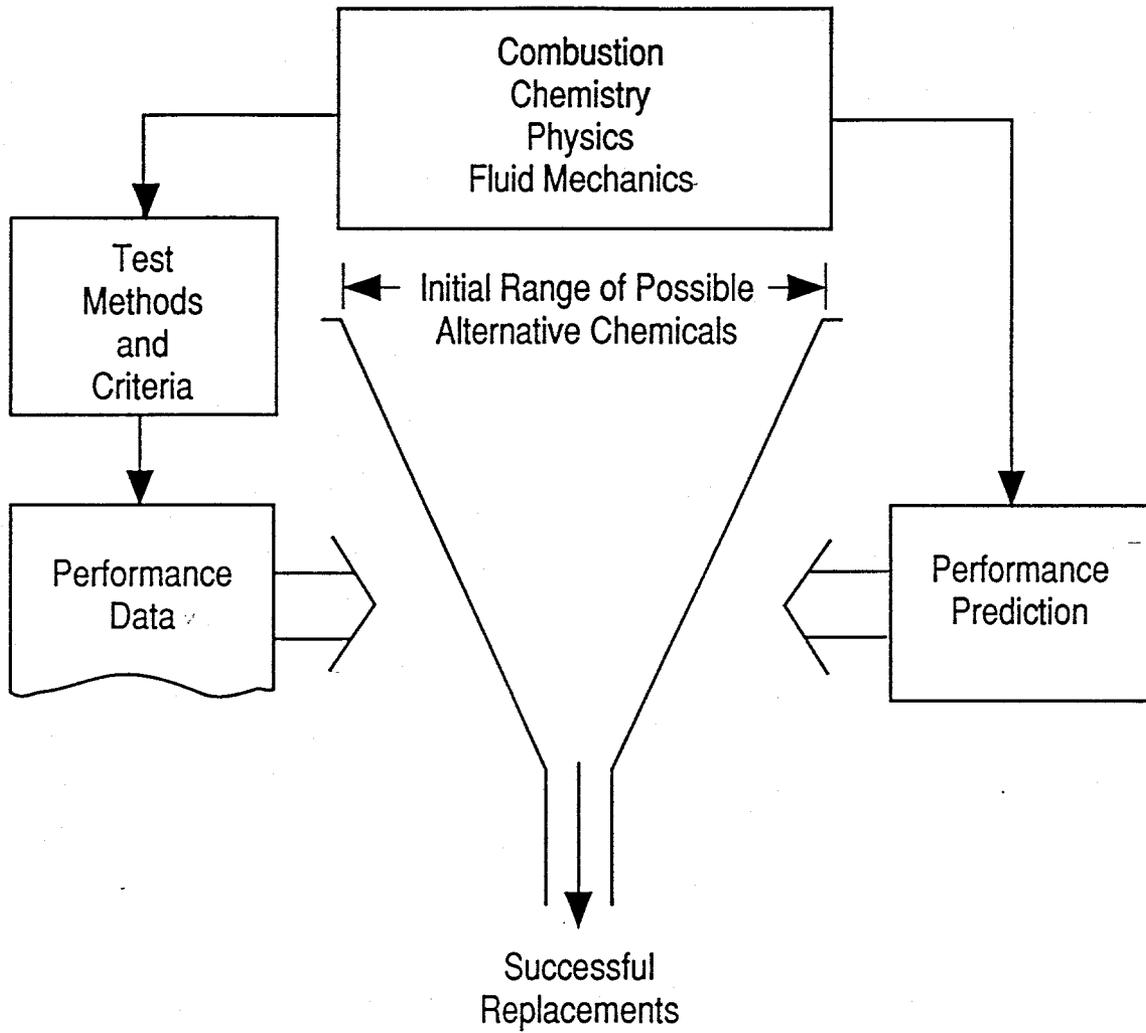


Figure A1. Research Strategy

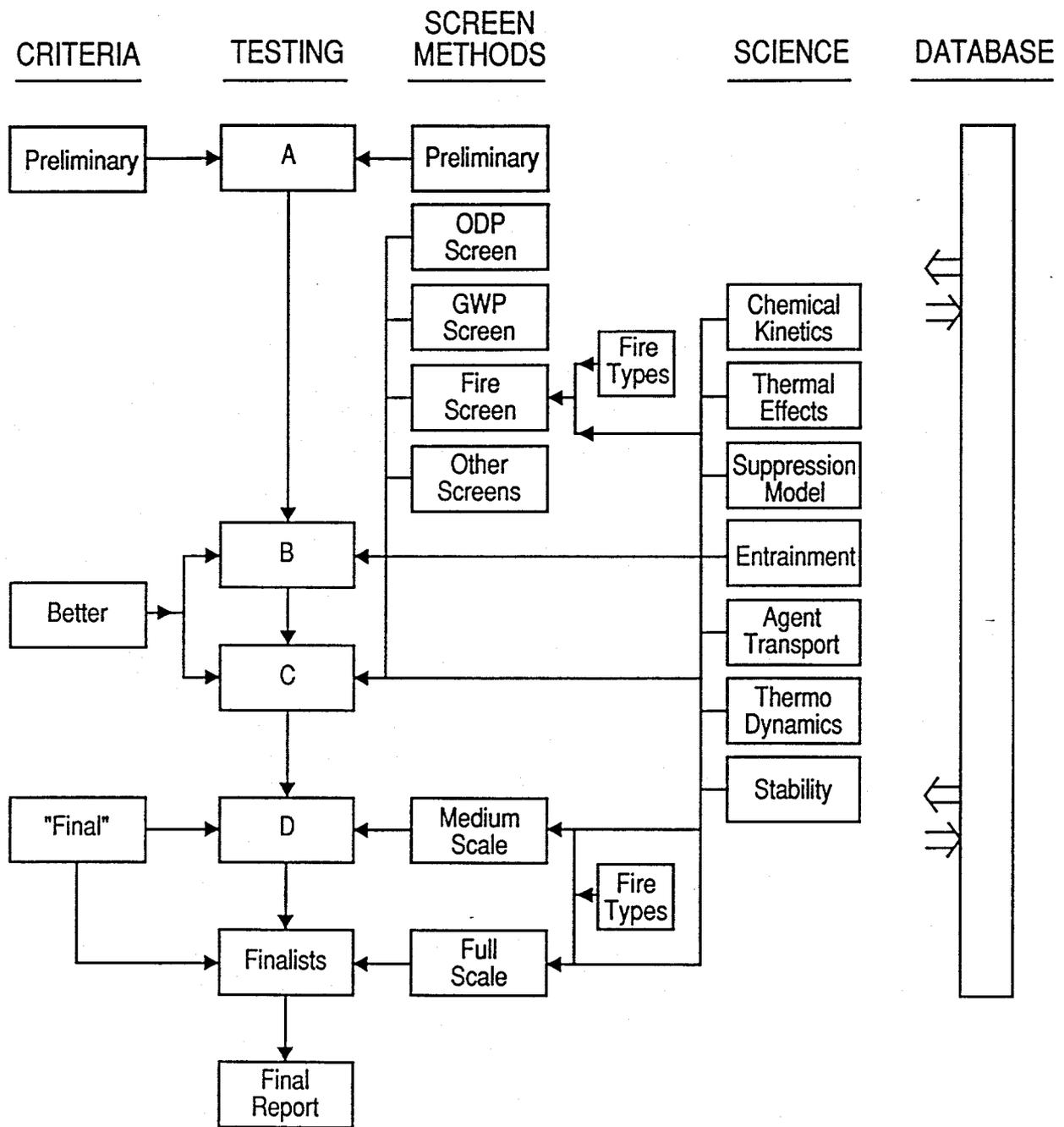


Figure A2. Program Flow Chart

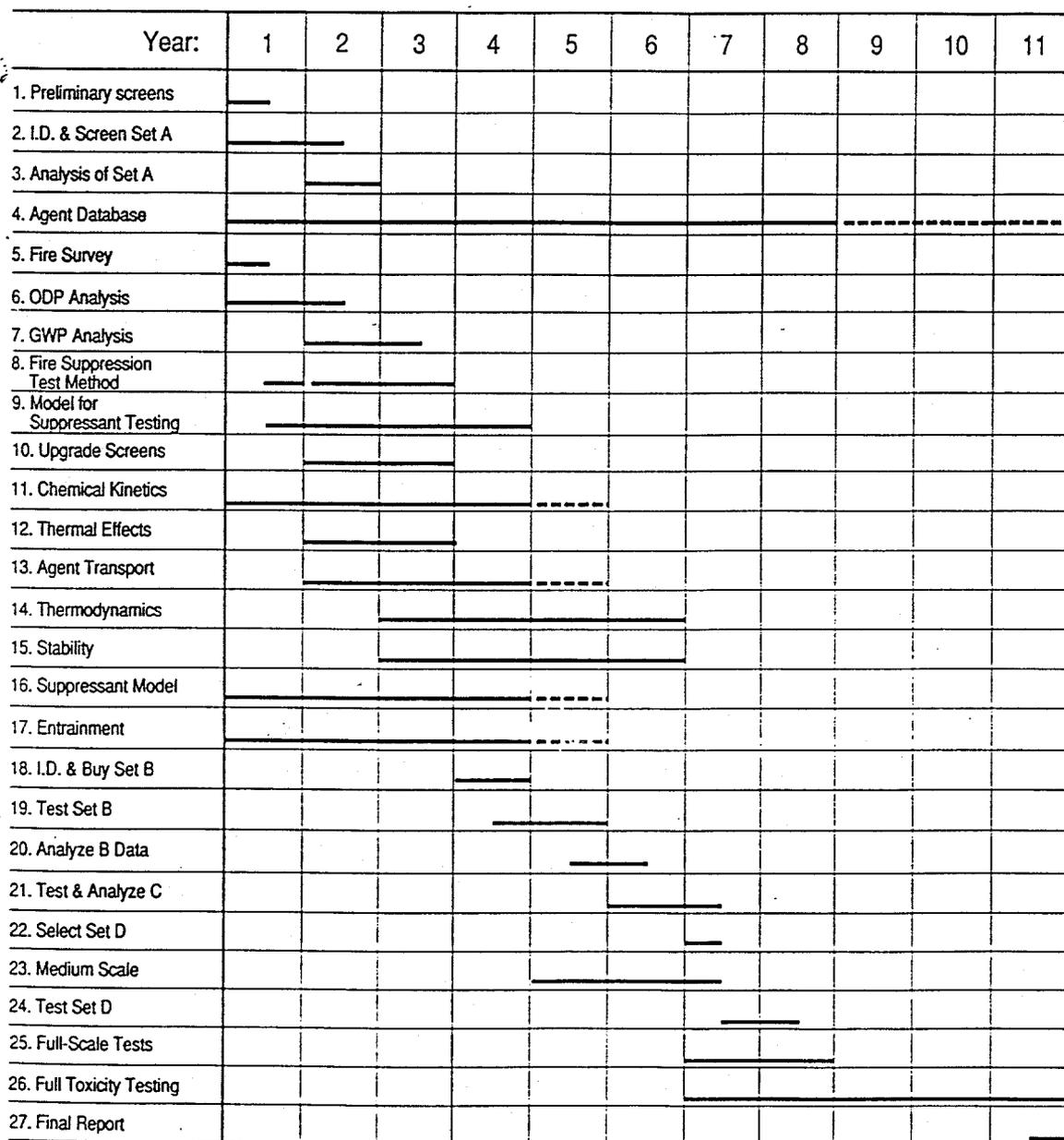


Figure A3. Project Schedule

## RESEARCH PLAN ELEMENTS

### 1. Preliminary Screening Procedures and Criteria (\$500k, 6 months)

**Objective:** Determine the most appropriate, currently available screening methods for fire suppression efficiency, residue level and electrical conductivity, ozone depletion potential, greenhouse warming potential, metals corrosion, materials compatibility, stability under long-term storage, and toxicity (inhalation and contact); determine reasonable first approximations for ratings of acceptable performance for each screen.

**Approach:** Compile descriptions of existing protocols; make (only) minor adaptations based on current fire science to use small quantities of chemical; estimate values for good performance from prior work of others; perform some calculations and tests as needed; analyze quality of results.

**Product:** Recommended selections with explicit rationale.

### 2. Exploratory Candidate Set (Set A)

**Objective:** (a) Identify and (b) screen  $\approx 100$  gases or liquids, covering a range of chemical and physical principles thought to affect flame suppression capability.

**Approach:** (a) Use expert knowledge of flame suppression chemistry and physics, combined with knowledge of prior successes and failures; list should avoid known problems with other critical properties; compounds to have broad range of chemical nature, e.g., substituted saturated halocarbons, unsaturated and aromatic organic halides, perfluorocarbons, organometallics, and inorganics; list to include some of the substitutes for CFCs; identify sources of each compound.

(b) Procure compounds; identify locales with testing capability; organize/perform screen testing.

**Product:** Matrix of performance data for Set A compounds.

### 3. Analysis of Set A Data

**Objective:** Identify potential winners, if any; extract guidelines for selection of further candidates and for elimination of classes of compounds.

**Approach:** Apply expert knowledge of flame suppression chemistry and physics; focus capability of other experts.

**Product:** Guidance document for selection of further candidate compounds.

### 4. Candidate Agent Database

**Objective:** Create and maintain an accessible tabulation of all chemicals that have been or are being considered as fire suppressants; database to include physical and chemical properties and performance data from tests for parameters in element 1; all data to be referenced.

**Approach:** Create multi-field database using commercial software; enter data on chemicals from published or unpublished reports; assure easy access and search capability for remote participants; keep current with data from all elements of HARC and other current programs.

**Product:** Common access to historical and current data.

### 5. Fire Type Survey

**Objective:** Determine the generic types of fires for which current halon systems are designed.

**Approach:** Survey principal users of current halons; analyze fires and delivery systems; include flaming and deep-seated fires; collate into few generic types; determine ranges of characteristics of a "drop-in" agent for such systems.

**Product:** Portrayal of (a) key types of fires which must be simulated in advanced suppressant performance tests and (b) ideal replacement agents.

**6. Ozone Depletion Potential Analysis**

**Objective:** Assess the capability of method(s) for determining ODP of current and potential alternatives to the current halons; determine best quick screen method and technical criterion for ODP.

**Approach:** Consulting with experts, identify the chemistry and physics included in the method(s); analyze the capability for current method(s) to expand to assess new chemicals; determine ease of obtaining ODP values for new chemicals; determine value of ODP for halon replacements that gives negligible added stratospheric ozone depletion.

**Product:** Technical criterion for ODP; accuracy of ODP determinations.

**7. Greenhouse Warming Potential Analysis**

**Objective:** Assess the capability of method(s) for determining GWP of current and potential alternatives to the current halons; determine best quick screen method and technical criterion for GWP.

**Approach:** Consulting with experts, identify the chemistry and physics included in the method(s); analyze the capability for current method(s) to expand to assess new chemicals; determine ease of obtaining GWP values for new chemicals; determine value of GWP for halon replacements that gives negligible added tropospheric warming.

**Product:** Technical criterion for GWP; accuracy of GWP determinations.

## 8. Fire Suppression Screen Test Feasibility

- Objective:**
- a: Determine the extent to which a small-scale test method for liquid and gaseous fire suppressant efficiency, using small amounts of agent, can replicate the suppression of real scale fires of liquid and solid fuels.
  - b: If reasonable, develop such a method.
- Approach:**
- a: Identify the key factors affecting fire suppression efficiency, from both the fire and the fire suppressant perspectives; use results of element 5; perform necessary calculations to determine scaling rules, etc.; use expert judgment to determine potential for accurate small-scale test.
  - b: If small-scale test appears promising, use results of (a) to design and proof test such a method; conduct suppressant tests and relate to prior medium- and real-scale tests using new or existing flame models; document fully.
- Product:** Assessment of feasibility of an accurate small-scale test method for fire suppressant efficiency. If appropriate, develop such a method; otherwise, defer to element 9.

## 9. Modelling of Suppressants In Turbulent Fires

- Objective:** Develop computational fire suppression model for "experiments" to optimize fire suppressant selection.
- Approach:** Evaluate existing computer models of combustion processes against each other and available data from experiments with similarity to fires being suppressed by a current halon; examine and couple existing turbulence, chemistry, and heat transfer sub-models; evaluate trade-offs between accuracy and complexity, detail and generality; adapt large eddy simulations based on both finite difference techniques and vortex methods to predict the time and 3-D distribution of temperature, reactants, and extinguishing agents; compute these for representative fire hazards (element 5); develop a methodology, such as the  $k-\epsilon-g$  field equation description of the mixing processes to include large-scale eddy effects and to imbed simplified chemistry into the local turbulent environment; document, describing the needed input data for a candidate suppressant.
- Product:** Ability to screen large numbers of candidate agents on the computer using chemical and physical properties and results from small-scale measurement methods.

**10. Upgrade of Preliminary Screening Methods**

**Objective:** Review and upgrade, as needed, the previous screening protocols for assessing residue level, metals corrosion, materials compatibility, stability under long-term storage, electrical conductivity, and especially toxicity (inhalation and contact) of chemicals and combustion products; must use small quantities of chemical.

**Approach:** Convene experts; compare screens with compliance tests; supervise/perform sample tests; determine necessary levels of performance; document approaches.

**Product:** Documentation of recommended protocols and performance criteria.

**11. Chemical Kinetics of Suppression**

**Objective:** Determine the chemical pathways and reaction rate data for flame extinction by potential halon replacements.

**Approach:** Identify families of potential chemicals from initial screens or literature survey; use multiple investigators with existing capability in flame measurements and reaction kinetics to determine key data as a function of family chemistry; measure, estimate, or compile data on, e.g., initial and free radical scavenging reactions; use current halons as reference points; incremental funding, depending on number of chemicals identified; single coordinator.

**Product:** Data to make the model in element 10 usable; determination of the types of molecular chemistry that result in efficient fire suppression.

**12. Thermal Effects of Suppressants**

**Objective:** Determine the contribution of the heat capacity and thermal decomposition of molecules to suppression.

**Approach:** Review prior work on thermal mechanisms; insert data for a range of compounds into the model from element 10; test the model in a diffusion flame using select molecules of varying thermal and chemical properties.

**Product:** Knowledge of the extent to which thermal properties determine flame suppressant effectiveness and a tabulation of those properties for a range of chemical species.

**13. Agent Transport Physics**

**Objective:** Develop numerical methods for calculating an agent's delivery characteristics as a function of its physical properties.

**Approach:** Review fluid flow modeling of nozzle systems; adapt for fire suppressants; develop computer code; compare predictions against a range of experimental data.

**Product:** Prediction method for the delivery of replacement agents; ability to determine whether a candidate chemical is within the "drop-in" range.

**14. Thermodynamic and Transport Properties**

**Objective:** Determine the data needed for the model in element 13.

**Approach:** Compile and/or measure specific heat, viscosity, thermal conductivity, diffusivity in air, and PVT relationships, including boiling temperatures and vapor pressures; all measurements as a function of temperature for both liquid and gaseous phases.

**Product:** Data to make the model in element 13 usable; determination of the values of physical properties that result in efficient and/or "drop-in" fire suppression.

**15. Thermal Stability and Decomposition**

**Objective:** Assess stability of replacement chemicals under long-term storage.

**Approach:** Determine homogeneous and wall-catalyzed decomposition rates under range of potential storage temperatures and pressures; analyze nature and quantity of decomposition products.

**Product:** Accurate extrapolation of short-term stability and corrosion tests to realistic storage life.

**16. Modelling of Suppressants In Turbulent Fires**

**Objective:** Develop computations of the injection into and distribution of extinguishing agents in a fire bed and adjacent fire plume.

**Approach:** Adapt large eddy simulations based on both finite difference techniques and vortex methods to predict the time and 3-D distribution of temperature, reactants, and extinguishing agents; compute these for carefully chosen scenarios representative of serious fire hazards; develop a methodology capable of combining simplified chemistry; supplement the  $k-\epsilon-g$  field equation description of the mixing processes to include large-scale eddy effects and to imbed the simplified chemistry into the local turbulent environment.

**Product:** Estimates of agent efficiency in penetrating and/or covering the fire bed, lowering bulk temperatures, and diluting the fuel/oxidizer mixture for a given intervention/application strategy.

**17. Agent Entrainment In Turbulent Combustion**

**Objective:** Determine experimentally the effect of variations in physical and chemical properties of flame suppression agents on their entrainment behavior in a turbulent fire plume and the effectiveness with which the agent is mixed molecularly with the plume gases.

**Approach:** Characterize the entrainment of gaseous and liquid compounds of diverse physical properties into isothermal, buoyancy-driven turbulent plumes using intrusive and optical methods; analyze the molecular mixing of the gases throughout the plume; elucidate the role of large scale and small scale turbulent structures in the mixing; characterize the effects of chemical heat release and stoichiometry on temperature in buoyancy-driven, turbulent fires of various fuels using techniques which have high spatial and temporal resolution; develop method for estimating the temperature behavior of a "typical" fire plume.

**Product:** Relationships to guide element 9; input data for the model developed in element 9; identification of the physical properties that best get the fire suppressant to the optimal location(s) in the fire.

- 18. Select and Procure Candidate Set B**
- Objective: Identify a set of  $\approx 100$  potentially successful candidate suppressants and obtain the quantities needed for screen testing as refined in elements 6-10.
- Approach: Incorporate analysis of set A data and fundamental research.
- Product: A set of  $\approx 100$  chemicals for further testing.
- 19. Test Candidate Set B**
- Objective: Obtain performance data for Candidate Set B chemicals.
- Approach: Use the screens from elements 6-10.
- Product: Matrix of performance data on Candidate Set B.
- 20. Analyze Data from Set B**
- Objective: Determine additional compounds for screen testing.
- Approach: Analyze results from element 19; expert judgment.
- Product: Additional ( $\approx 50$ ) compounds for screening: Set C.
- 21. Test And Analyze Set C**
- Objective: Determine the performance of compounds in Candidate Set C.
- Approach: Use the screens from elements 6-10; estimate cost of producing the chemicals; integrate with Set B data.
- Product: Matrix of performance data on Candidate Sets B and C.
- 22. Select Candidate Set D**
- Objective: Identify reduced list of compounds for further testing.
- Approach: Expert analysis of prior data and fundamental research.
- Product: List of  $\approx 20$  compounds.

- 23. Medium Scale Test Protocols**
- Objective: Design more realistic, larger-scale, potentially more costly, fire suppression methods for testing.
- Approach: Literature review; use fire type survey and suppression model from elements 5, 8 and 9; engineering design.
- Product: Methods for more realistic fire suppression data for compounds in Candidate Set D.
- 24. Test Candidate Set D**
- Objective: More realistic data on Candidate Set D compounds.
- Approach: Use protocols from element 23; analyze data for presentation to full Technical Committee.
- Product: Recommendation of final replacement agents: 2-5 compounds with high likelihood of effectiveness as fire suppressants and low vulnerability under other criteria.
- 25. Full-Scale Suppression Tests**
- Objective: Develop and perform realistic fire-suppression tests.
- Approach: Review of key fire types, delivery systems, and past tests; survey of testing needed to convince users, code officials, etc. of value of new agents; design and operation of real-scale proof tests.
- Product: Demonstration/confirmation of effectiveness of replacement agents.
- 26. Full Toxicity Testing**
- Objective: Perform toxicity tests needed for acceptance of new agents.
- Approach: Summarize tests needed by health regulators; procure sufficient quantity of agents identified in element 24; perform toxicity tests.
- Product: Demonstration of acceptance of replacement agents.
- 27. Prepare Final Report (\$300k, 6 months)**

**SECTION II**  
**RESIDUE LEVEL**

Richard H. Harris, Jr.  
Fire Toxicity Measurement Group  
Center for Fire Research

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## SECTION II

### RESIDUE LEVEL

#### SECTION SUMMARY

Residue level, defined here as a contamination resulting from synthesis, manufacturing, or processing of halon substitutes, but not as a result of reaction of the suppressants with the fire, was determined by an analytical method developed for this project at the Center for Fire Research. The method is a combination of procedures derived from standard test methods. The method requires only 1 ml of material, is easy to use, and is rapid. Results of tests on three halons and one halon/oil mixture indicated the test method is not only accurate, but also precise. The method requires only a technician to perform the procedure. Minimal professional time is needed to interpret the results. The method is adaptable to materials that are gases at ambient conditions, low-boiling liquids, or even solids. It is estimated that one sample can be evaluated in less than one-half day using about 0.02 mole of chemical for a cost of about \$50 (not including the cost of the chemical). As many as five samples can be run concurrently.

For screening purposes, three classes of residue level performance are proposed. They are:

- Class 1: no residue, within measurement limits, which would be expected of a pure, low-boiling compound. The currently-used halons should fall into this category, if pure.
- Class 2: less than 1 percent measurable residue, which might result from processing or container contamination. These chemicals are often worth further examination for some uses.
- Class 3: over 1 percent residue, which could result from a high boiling material or a major by-product from the synthesis that was not removed. A Class 3 material would be discarded initially, but could be evaluated again if purity were the problem.

#### A. BACKGROUND

The currently-used halons are ideal for sensitive environments and for situations that allow for no clean-up time. The two most widely used halons, 1211 and 1301, are gases at room temperature. In the pure state, and barring possible residues from combustion products, no residue is expected because of rapid evaporation. The halon can be deployed in a sensitive environment, such as a computer room or library, extinguish the fire, and leave no residue that might foul circuit boards or cause irreparable damage to valuable possessions. Similarly, these suppressants can be used to extinguish an engine fire on an aircraft and not deposit a residue that will prevent the engine from being restarted. Replacements for halon 1211 or 1301 should have the same no residue or, at worst, slight residue property.

Candidate halon replacements could, in principle, be gases, liquids or even solids. In practice, solid compounds need not be tested, for they are sure to leave a residue. In the case of a high boiling, pure liquid, some residue might remain for a time; a user must decide how long this residue could be allowed to remain. A pure gas or a pure liquid with a low boiling point will not leave a residue upon deployment. However, impurities can be introduced during the synthesis process or manufacturing and handling of a compound.

Ideally, in the screening process, one would only consider pure chemicals or intentional mixtures of them. There are cases, however, where a test for fire suppression appropriateness of a commercial product in its currently-manufactured state might be desired. This might contain additional chemicals, and a screen for residue level would become appropriate.

A screening test for residue levels in experimental products should use as little material as possible. Therefore, a procedure was investigated with this idea in mind.

## **B. EXISTING TEST METHODS**

A review of the literature yielded several standard methods for determining contaminating residue levels by evaporative techniques. ASTM methods include tests for materials with a range of boiling points from liquefied petroleum gases to solid compounds that sublime. An ISO standard provided an excellent reference for developing a test method for the screening of halon substitutes. Also, an industrial method used by E.I. du Pont, similar to one of the ASTM tests, was considered for use as a screening test. From this group of tests, there appeared to be sufficient test methods that, with modifications, even unusual halon substitutes could be screened.

The disadvantage of the methods most applicable to our goal was the amount of material required to determine a residue level. The tests performed on liquefied gases required from 100 to 500 ml of liquid. This was considered prohibitive for a screening test of a new compound which might be in short supply.

The test methods considered follow, with a brief description of each. The test methods are listed in order of their applicability to a halon substitute which would most likely be a gas at room temperature or a low boiling liquid. After this list, a modified method which incorporates techniques learned from these tests, but uses a small amount of material, is described in detail.

### **1. ISO 5789: Fluorinated Hydrocarbons for Industrial Use--Determination of Nonvolatile Residue.**

This International Standard [1] specifies a method for determining the nonvolatile residue of fluorinated hydrocarbons. The principle entails evaporation of a measured portion under specified conditions, using special apparatus, and weighing of the residue after evaporation. A diagram of the apparatus is shown in Figure 1. The method requires a jacketed glass container equipped with a vacuum connection and a detachable glass element. The detachable glass element is dried and weighed, the jacketed glass container is filled with 500 ml of test material, the test material is evaporated uniformly over a period of 1.5 to 2 hours, and the detachable element is removed, dried and reweighed. The increase in mass of the detachable element corresponds to the nonvolatile residue of the test portion.

This is the most applicable standard method; the equipment involved is easy to use and the procedure is easy to employ. The major drawback is the large amount of liquid required.

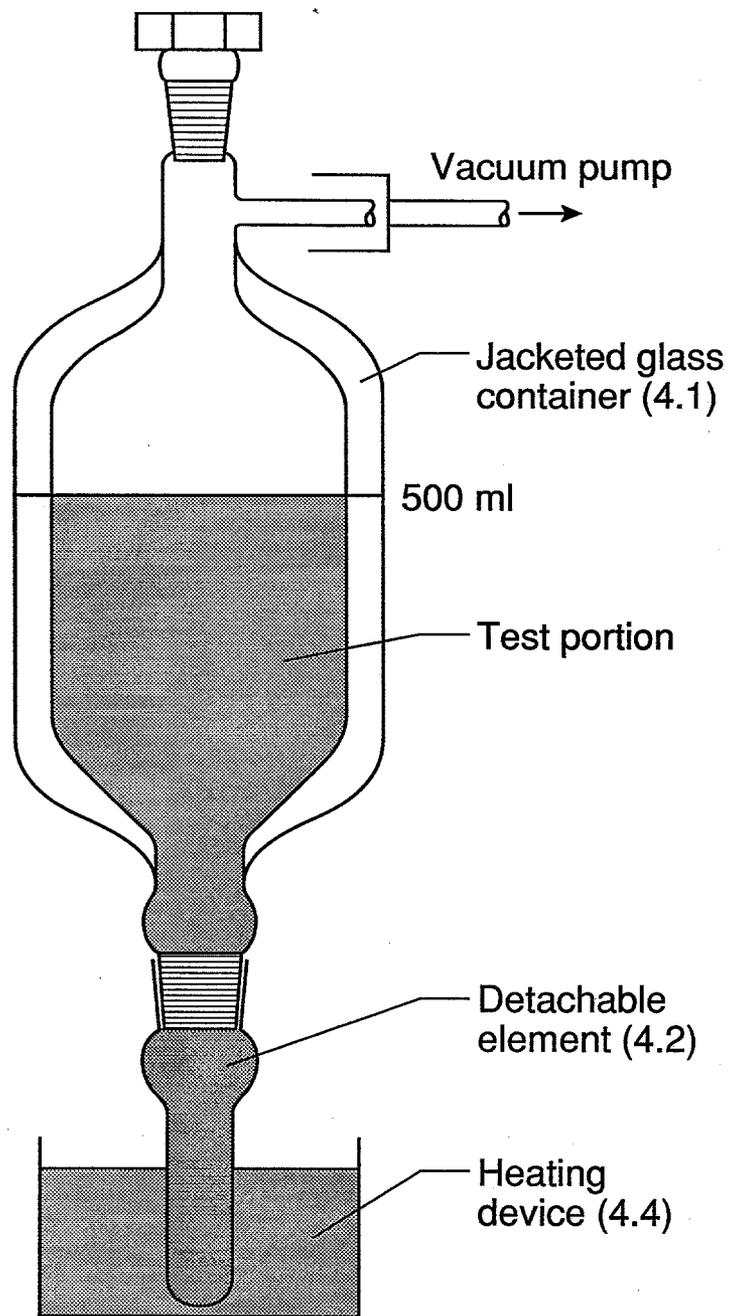


Figure 1. Apparatus for Determining Nonvolatile Residue in Fluorinated Hydrocarbons

**2. ASTM D 2158: Standard Test Method for Residues in Liquefied Petroleum (LP) Gases**

This standard test method [2] covers the determination of the extraneous materials weathering above 37.8°C (100°F). A 100 ml sample of liquefied petroleum gas is weathered in a 100 ml centrifuge tube. The volume of the residue remaining at 37.8°C (100°F) is measured and recorded, as is the appearance of a filter paper to which the residue has been added in measured increments. The method requires a graduated centrifuge tube with the first 0.5 ml graduated in 0.05 ml increments and a cooling coil and low temperature bath. A diagram of the apparatus is shown in Figure 2.

This standard method, like the ISO method, is applicable to a screening method. However, this method also requires a considerable amount of liquid.

**3. E.I. Du Pont's Goetz Tube Apparatus**

This industrial method<sup>1</sup> follows closely the previously described ASTM D 2158, except that the test portion is evaporated in a pear-shaped glass tube of 100 ml volume with a tip of 1.0 ml volume graduated to 0.05 ml volume. A photograph of the apparatus is shown in Figure 3.

This industrial method would be a very good screening method, except that it also requires a prohibitive amount of liquid.

**4. ASTM D 381: Standard Test Method for Existent Gum in Fuels by Jet Evaporation**

This standard test method [3] is for the determination of the existent gum in engine gasoline and aircraft fuels. A measured quantity of fuel is evaporated under controlled conditions of temperature and air or steam flow. For aviation gasoline and aircraft turbine fuel, the resulting residue is weighed and reported as milligrams per 100 ml. For engine gasoline, the residue is weighed before and after extracting with n-heptane and the results reported as milligrams per 100 ml. A diagram of the apparatus is shown in Figure 4.

This standard method requires a more sophisticated apparatus than the previous methods. Use of this method is probably too complex for a simple screen.

**5. ASTM D 2232: Standard Test Method for Evaporating Residue of Naphthalene**

This standard test method [4] is used to determine the evaporation residue of naphthalene. The evaporation residue is an empirical measure of nonvolatile impurities in naphthalene. A weighed quantity of naphthalene is heated in a tared dish for 3 hours at 105°C in a forced-draft oven and the residue weighed.

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<sup>1</sup> Personal communication from Daniel Moore, E.I. du Pont, to Richard H. Harris regarding the nature of this internally used test method.

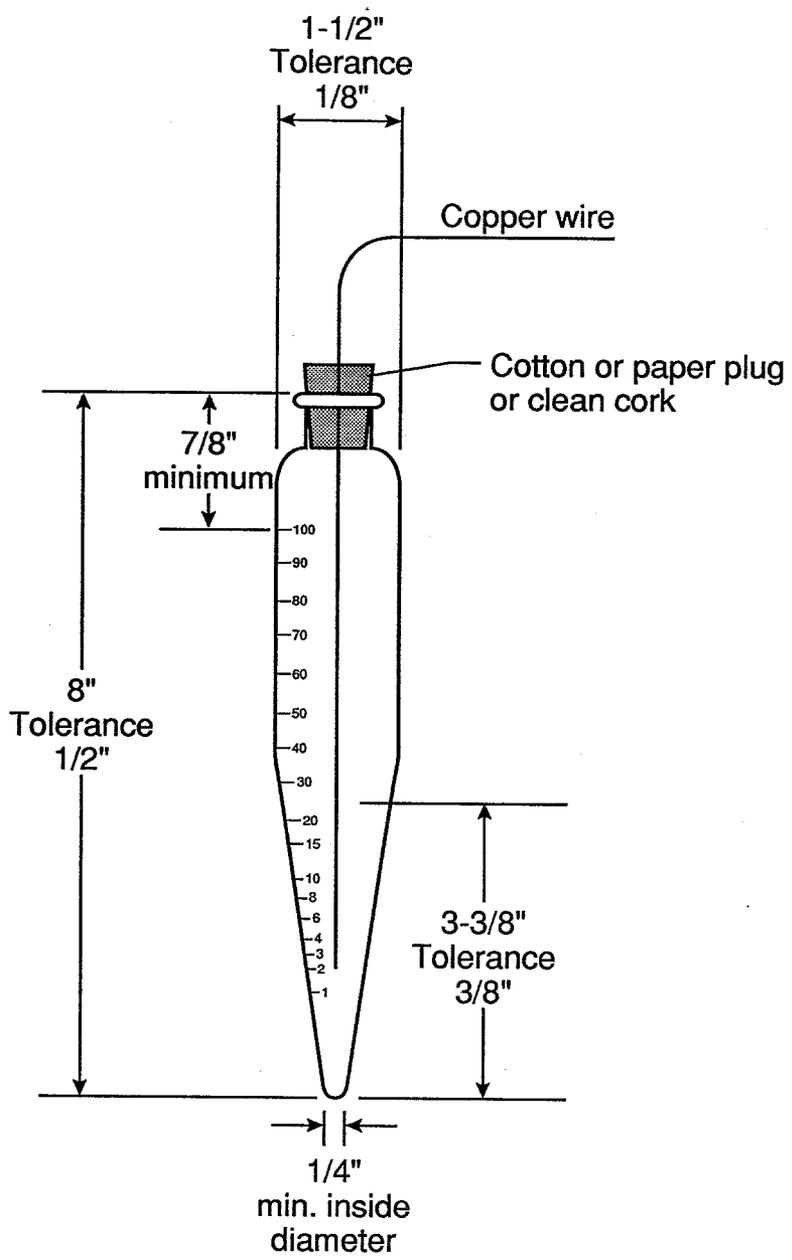


Figure 2. Apparatus for Determining Residues in Liquefied Gases

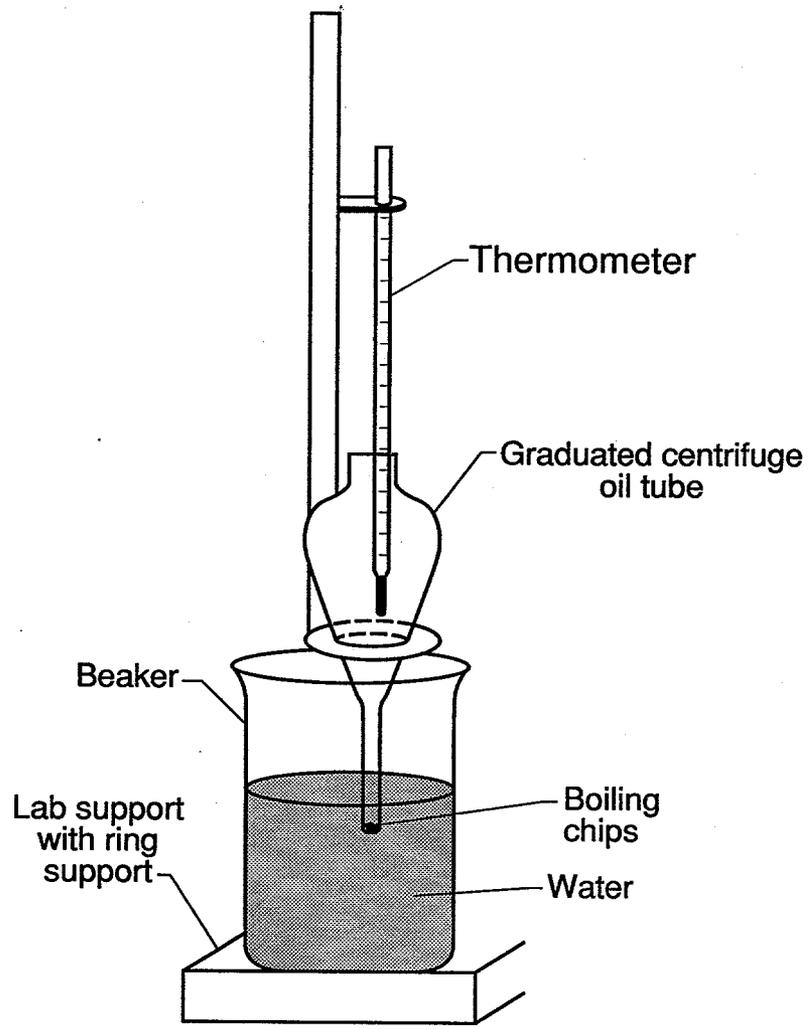


Figure 3. Goetz Tube Apparatus for Determining Residue of Halons

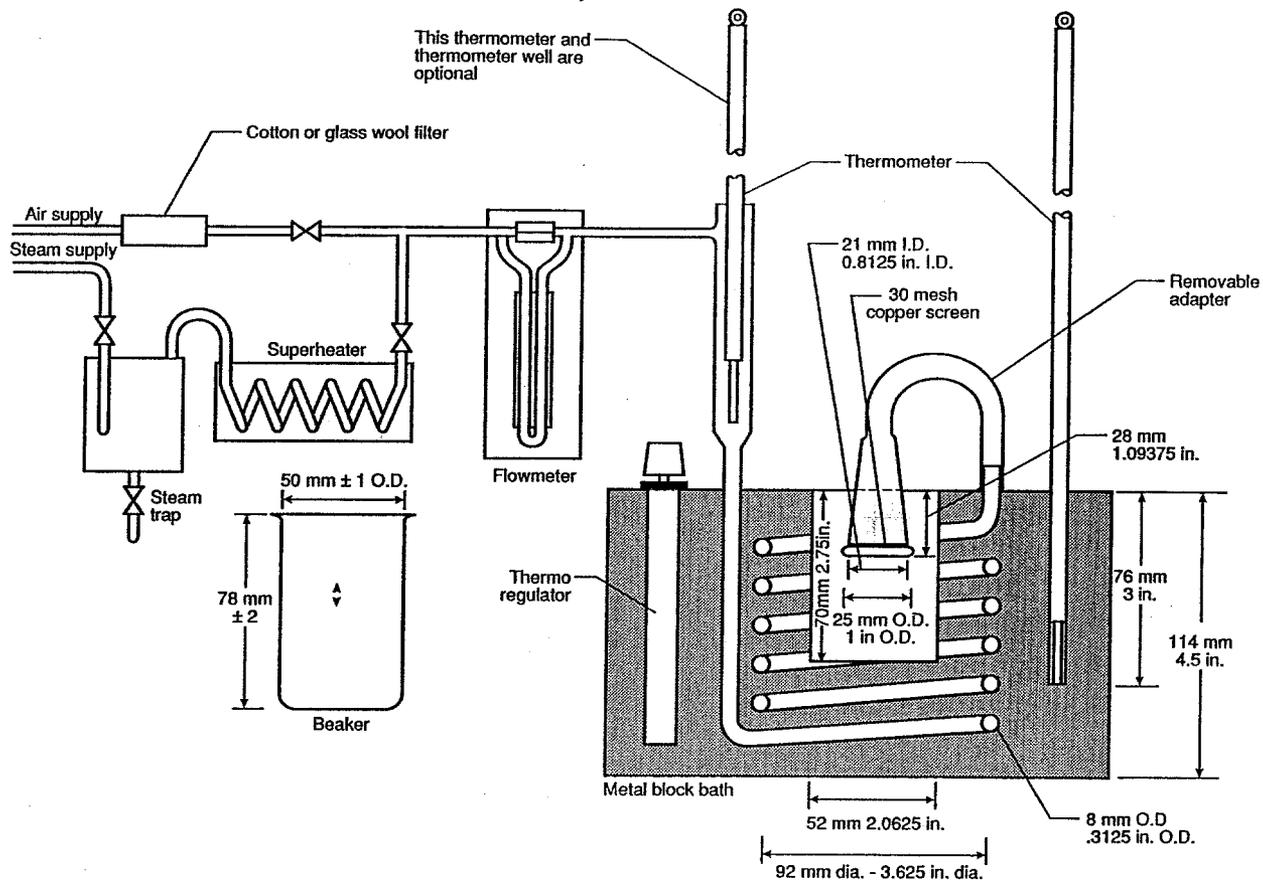


Figure 4. Apparatus for Determining Residue by Jet Evaporation

This test method is probably not relevant to halon replacements; but, if a solid material or one that sublimates is developed, a procedure is available.

### C. SCREENING METHOD

Since all of the standard procedures for evaluating residue level required too much liquid, an analytical technique requiring as little as 1 ml of liquid was developed. Essentially, the method requires drying and weighing small containers, adding the candidate halon substitute, and evaporating, and then drying and reweighing to determine a mass difference. The detailed procedure and equipment needed for determining residue levels are described in the Appendix.

The capability of this approach was tested using halons 1211 and 1301, as well as a third chemical, halon 233. In order to determine whether a residue would be detected, samples of halon 233 containing a small amount of a heavy oil were also tested.

### D. CRITERIA

It is difficult to determine at this time how much or what kinds of residue will present problems in a particular application. However, for screening purposes, three possible classifications of residue level have been proposed. They are:

- Class 1: no residue, within measurement limits, which would be expected of a pure, low-boiling compound. The currently used halons should fall into this category, if pure.
- Class 2: less than 1 percent measurable residue, which might result from processing or container contamination. These chemicals are often worth further examination for some uses.
- Class 3: over 1 percent residue, which would result from a high boiling material or a major by-product from the synthesis that was not removed. A Class 3 material would be discarded initially, but could be evaluated again if purity were the problem.

### E. PERFORMANCE DATA

The results of screening tests on halons 1301, 1211, and 233 indicate that this procedure is feasible and accurate. Three tests were performed for each halon to determine the reliability of the method. The average value of the residue and its standard deviation are reported in Table 1. Because of the quality of these results, it is anticipated that in actual screening a single test will be sufficient to determine any residue. Replication of the screen test would only be required in the case of error or questionable results.

The results indicate no residue from halons 1301 and 233. Therefore, these halons represent Class 1 compounds. A small residue (0.3 mg/ml or about 0.01 percent by weight based on a halon 1211 density of 1.83 g/ml) was found for halon 1211. This small amount is apparently not a problem, since this halon is currently in widespread use. Thus, halon 1211 barely represents a Class 2 compound. The last row of data in the table is from a mixture of halon 233 and a heavy oil, such as might result from careless filling of the halon storage tank. One hundred mg of the heavy oil was added to 100 ml of halon 233 in a volumetric flask. A 1.0 ml aliquot of this mixture was evaporated; a 1.0 mg residue should have been found. The test result

TABLE 1. RESIDUE LEVELS FROM HALON COMPOUNDS

Halon	Boiling Point (°C)	Residue (mg)
1211	-4	0.27 ± 0.06
1301	-58	0 ± 0
233	48	0 ± 0
233/oil	--	0.90 ± 0.1

was 0.9 mg of residue (0.8, 0.9, 1.0 mg replicates) recovered. Since the density of halon 233 is 1.58 g/ml, this results in an impurity level of 0.06 percent by weight. This demonstrates the sufficient reproducibility and accuracy of the method. The 0.06 wt. percent residue from this impure halon 233 would result in a Class 2 designation unless the chemical were purified and retested.

#### F. EVALUATION OF SCREENING METHOD

The proposed method is feasible for determining residue levels. The advantage of this method over the ASTM or ISO methods is the considerably smaller amount of compound required. The procedure can be carried out by a technician; minimal professional time will be required. The procedure, described in Appendix A, is not complicated or difficult to run, so any analytical or physical testing lab could obtain the equipment and start testing in a short time. Preliminary results indicate a high degree of accuracy in weighing the residue along with good precision. The residue can be recovered quite easily for further identifying tests, if needed.

#### G. LABORATORIES/COST

The screening method can be carried out quickly. It is estimated that one sample can be evaluated in less than ½ day using less than 0.02 mole of agent. However, as many as five samples can be run concurrently if necessary. If this were the case, then ten samples could be screened in one 8-hour day. It is estimated that the cost for performing this test is about \$50 (plus the cost of the chemical). Because this is not a standard test, no laboratories have been identified for performing this screen; however, because of its simplicity, any number of independent laboratories could perform the test as described in this chapter.

#### H. CONCLUSIONS

We have developed a screening method that is easy to use, requires a small amount of material, and can be performed by most laboratories. This would be the first screen of a candidate compound to determine if it has the "cleanliness" to be carried through the more difficult and time consuming screens. Often, a knowledge of the chemical structure and known physical properties would allow this test to be eliminated, e.g.,

if the compound is known to be a pure, low-boiling chemical. For these chemicals, this screening method would be used only if the purity is in question.

## **I. REFERENCES**

- [1] "Fluorinated Hydrocarbons for Industrial Use-- Determination of Nonvolatile Residue," ISO 5789-1979, A 401-1283, International Organization for Standardization, Geneva, Switzerland, (1979).
- [2] "Standard Test Method for Residues in Liquefied Petroleum (LP) Gases, D 2158-85," 1989 Annual Book of ASTM Standards, Vol. 05.02, p.34, American Society for Testing and Materials, Philadelphia, PA, (1989).
- [3] "Standard Test Method for Existent Gum in Fuels by Jet Evaporation, D 381-86," 1989 Annual Book of ASTM Standards, Vol. 05.01, p. 147, American Society for Testing and Materials, Philadelphia, PA, (1989).
- [4] "Standard Test Method for Evaporating Residue of Naphthalene," D 2232-81, 1989 Annual Book of ASTM Standards, vol. 06.03, p.612, American Society for Testing and Materials, Philadelphia, PA, (1989).

## APPENDIX A

### ANALYTICAL METHOD FOR DETERMINING RESIDUE LEVELS IN HALON ALTERNATIVES

#### Equipment:

- 5 ml containers (crucibles work well)
- Drying oven maintained at  $105 \pm 2^\circ\text{C}$
- Desiccator with desiccant
- Small copper cooling coil (if gas at ambient temperature)
- Low temperature bath of dry ice and acetone (if gas at ambient temperature)
- Analytical balance (0.1 mg accuracy).

#### Procedure:

Five ml containers are cleaned and dried at  $105 \pm 2^\circ\text{C}$  for 30 minutes. The containers are then cooled in a desiccator for 30 minutes and weighed to the nearest 0.1 mg using an analytical balance. Care should be taken in handling the containers to avoid oil residues from the fingers.

The sample(s) to be screened are then added into the tared containers. If the compound is a liquid at room temperature, a pipet can be used to deliver a 1 ml aliquot. If the compound is a gas at room temperature and contamination is suspected, it must be cooled to dry ice/acetone temperature in a cooling coil and then metered into the tared containers. The containers receiving the cooled liquid should be at dry ice temperature to prevent rapid boiling of the compound as it is added. This is done by sitting the containers in a small box containing finely crushed dry ice. For these samples, an estimate of 1 ml of compound is made. The containers are then held several inches above the dry ice container to promote even evaporation without bumping. In the case of the liquid samples at room temperature, evaporation can be achieved at ambient temperature or with mild heating, depending on the boiling point of the compound.

After evaporation is completed, the containers are placed in the drying oven at  $105 \pm 2^\circ\text{C}$  for 30 minutes, removed from the oven and placed in a desiccator for 30 minutes, and weighed with the analytical balance. The amount of residue is the difference between the weight of the container with residue and the clean, dry container.

# SECTION III

## FIRE SUPPRESSION EFFICIENCY

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## SECTION III

### FIRE SUPPRESSION EFFICIENCY

#### SECTION SUMMARY

At present, there is no standardized test for fire suppression efficiency. Therefore, the existing laboratory test methods for fire suppression efficiency were surveyed, and individually analyzed for appropriateness as a preliminary screen. Two approaches that have been used are: (1) inerting tests and (2) flame extinguishment tests. The flame extinguishment method was selected as a more appropriate screening test because it uses less agent, its variables are better understood than the inerting method, and it has been shown to be both repeatable and reliable.

An apparatus was constructed, based on the prior literature on suppression of cup burner diffusion flames. The fuel source was modified to be a polymer stick as is used in ASTM D 2863, the Limiting Oxygen Index Test, thus eliminating problems associated with maintaining a constant fuel level in the cup.

The figure of merit is the concentration of agent in air needed to extinguish the pre-existing diffusion flame. New chemicals will be evaluated relative to the performance of halons 1211 and 1301, each of which requires about three percent by volume to suppress the flaming polymer stick. The potential replacement agents are placed into four classes.

- Class 1: At least as effective as halons 1211 and 1301; quenches the test flame at less than 3 percent by volume.
- Class 2: Not as effective as halons 1211 and 1301; quenches the test flame at 3 to 6 percent by volume.
- Class 3: Much less effective than halons 1211 and 1301; quenches the test flame at 6 to 12 percent by volume.
- Class 4: Not a chemical fire suppressant; requires at least 12 percent by volume to quench the test flame.

Halons 131, 14, 1202, and 113 were tested and found to be in Classes 2, 3, 1, and 3, respectively. Halons 131 and 14 are gases at room temperature, and halons 1202 and 113 are liquids.

Since the toxicity screen relies on this screen for the concentration, it may be useful to further test Class 1 chemicals at  $\frac{1}{2}$  and  $\frac{1}{4}$  of the halon 1301 value. If cost and quantity of chemical are not critical, then it may be useful to determine the actual percent needed for flame extinguishment.

Tests conducted showed the test was easy to operate and required only small amounts of chemical. About one-half day, requiring about 0.5 mole of chemical, is needed to perform this test. An estimated cost of testing is \$100-400. This does not include any costs of modifying the apparatus to test liquid agents.

This test method quantifies the vapor-phase performance of candidate agents as fire suppressants. If the agent is to be used as a replacement for halon 1211, its ability to be sprayed or streamed at the fire needs to be considered along with the agent's performance in this screen. No small-scale protocol exists at present to determine this. This procedure is not applicable to agents which are solids or are liquids of low vapor pressures.

## A. BACKGROUND

Today's halons are used primarily for the protection of vital electronic equipment facilities. This includes computer rooms, magnetic tape storage vaults, electronic control rooms, and communication equipment rooms, such as telephone switching operations. Halons also have significant application in records storage, museums, engine and machinery spaces, aerosol filling rooms, areas of use and/or storage of flammable liquids, and pipeline pumping stations [1-4].

The two primary application methods of the halons are total flooding and direct attack. In total flooding, the agent is dispersed primarily as a gas. Upon discharge, the agent rapidly mixes with air to fill the enclosure volume to a predetermined extinguishing concentration. This concentration must be held for sufficient time to allow extinguishment of the fire. For total flooding systems, the amount of suppressant needed is not a function of fire size or location; however, it is a function of fire type.

In direct attack, the agent is dispersed primarily as a liquid. The agent is sprayed or "streamed" at the fire. Examples of direct attack systems are portable extinguishers, local fixed systems, and large-capacity handline equipment. In direct attack, the needed quantity of suppressant is directly related to the size of fire and the efficiency of the agent. This efficiency may differ from the efficiency of the same chemical used for total flooding.

The suitability of an agent to be used in total flooding applications depends upon its chemical and physical effectiveness near the fire zone. The effectiveness of an agent used in direct attack applications depends additionally on its ability to be sprayed or streamed at the fire.

Halon 1301 is a gas at 21°C (70°F) with a vapor pressure of 1372 kPa (199 psig) and a boiling point of -57.75°C. Halon 1301 containers are usually pressurized with dry nitrogen either to 360 or 600 psig at 21°C. This ensures adequate performance at all temperatures. Because of its low boiling point, halon 1301 is widely used as a total flooding agent [5,6].

Halon 1211 is also a gas at 21°C, with a vapor pressure of 152 kPa (22 psig) and a boiling point of -4°C (25°F). Its relatively high boiling point allows it to be projected as a liquid stream, thus enabling portable extinguishers and local application systems to have a greater range than possible with other gaseous materials [7].

## B. EXISTING TEST METHODS

No standardized laboratory-scale test method for evaluation of fire suppression efficiency now exists. Fire suppression efficiency can be defined in absolute or relative terms. Absolute effectiveness measures how well an agent or system is able to cope with a specific hazard. Relative effectiveness measures the performance compared to some reference agents or systems. Since it would be impossible to measure the absolute effectiveness of each agent for each specific hazard, the agent's effectiveness is often measured relative to a known "good" fire suppressant. Effectiveness measurements can be made based on volume percent, weight percent, or mole percent [8].

Two types of laboratory-scale methods to determine relative effectiveness of fire suppression agents have been used to date. One is based on an agent's ability to prevent ignition of (inert) a flammable mixture of fuel in air. The other is based on the vapor phase performance of the agent in extinguishing a diffusion flame. These two approaches and previous studies are summarized below. These previous studies were examined to devise a simple, quick, and reliable method of screening potential replacement agents.

## **1. Inerting Tests**

### **a. Description**

Inerting evaluations are performed to determine the minimum concentration of agent which will render all proportions of fuel and air in a system nonflammable. A typical apparatus used for inerting determinations is a long slender glass tube, called an explosion burette (Figure 1). Calibrated rotameters are used to produce a three-component test mixture of flammable vapor, air, and suppressant in the system. The gas mixture is well-mixed in the tube, and then an ignition source is activated near the bottom of the tube. Ignition sources vary from a match head to an A-C or D-C spark of some specified energy.

### **b. Figures of Merit**

Performance of an agent concentration is by visual observance. A mixture is deemed flammable if a flame propagates the full length of the tube. Some laboratories, however, introduce a factor of safety into the test results by considering a mixture flammable if a flame propagates some fraction of the tube length, such as halfway up. At the extreme, a mixture can be deemed flammable if there is any flame propagation beyond the ignition source [9].

The minimum concentration of agent in the combustible mixture that will inhibit flame propagation for any concentration of combustible material is labeled the "peak concentration," and is taken as an indication of the effectiveness of the agent in inhibiting flame propagation. This peak can be determined graphically by plotting the volume percent of combustible vapor against the volume percent of agent for all mixtures deemed nonflammable. The curve drawn includes within its envelope all the points that are flammable. The Y-axis intercepts (zero suppressant in the mixture) represent the upper and lower flammable limits of the fuel. As increasing concentrations of agent are added, these limits are narrowed (Figure 2) [9,10].

### **c. Historical Approaches**

(1) **Early Methods.** In the 1940's, E.I. du Pont de Nemours and Company, Inc., conducted comparative tests of halogenated agents [11]. Their apparatus consisted of a 100 ml explosion pipette, 25 mm in diameter and 330 mm high. An explosive mixture consisting of 9.9 volume percent of methane in air was used as the test mixture. A known volume of extinguishing agent was added to the mixture. The gases were transferred to the pipette and back to the makeup flask eight to ten times before testing their flammability. The concentration of the methane and extinguishing agent was obtained by measuring the pressure of the mixture. A platinum electrode in the top of the pipette provided ignition, thus the direction of flame propagation was downward. An average of the agent concentration that just prevented burning and the concentration present when combustion first occurred was used to measure its effectiveness.

Also in the late 1940s, the U.S. Army Engineer Research and Development Laboratories contracted with the Purdue Research Foundation to carry out laboratory studies of vaporizing liquids. Some sixty candidate agents were evaluated [12]. The Purdue Research Foundation chose the test procedure used by the Bureau of Mines to determine flammable limits of various fuels, requiring only a small amount of chemical for evaluation. The tube was 51 mm inner diameter (i.d.) x 120 mm high, with venting at the lower end of the tube. The spark source was a Ford ignition coil of unspecified energy. Varying amounts of test agent were evaluated for their inerting ability on mixtures of combustible vapor in air. Instances of flame propagation or non-propagation and the concentrations of the three components were recorded. The "flammability peak" data for various agents were compared to determine the relative effectiveness of the agents on a volume basis. From the observed flammability peak concentrations, the weight

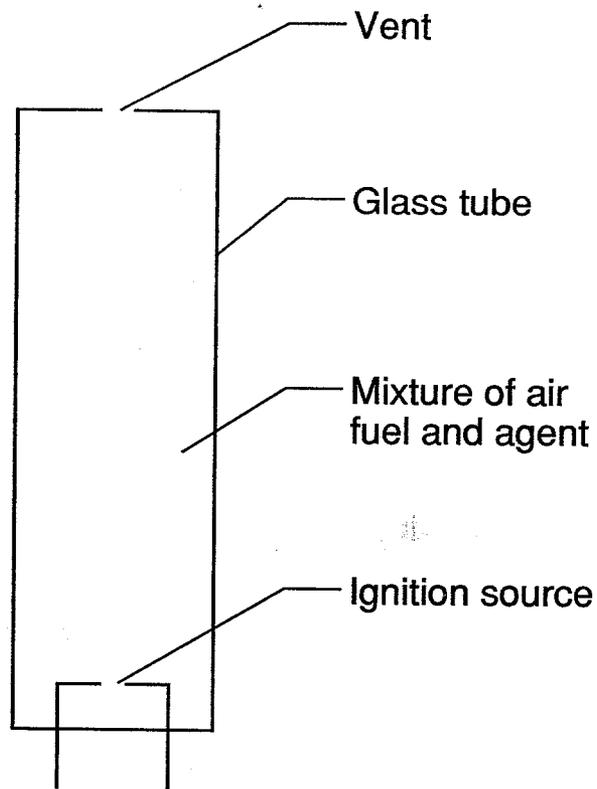


Figure 1. Explosion Burette



effectiveness of each agent was determined by multiplying by the molecular weight and expressing the result as a percent of the requirement for halon 1001, which was taken to be 100.

(2) Du Pont Mason Jar. In 1971, Du Pont performed further agent evaluation tests [13]. To reduce wall-quenching effects, a 1-quart mason (Figure 3) jar was used in place of the Bureau of Mines long slender burette. An ignition source of 176 J (kitchen match) was used. Test mixtures were made by evacuating the jar and admitting suppressant and fuel by partial pressures. The contents were mixed, the cap was switched to one containing a match head, the match head was activated, and the degree of flame propagation observed. The criterion for non-flammability was that no visible flame extension was permitted beyond that produced by the match head in air. For each determination, a new jar was employed. Flammability peak diagrams were drawn from the data, and the flammability peak concentrations of the various agents compared.

The peak concentrations determined from the mason jar technique were considerably higher than those previously reported. This could be due to the severe criterion of "zero" permissible flame propagation, the high ignition source strength vs. volume of the jar, and/or the exposure of the test mixture to air when switching from the mixing cap to the igniting cap [9,10].

(3) Du Pont Explosion Burette. In 1972, Du Pont also did agent effectiveness evaluations using a long vertical burette [14]. The apparatus measured 102 mm i.d. x 1.22 m long, and was vented at the top. Varying ignition energies from both A-C sparks and D-C sparks were examined. The effect of flame propagation criteria, ranging from essentially none to 50 percent of the tube length, was evaluated. At equal ignition energies, peak concentrations obtained in the 102 mm burette were lower than those obtained in the mason jar, thus suggesting a relationship between ignition source strength and volume of apparatus. Flame propagation criteria also played a major role in extinguishment concentration determined. As the ignition source strength increased, the difference in observed extinction concentration becomes more significant. The halon 1301 concentration nearly doubled if zero flame propagation was used as a criterion instead of 50 percent of the tube length.

(4) ICI Explosion Burette. In 1973, ICI performed evaluation tests using a 56 mm i.d. x 1.49 m long burette [9,10]. The burette was vented at the bottom. For a single fuel, determinations were made with halon 1211 at temperatures of up to 200°C. The ignition source was an A-C spark coil providing 20 to 30 J/s of energy at approximately 40 Hz. An effective flame propagation criterion of half the tube length was employed. Temperature was shown to be a major factor in the inerting concentration. N-hexane, for example, showed an increase in halon 1211 requirement of about 35 percent as the temperature increased from 25 to 140°C; at 160°C, the amount of halon 1211 needed had tripled; and at 200°C, the amount needed was almost four times higher than the room temperature value.

(5) Factory Mutual Research Corporation Explosion Burette. In 1973, Factory Mutual Research Corporation (FMRC) investigated differences caused by venting the burette at the top vs. venting at the bottom [9,10]. The apparatus was a 57.5 mm i.d. x 1.35 m long vertical tube. The ignition source was the same as that of the Du Pont and ICI burette tests, an A-C spark of 20 to 30 J/s at 40 Hz. An effective flame propagation criterion of 25 percent of tube length was employed. Six fuels were investigated; and, for all six fuels, the peak concentrations of both agents obtained with bottom venting were lower than those obtained with top venting. Peak concentrations for halon 1301 were higher than for halon 1211, a reversal from the Purdue and ICI results. Neither the top-vented or bottom-vented data agree with ICI's results.

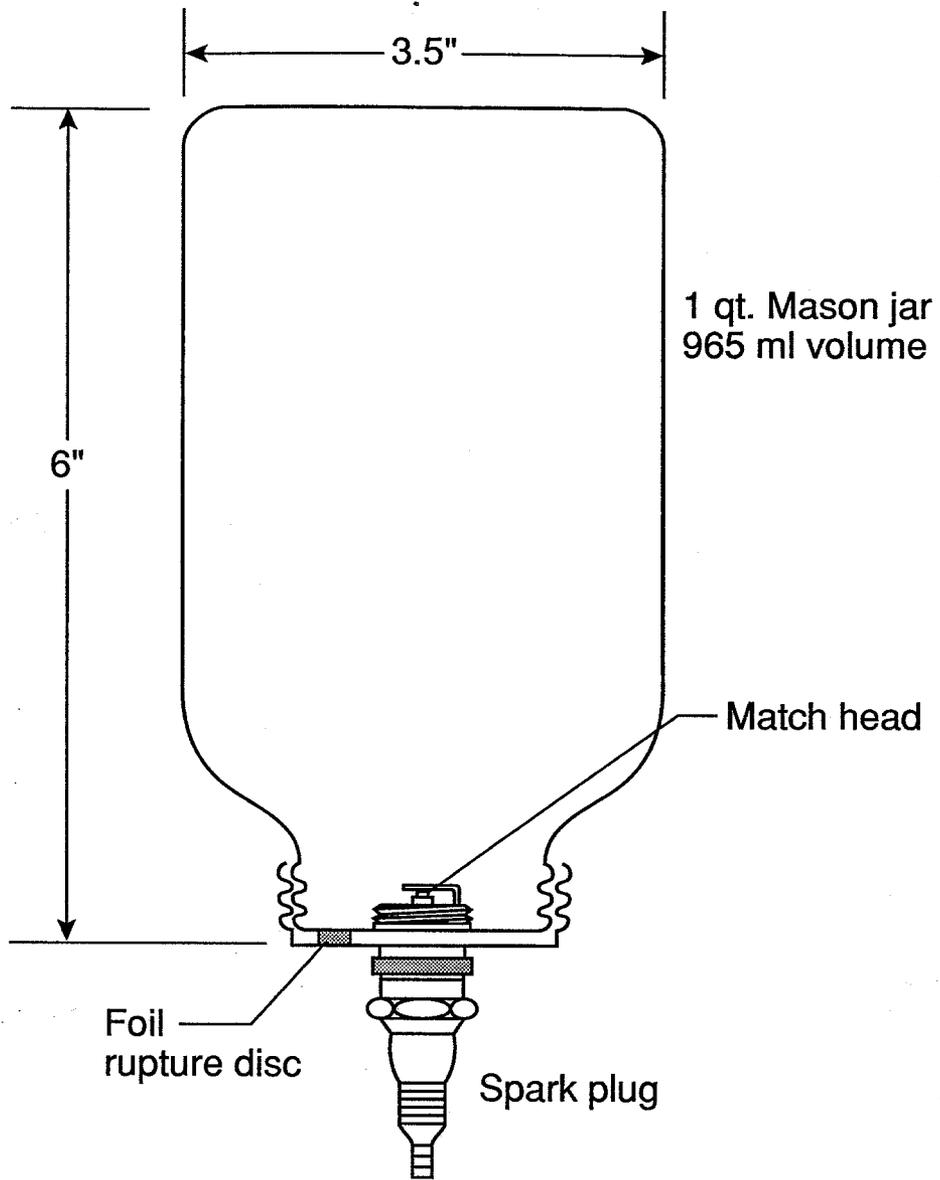


Figure 3. Du Pont Mason Jar Apparatus

(6) **Fenwal Explosion Sphere.** Fenwal conducted inerting tests using a 5.61-liter spherical stainless steel vessel consisting of two hemispheres (Figure 4) [10]. Pipe thread penetrations in the bottom half were used for loading fuel, agent, and air, as well as for attaching instrumentation and creating a vacuum. The top half of the vessel was equipped with a rupture disk. The ignition source was an electric spark with an energy of 11 J, placed at the geometric center of the vessel.

The combustible fuel-air and agent mixtures were introduced into the test vessel on a volume percent basis as determined by the partial pressure exerted by each constituent in the mixture. The spark was ignited, and the resulting explosion pressures were recorded. A mixture was considered nonflammable or inert if the maximum pressure developed was less than one psig.

In 1986, Worcester Polytechnic Institute, Center for Fire Safety Studies, also conducted a series of inerting tests in the 5.61-liter Fenwal spherical vessel using pyrotechnic ignition sources of different energy levels [10]. Inerting concentrations of halon 1301 for propane and iso-butane were investigated using inerting criteria based on a pressure rise of no more than one psig. The results show a strong relationship between inerting concentration and ignition source energy level, the inerting concentration increasing with ignition source strength up to a certain point and thereafter becoming independent of ignition source strength.

#### **d. Advantages and Limitations of Inerting Measurements**

Inerting requirements for halogenated agents vary with fuel type, temperature, and container geometry. Inerting concentrations also vary with ignition energy vs. container volume, and the criterion of "flammability," i.e., the length of flame propagation, permitted in the tube.

There is no standardized test for peak inerting concentration. The descriptions of the various test methods reveals that the apparatus varied considerably from a long slender tube to a large spherical vessel. Ignition sources were both A-C and D-C and varied in strength from 11 to 176 J, and 20 to 1300 J/s. The criterion used for determination of "inerting" also varied for the different experiments. ICI considered a mixture inert when flame propagation in the burette was less than 50 percent of the tube length with the ignition source at the bottom of the burette. FMRC considered the mixture inert when flame propagation was limited to 25 percent of the burette length, whereas Du Pont considered a mixture inert when no visible flame was observed beyond the ignition point except for the match head flame itself. The inerting concentration fixed by Fenwal was done on the basis of pressure rise, i.e., if the pressure rise in the container was no more than one psig after ignition, the system was considered inert.

ICI's vessel was vented at the bottom, Du Pont's at the top. FMRC investigated the difference caused by venting a burette at the top versus at the bottom. In all cases, peak concentrations of halons 1301 and 1211 obtained with bottom venting were lower than those obtained with top venting. Neither FMRC's top-vented or bottom-vented data agreed with ICI's results. Table 1 shows some test results for isobutane and propane. Wide variations are found in the results obtained from the different experiments although the same basic phenomena were being evaluated in each test series. For halon 1301, inerting concentrations for isobutane fires varied from 4.75 percent (reported in the FMRC explosion burette data) to 31 percent reported by Du Pont in the mason jar study.

It is seen from these test results that the fuel type affects required concentration, increasing the temperature increases the flammability peak concentration, and increasing ignition energy increases inerting requirements for a given fuel. The extent of each of these effects is dependent on fuel type. Increasing the amount of flame propagation permitted in the system permits lower concentrations for inerting. This effect is greater when a high ignition energy is used. At high ignition energies, smaller scale equipment produces higher inerting requirements.

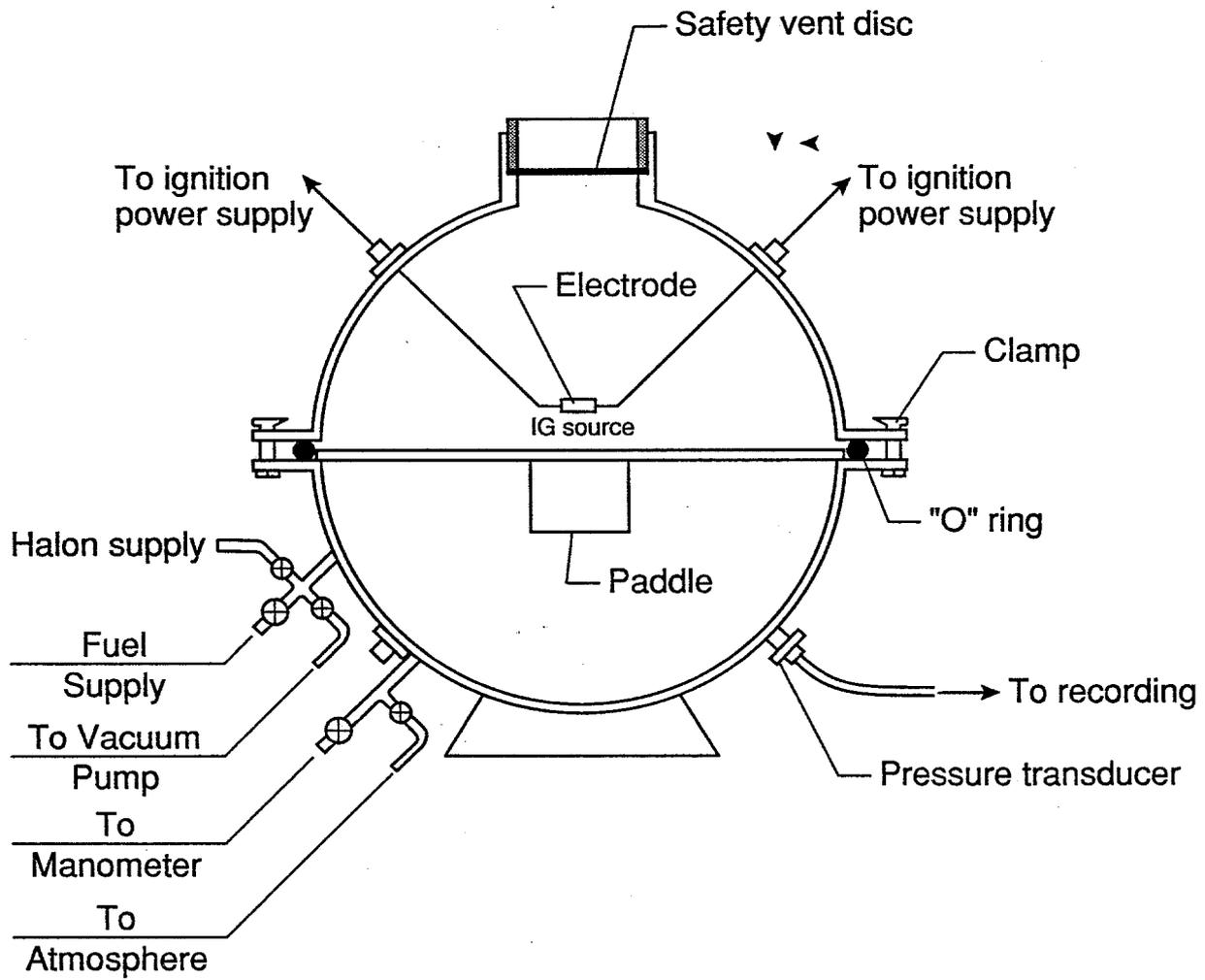


Figure 4. Fenwal Explosion Sphere

TABLE 1. INERTING TEST RESULTS

Apparatus	Vol, ℓ	Ignition		Flammability Criterion (% of tube length)	Vol. % of Halon 1301 i-butane/ propane	
		strength	source			
Mason Jar	1	176J	match	no flame propg.	9.0	9.0
"		27J/s	A-C spark	"	6.5	4.3
"		1300J/s	A-C spark	"	31.0	40.0
Du Pont Expl. Burette	9.8	176J	match	"	6.25	5.5
"		176J	match	50%-top vent	6.5	6.75
"		27J/s	A-C spark	none	6.25	4.25
"		27J/s	A-C spark	50%	6.25	4.25
"		1300J/s	A-C spark	none	11.0	10.0
"		1300J/s	A-C spark	50%	6.5	5.25
FMRC Expl. Burette	3.5	20-30J/s	A-C spark	25%-top vent	4.75	4.0
Fenwal Sphere	5.6	11J	D-C spark	$\Delta p < 1p$ sig.		7.0

It is clear that before this method can produce repeatable and/or reliable results, conditions and apparatus for determining inerting concentrations would require further investigation and quantification. This method is not easy to operate accurately due to inaccuracies in making gas mixtures and/or inadequate gas mixing. It is not precise because the oxygen concentration is critically reduced at high concentrations of agent; flammability peak diagrams also are only as good as the measurements of agent and combustible vapor.

This approach does offer limited advantages:

- It uses small amounts of the agent per test, although many tests are needed to find the peak concentration.
- It probably gives conservative results; more agent is needed for inerting than for flame extinguishment. This is offset by the fact that there is no known quantitative relationship between inerting and suppression of actual flame, and small-scale inerting measurements have not been proven reliable at full-scale.

## 2. Flame Extinguishment Tests

Effectiveness of fire suppression agents can also be measured by their ability to extinguish a pre-existing diffusion flame. Two types of test methods have been used that measure flame extinguishment. These are referred to as "dynamic" tests and "static" tests.

In a dynamic test, a diffusion flame is surrounded by a mixture of air and agent that flows past the flame. The agent concentration is increased until the flame goes out. Combustion and decomposition products are not recirculated into the fire zone.

In static tests, pure agent is dispersed into an enclosure containing a fire, filling the enclosure to a particular concentration of agent. Static tests closely approximate conditions under which a total flooding system would operate and usually are performed on a large scale. Static tests are less conservative, however, since the oxygen in the room depletes during the course of the test. This would have a dramatic effect if employed in a laboratory-scale test.

### a. Dynamic Tests

A number of experiments have been performed by various laboratories to determine concentrations of agents needed to extinguish diffusion flames of various types of fuel. These tests provide insight into the variables affecting flame extinguishment test results. The basic test apparatus hosts a diffusion flame, which can be produced from a gas, liquid, or solid fuel. The flame is surrounded by a glass chimney. A mixture of air and agent is flowed past the flame. The concentration of agent in that air flow is increased until extinguishment is obtained.

(1) National Bureau of Standards. In 1961, Creitz at the National Bureau of Standards (NBS) conducted flame extinguishment tests on four gaseous hydrocarbon fuels, plus carbon monoxide and hydrogen, using halons 1001 and 1301 [15]. His apparatus consisted of a 5.4 mm i.d. tube supporting a diffusion flame. The flame was surrounded by a 50 mm i.d. chimney through which the air and agent mixture flowed upwards past the flame (Figure 5). The air flow rate past the flame was 16 cm/s. Fuel, agent, and air were at room temperature. Creitz sometimes considered the point of extinguishment to be the point at which the flame lifted off the 5.4 mm tube.

(2) ICI Burners. In 1970, Hirst and Booth, at ICI, conducted flame extinguishment tests on eighteen liquid and gaseous fuels using halon 1211 [16]. The apparatus was a 28.5 mm diameter porous metal hemisphere surrounded by a 98 mm glass chimney (Figure 6). The air flow rate was held constant at 45  $\ell$ /min, which produced a velocity past the burner of approximately 13 cm/s. The fuel flow rate was adjusted in order to provide a flame height of 6 to 9 inches before addition of the suppressant. Fuel, agent, and air were all at room temperature. Results obtained in the ICI hemispherical burner were higher than those obtained by Creitz at NBS. Because some back diffusion of agent decomposition products onto the surface of the hemisphere occurred and, because the burner proved difficult to clean, this apparatus was discarded.

ICI then modified the burner by replacing the hemisphere with a streamlined 28.5 mm o.d. glass cup (Figure 7) [17]. Fifty-eight gaseous and liquid fuels were tested with halon 1211 and some with 1301 as well. For liquids, the level of the fuel was maintained at the very outside edge of the cup by grinding the cup to a sharp 45° edge. The air flow rate through the system was 40  $\ell$ /min, which produced a velocity past the cup of 13 cm/s. For gaseous fuels, the cup was replaced with an 8 mm outer diameter (o.d.) glass tube having the same length as the cup. The linear velocity of the gas stream was matched to that of the combined air and agent stream. In 1974, a heating coil was added within the structure of the cup itself [18]. The heating coil provided the capability of testing agent performance on fuels at elevated temperatures

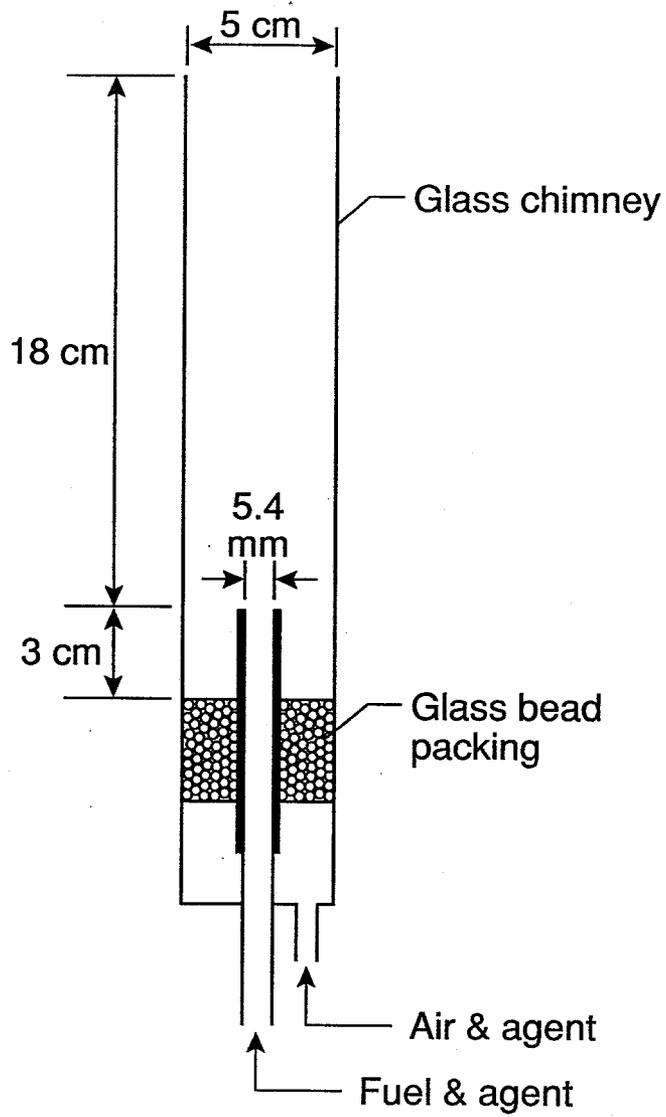


Figure 5. NBS Cup Burner

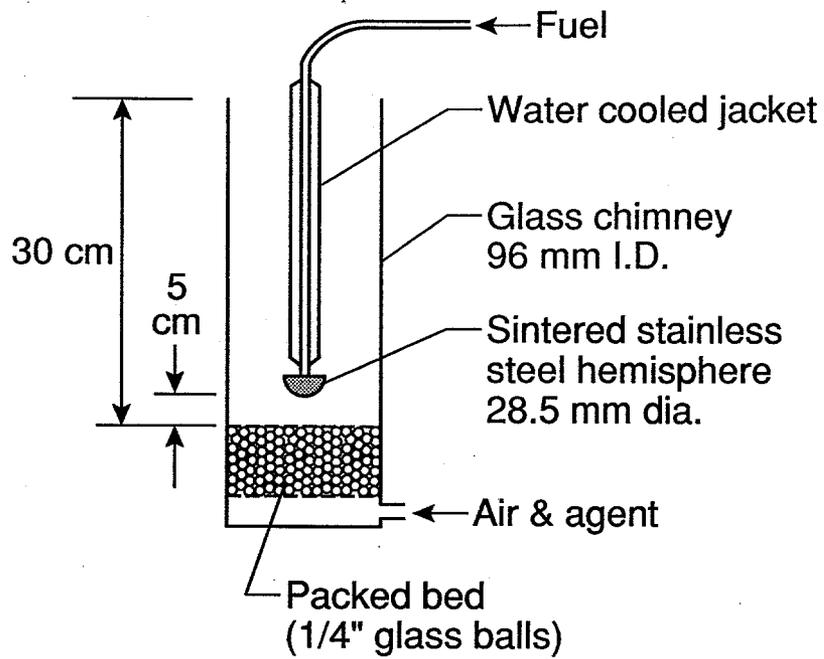


Figure 6. ICI Hemispherical Burner

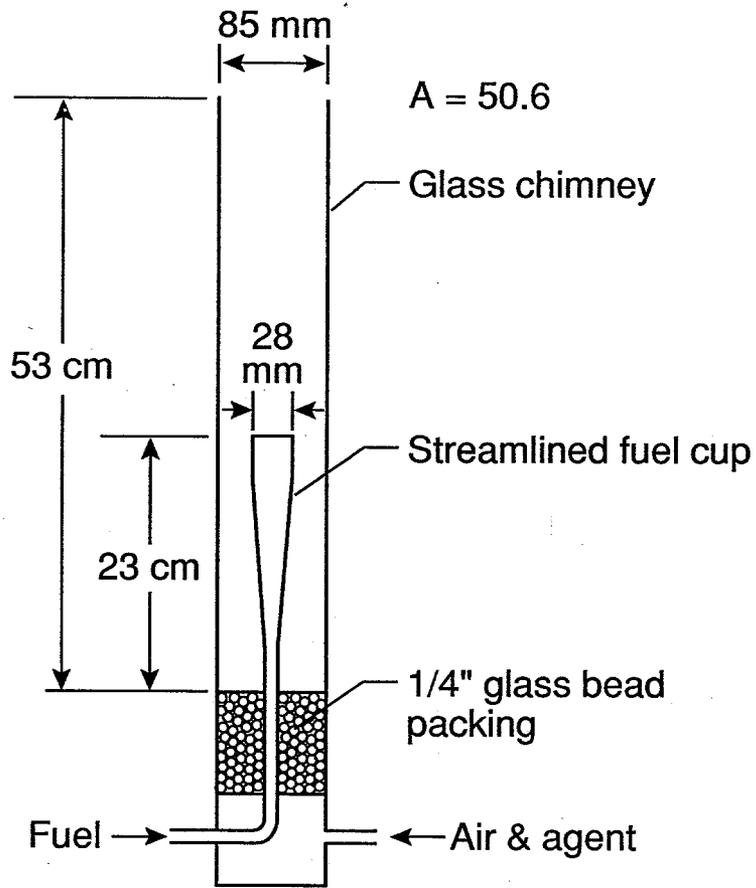


Figure 7. ICI Cup Burner

near the boiling point of the fuel. The results for fuels at room temperature were similar to Creitz's. Some fuels needed a higher concentration of agent for extinguishment when tested near their boiling points; for others this difference was only marginal.

(3) Factory Mutual Research Corporation Burners. In 1973, Factory Mutual Research Corporation (FMRC) ran cup burner tests with the intent of trying to reproduce the ICI results [19]. The FMRC cup burner apparatus was a 28 mm cup surrounded by a 105 mm glass chimney (Figure 8). It contained an internal heater. The volumetric flow rate through the system was equal to that of the ICI cup burner tests; however, due to the larger diameter chimney used by FMRC, the velocity past the cup was only 60 percent of that in the ICI apparatus. Ten liquid fuels were tested with halons 1211 and 1301. Some of these fuels were tested at elevated temperatures. The FMRC room temperature data show the same relationships as observed by ICI, but the concentrations necessary for extinguishment seem to be uniformly lower than ICI's by approximately 0.5 percent (absolute).

Following this series of tests, FMRC modified the cup burner apparatus in order to permit liquid fuels to be flash vaporized before being fed to the burner [20]. The burner tube was 38.5 mm in diameter. The vaporized fuel passed up the tube and was ignited at the top. Air containing the suppressant was fed at the bottom of the 105 mm i.d. glass chimney. The air flow rate and fuel flow rate were varied. The initial fuel temperature was 3 to 4° C above the boiling point. The peak extinguishing concentration was obtained from a plot of concentration at extinguishment vs. the ratio of air and agent velocity to fuel vapor velocity. In general, the peak extinguishing concentrations obtained in this "vapor burner" were higher than those determined in the FMRC cup burner; however, the same relationships between fuels was observed in this series as in the previous ones.

(4) Limiting Oxygen Index Test, ASTM D 2863. The oxygen index test can be thought of as a diffusion flame extinguishment test using nitrogen as the suppressant [21-23]. The fuel is generally a solid. The test determines the minimum percentage of oxygen (the "oxygen index") in a nitrogen-oxygen mix flowing upward in a test column that will just support combustion when measured under-equilibrium conditions of candle-like burning. The equilibrium is established by the relation between the heat generated by the combustion of the specimen and the heat lost to the surroundings as measured by one or the other of two arbitrary criteria, namely a time of burning or a length of specimen burned. This point is approached from both sides of the critical oxygen concentration to establish the oxygen index.

#### **b. Static Tests**

In a static test, pure agent is dispersed into an enclosure containing the fire. The system is designed to disperse agent to fill the enclosure to a particular concentration, and extinguishment is visually observed. This method closely approximates the conditions under which the system operates in practice. Static tests could not be performed at laboratory-scale due to the depletion of oxygen during the test and, therefore, were not considered as potential screening methods. Data from static tests reported in the literature, however, provide information regarding the scaleability (reliability) of the cup burner test method.

(1) ICI Total Flooding Tests. In 1970, ICI performed a series of large-scale total flooding tests to verify their laboratory-scale data [18]. The room volume was 71 m<sup>3</sup> (2,500 ft<sup>3</sup>) and measured 4.6 x 4.6 x 3.4 m high. The fire pan was a 0.46 m<sup>2</sup> circular pan elevated 0.76 m above the floor. Halon 1211 concentrations needed to extinguish fires with five different fuels were determined visually. With one exception, the cup burner flame has proved to be more difficult to extinguish (in terms of critical halon concentration) than any full-scale fire involving the same fuel. This applies to a variety of fires of large dimensions. Because of this built-in safety factor, the cup burner technique is ideally suited to the measurement of flame extinguishing concentrations.

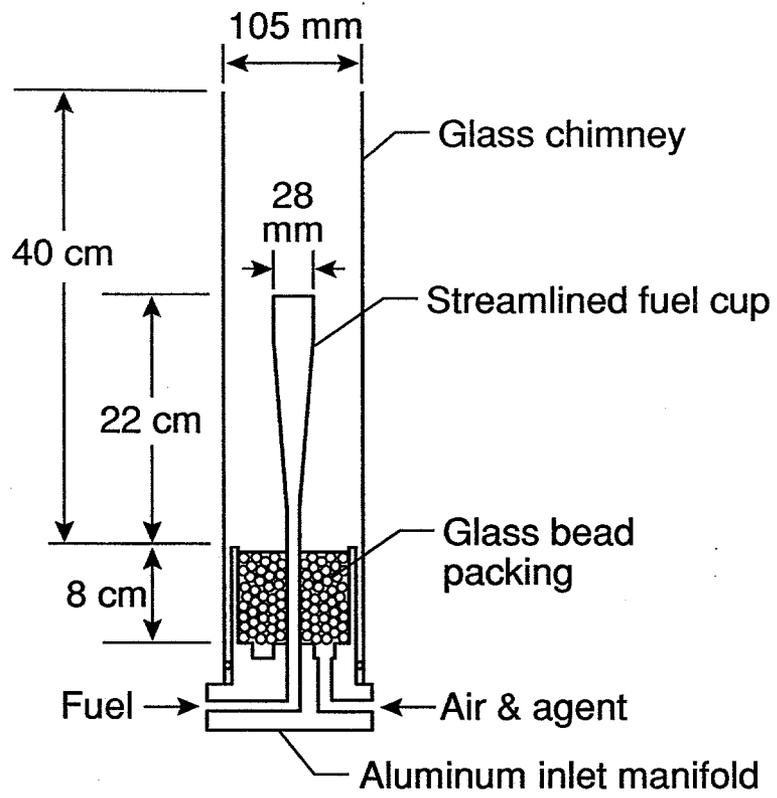


Figure 8. FMRC Cup Burner

(2) **Ansul Large-Scale Tests.** In 1972, the Ansul Company conducted a series of large-scale tests in a 284 m<sup>3</sup> test enclosure [24]. The extinguishment concentration of halon 1301 was determined for seven liquid fuels. The fire pan was 0.93 m<sup>2</sup>. Fuels were heated to near their boiling point prior to ignition.

Samples of the atmosphere were withdrawn from the room and analyzed by vapor-phase chromatography. These were averaged to obtain the mean agent concentration in each test. For each fuel, two values of extinguishing concentration were reported: a lower limit which was equal to the maximum concentration which did not extinguish the fire; and an upper limit, representing the minimum concentration of agent which did not produce extinction. Almost all the extinguishing concentrations for these fuels either agree with, or are somewhat lower than, those obtained in the small-scale laboratory cup burner.

**c. Analysis of Various Cup Burner Tests**

The cup burner is not a standardized test method. The apparatus used in previous studies varied somewhat. The apparatus and test conditions for each test series are summarized in Table 2.

**TABLE 2. MEASUREMENTS MADE IN CUP BURNERS**

	NBS	ICI	FMRC
Dimensions	5.4 mm i.d. tube 5 cm i.d. chimney	28.5 mm o.d. cup 85 mm chimney	28 mm cup 105 mm chimney
Flow velocity	16 cm/s	13 cm/s	v = 60% ICI (8 cm/s)
Temperature	Room temperature	20°C + near B.P.	24°C

Good agreement among the data was obtained as seen in Table 3. The flame extinguishment tests carried out by NBS, ICI, and FMRC provide insight into the various factors affecting the results of a cup burner test. Some of the factors found to have an effect are: the air flow rate, the fuel level in the cup, the removal of fuel after a determination, the removal vs. recirculation of combustion products, and the initial temperature of the fuel. The effect of each of these test parameters on the test results is fairly well understood.

(1) **Air Flow Rate.** The ICI studies show an increase in extinction concentration with increasing air flow rate up to a point. Then there is a plateau in the curve beyond which increasing the air flow rate does not affect extinguishment concentration until the point where the flame begins to lift off the burner, when the extinguishing concentration is again lowered. Bajpai, at FMRC, states the dependency of extinction concentration on mixture flow velocity is a consequence of eddy mixing at the flame boundary. Since the flame stream and agent/air mixture stream move in the same direction with different velocities, a boundary occurs between these two streams. When a discontinuity exists between the two velocities, this boundary becomes unstable and gives rise to a zone of eddy mixing that increases in width in the direction of flow. The concentration of agent in air needed to extinguish the flame is thus dependent upon two processes: (1) molecular diffusion of the agent due to a concentration gradient; and (2) eddy diffusion of the agent due to mixing at the flame boundary. The degree of mixing, expressed as an eddy diffusivity increases with increased velocity difference between the two streams. Thus, this influence will increase as the magnitude of velocity difference increases (resulting in lower extinction concentration) and will decrease when velocity differences are small (resulting in higher extinction concentration) [19].

TABLE 3. SUMMARY OF CUP BURNER TEST RESULTS

Fuel	Volume Percent				
	Halon 1301			Halon 1211	
	FMRC	ICI	NBS	FMRC	ICI
Methane		1.33	1.5		
Ethane		2.85	3.0		
Propane		3.1	2.7		
Butane		2.7	2.4		
Hydrogen		15.0	17.7		
Methanol	7.06	7.3		7.9	8.10
Ethanol	3.66	3.9		4.17	3.81
Acetone	3.29	3.5		3.62	3.78
Di-Ethyl Ether	3.67	3.9		4.17	4.32
Ethylene Glycol	4.66*	2.6		5.44*	2.97
Nitro-Methane	4.11	4.1		4.73	4.86
Heptane	3.29	3.5		3.56	3.78

(2) **Flame Stability.** Stability of a cup burner flame is attributed to an adequate supply of fresh air always being available to the flame. This is contrary to enclosed fire situations, where the air feeding the flames will be partially vitiated by the combustion. Also, the cup burner flame is undisturbed either by movements of the fuel surface or irregularities in the airflow. The flame is anchored at its base by a partially premixed region, formed by the small eddy that results from the flow of air past the edge of the burner. The reaction zone is blue in this area due to premixing. It is smooth and motionless in contrast to the turbulent conditions in a fire, where disturbances reduce critical agent requirements [18,24-26].

(3) **Removal of Combustion Products.** The burner assembly should be placed inside a fume cupboard, or some other provision made to exhaust the products of combustion, since the agent and/or the products of combustion may be toxic. [If vibrations of the exhaust fan cause disturbances of the fuel surface which affect the flame stability, it may be necessary to stand the apparatus on a rubber mat.]

(4) **Initial Fuel Temperature.** Studies conducted on fuels where the initial temperature of the fuel was between ambient and the fuel's boiling point showed an increase in critical agent concentration when certain fuels were preheated to temperatures near their boiling points. This phenomena was not observed for all fuels. Ethylene glycol in the ICI study needed an extinguishing concentration of 3.0 volume percent with the fuel at ambient temperature; this increased to 5.0 volume percent when the initial

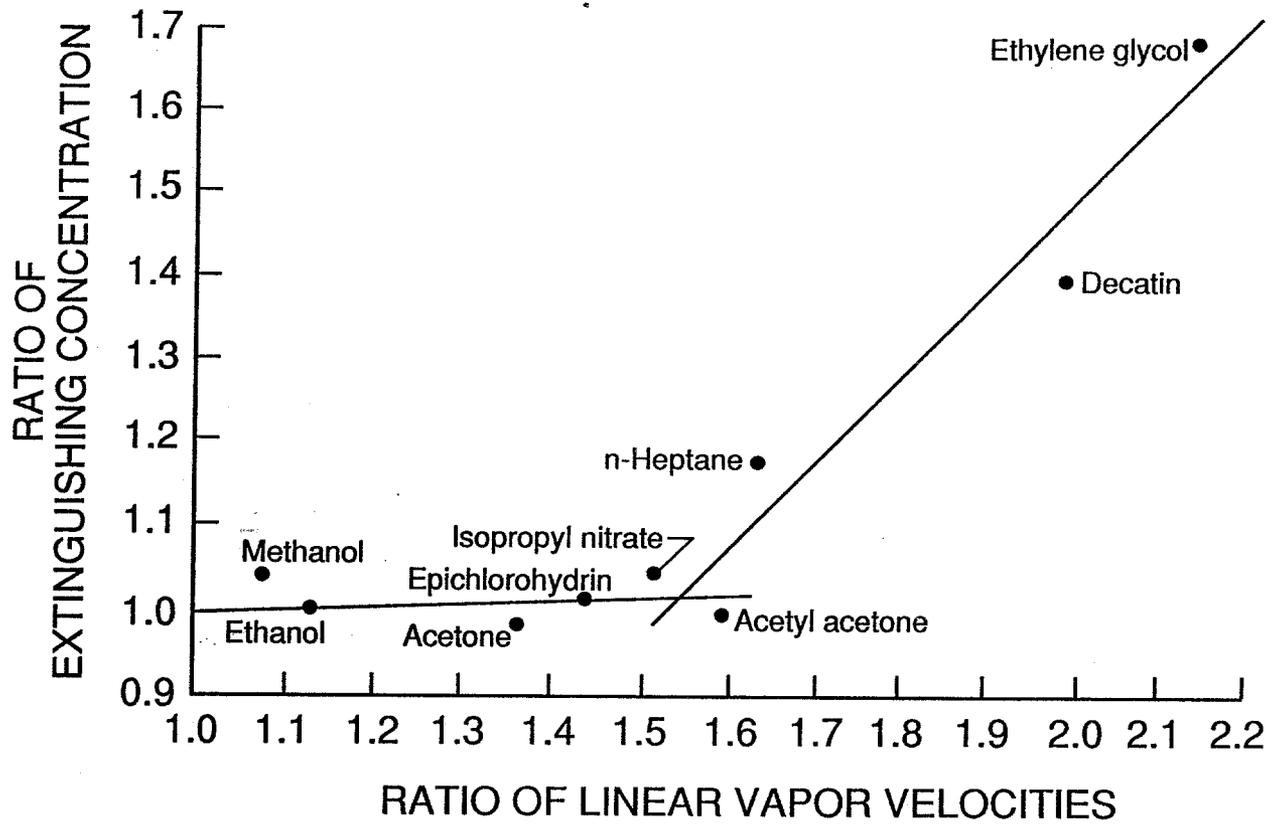


Figure 9. Extinguishment Concentration vs. Ratio of Linear Vapor Velocities, Elevated/hot

fuel temperature was elevated to near the agent's boiling point. There is no evidence that heating the fuel had caused any appreciable chemical changes either in the composition of the fuel vapor or in the combustion mechanism. An explanation must therefore be sought in the physical processes, and the most obvious of these is the increased rate of volatilization of the fuel. This must result in an increase in the linear velocity of the vapor leaving the surface. The relationship of this velocity to that of the air flowing past the burner affects the composition of the premixed region at the base of the flame. This, in turn, affects the stability of the flame. Figure 9, from Booth and Hirst, shows that fuels exhibiting an increase in extinguishing concentration with increase in linear vapor velocity have a greater than 1.55 ratio of hot vapor velocity to ambient vapor velocity; this means that for these fuels, the temperature increase caused an increase in the volatilization rate of the fuel. Thus the apparent temperature sensitivity is really the effect of relative vapor and air flow rate on the formation of the premixed region at the base of the flame. For some of the more volatile fuels (acetone, acetyl acetone, and gasoline), the effect is reversed: a lower agent concentration is required at the higher fuel temperature. This is presumably due to the formation of over-rich mixtures in the premixed region of the flame or, perhaps, to the extension of the base of the flame to a position outside the edge of the burner [18].

(5) Fuel Level in Cup. The fuel level should be maintained at the top of the burner during each determination. A 45° edge should be ground into the top edge of the burner to make it easier to maintain the correct fuel level, to reduce the tendency for the fuel to run over the edge, and to bring the fuel surface closer to the air supply [18,19]. It is sometimes hard to maintain a stable fuel level in the cup, and impurities in the fuel may affect the meniscus.

(6) Removal of Fuel after a Determination. For accurate test results, the fuel should be removed and replaced after a determination because of contamination by the diffusion of breakdown products from the flame.

If all these test parameters were to be standardized, the reproducibility of cup burner results would likely increase beyond what is shown in Table 3.

#### d. Comparison to Full-Scale/Reliability

Table 4 compares FMRC cup burner data with some full-scale turbulent flame data obtained in the Ansul 284 m<sup>3</sup> room. Ansul conducted 62 fire tests. From the test results, it was concluded that seven liquid fuels agreed within 0.5 percent by volume with laboratory-scale data. The ranges found for flammable gases were lower, by about two percent by volume, than those found in the laboratory-scale tests.

ICI (Booth and Hirst) also correlated laboratory-scale data with full-scale fires of both gaseous and liquid fuels and, in every case, a higher concentration was needed to extinguish a flame in the cup burner than to extinguish a large fire involving the same fuel. This applies to spray, running, pool, and obscured fires. ICI used a 70 m<sup>3</sup> room; n-heptane needed a concentration of halon between 3.3 to 3.4 percent for extinguishment on a full-scale as compared to a concentration of 3.8 percent in the cup burner. Ethanol took 3.7 to 3.8 percent in the full-scale tests compared with 4.2 percent in the cup burner, and methanol took 7.5 to 7.7 percent compared with 8.2 percent in the cup burner. Thus good absolute agreement is much better than is needed for a screening procedure.

In summary, cup burner tests are excellent for testing the fire suppression efficiency of gases or vaporized liquids. The results are not too sensitive to small changes in apparatus and correlate well with real-scale testing. There is, however, an operational problem with maintaining the liquid level.

No published data were found on testing liquid agents as liquids on a laboratory-scale. This could not be done in a burette [27-30]. Agents that are liquids at room temperature can be tested in the cup burner, after some method of vaporization. This will be discussed later. A bench-scale method, in which

TABLE 4. EFFECT OF SCALE

Fuel	Volume Percent 1301	
	FMRC Cup Burner	Ansul 10,000 ft <sup>3</sup> Room
Acetone	3.29	3.0
Diethyl Ether	3.66	3.34-3.95
Ethylene Glycol	4.65	3.72-3.96
Methanol	7.05	6.33-6.36
Nitromethane	4.13	5.00-5.82
Xylene	2.08	1.60-1.81

liquid agents are sprayed at the flame, is being developed at New Mexico Engineering Research Institute (NMERI).<sup>1</sup>

## C. SCREENING METHOD DEVELOPED

### 1. Rationale

Of the two types of methods that have been used previously, the diffusion flame extinguishment approach was selected as more appropriate than the inerting approach for screening a candidate agent for fire suppression efficiency.

- A flame extinguishment test requires less chemical (about 0.5 mole) for evaluation than the inerting tests. The amount of chemical needed to run a screening procedure is an important consideration due to the fact that some candidate agents will not be commercially available and may require expensive synthesis.
- For flame extinguishment tests, the quantitative effects of the test variables on the results are better known and easier to control.
- Flame extinguishment tests are insensitive to modest variations in apparatus and test conditions. With standardization of these test parameters, such as dimensions of apparatus, flow rates, and experimental procedure, repeatable results can be obtained.
- Flame extinguishment test results correlate well with full-scale test data. The laboratory-scale results are slightly conservative (by about one-half to two percent), since the diffusion flame in the burner is stable and is slightly harder to extinguish than a full-scale turbulent flame.

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<sup>1</sup> Private communication from Robert Tapscott, New Mexico Engineering Research Institute to Richard Gann regarding recent advances in fire suppressant testing.

- Inerting tests are not easily operated, and inaccuracies in making gas mixtures and inadequate gas mixing affect the accuracy of the results.
- Inerting tests have shown no consistency of results; inerting concentrations reported in the literature for halons 1211 and 1301 on a range of fuels vary by as much as an order of magnitude (Table 1).
- Many inerting test parameters such as container geometry, temperature, ignition source strength and type, ignition energy vs. container volume, venting at the top vs. bottom of apparatus, and criteria for defining "flammability" have been shown to have significant effect on inerting test results. The magnitude of the effect of each of these parameters on the final test results is not well quantified, but can be quite large (e.g., ignition source strength).
- It is unclear from the inerting test results which extinction criterion is the most meaningful. A mixture has been deemed flammable if flame propagated the full length of the tube, or one-half or one-quarter. Flammability of a test mixture has also been defined in terms of pressure rise, the mixture being deemed flammable if the pressure in the system rose more than one psig.
- It is difficult to perform full-scale inerting tests since there are too many variables involved; including the effect of turbulence in the system. There is also no known relationship between inerting and extinguishing concentrations.

## 2. Suggested Modifications

### a. Hardware

To alleviate problems related to maintaining fuel levels in the cup, and for overall simplification of the apparatus/procedure, it was decided to use a solid plastic for the fuel. The fuel "candle" and its support are modeled after the ASTM D 2863, Standard Test Method for Measuring the Minimum Oxygen Concentration to Support Candle-Like Combustion of Plastics (Oxygen Index) [22].

A diagram of the fire suppression efficiency screen apparatus is shown in Figure 10. For convenience, it will hence be referred to as the NIST PMMA burner. The shell closely approximates the cup burners used previously by FMRC and ICI. The specific design parameters were selected based on an evaluation of previous data in the literature and evaluation of applicable standardized tests. The apparatus consists of a pyrex glass chimney of dimensions 105 mm i.d. x 480 mm long. The chimney is supported on a brass base through which a mixture of air and agent is flowed. The air/agent stream is dispersed through a perforated circular plate and then through glass beads at the base of the chimney. It flows up past the flame which is supported in the center of the chimney.

Since the apparatus and combustion conditions strongly resemble those of ASTM D 2863, it is appropriate to use its standard operating procedure. This protocol can be found in Reference 22.

### b. Operating Conditions

Increasing the flow rate through the system has been shown to increase the concentration of agent needed for extinguishment up to a point. After this, increasing the flow rate has no effect on extinguishing concentration until lift-off of the flame occurs. Tests were conducted with halons 1211 and 1301, in the NIST PMMA burner at flow rates of 10, 20, and 30  $\ell$ /min. No measurable difference in

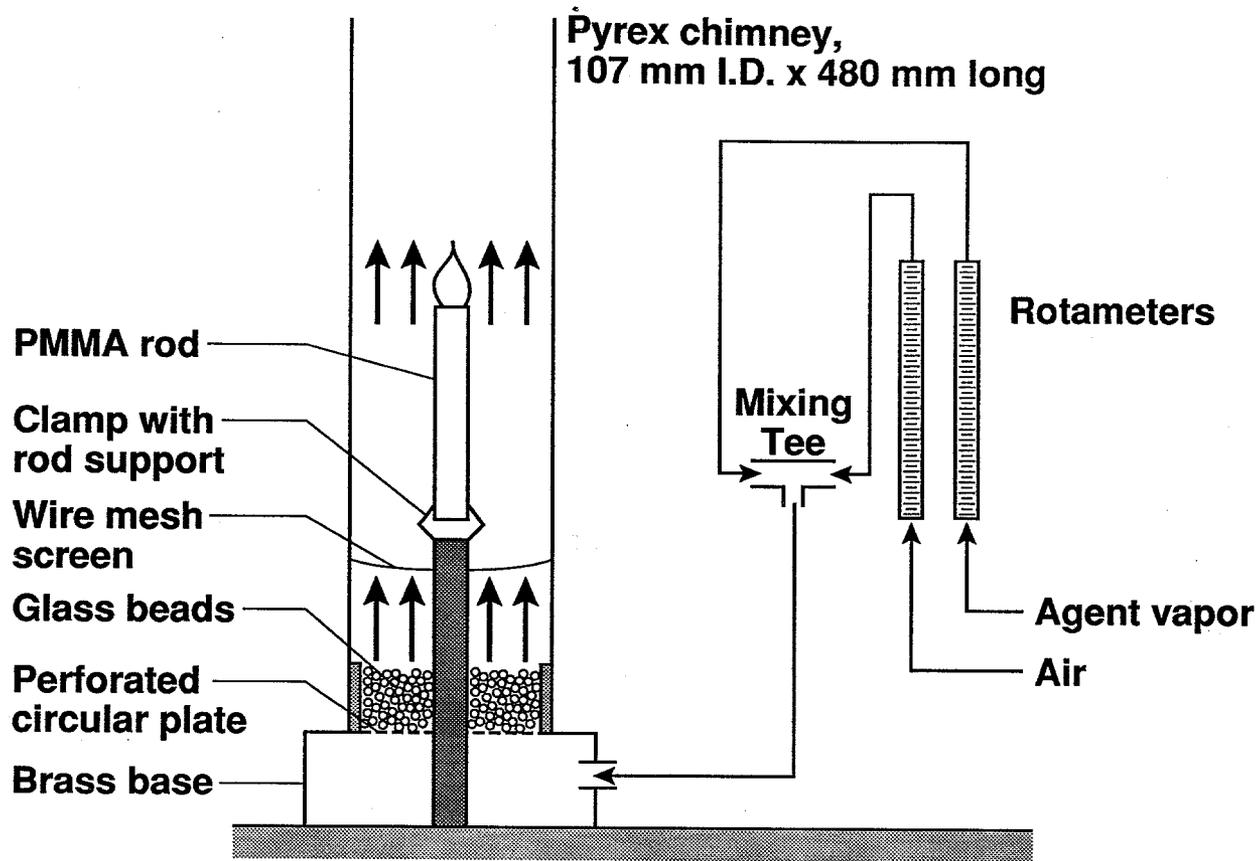


Figure 10. NIST PMMA Burner

extinguishant concentration was found. The lower end of the range, 10  $\ell$ /min, was thus chosen so that tests could be conducted using the least amount of agent and still give reliable test results.

Tests are conducted under a hood to provide a safeguard from possible toxicity of agents and/or decomposition products, and also for removal of combustion products away from the apparatus, thus preventing vitiation of the flame. All tests are conducted with the fuel initially at room temperature. Although initial fuel temperature has been shown to affect extinguishing concentration of some fuels due to increases in burning rates, relative performance of the agents did not change. The purpose of this screen is not to determine an exact extinguishing concentration at which the agent is to be applied, but to be able to compare relative performance between the candidate agents and halon 1211 and 1301.

To run volatile liquid agents through the screen, a method of vaporizing them is necessary. The best way to accomplish this is dependent on the specific chemical's vapor pressure and boiling point. Two possibilities exist. One is to meter the fluid through a heater using a syringe pump. This works for most liquids. The problem arises, however, with the potential of the chemical to condense while passing through the rotameter; this will depend on its boiling point.

The other method involves evacuating a cylinder and mixing the agent with air in the cylinder by the partial pressure method. The effectiveness of this method depends on the vapor pressure of the chemical being evaluated. The agent must be sufficiently volatile that its fraction of the cylinder mixture is larger than the greatest fraction of agent to be tested. [If the needed partial pressure of the agent in the mixture exceeds its vapor pressure, the agent will condense out of the mixture.] An air/agent mixture is prepared in a cylinder to the concentration to be tested in the screen. This mixture is then run through a rotameter and into the NIST PMMA apparatus.

The procedure for preparing an air/agent mixture is as follows:

- Evacuate cylinder using a vacuum pump.
- Calculate the volume of liquid agent needed to create a mixture of an air/agent at the desired concentration and total pressure. This is a function of the density and molecular weight of the liquid agent and of the volume of cylinder.
- Inject the agent into the evacuated cylinder using a syringe. If the boiling point of the agent is near room temperature, chill the syringe and liquid before injection to avoid vaporization.
- Fill the cylinder to the desired total pressure with air.

**c. Calibration of Rotameters**

The first step in the operational procedure is to calibrate the rotameters. This can be done for each agent by:

- calibrating with the specific gas to be tested, which is the most rigorous method;
- obtaining calibration curves if available from the gas supplier; or
- using the ratio of the specific gravities, temperatures, and pressures of the agent to the values for a gas for which the rotameter was calibrated.

Mathematically ratioing the physical properties will introduce a five to 20 percent error. This is acceptable for the purposes of this screen and saves considerable time and money.

The gases should be uniformly regulated down to a standardized pressure (20 psig if available) before entering the rotameters. Clean and dry air should be used in all tests.

**d. Test Procedure**

The test is conducted under a hood to help remove products of combustion. A new sample of PMMA (fuel) is used for each determination due to possible contamination by agent's decomposition products. All apparatus joints must be checked carefully for leaks. This can be accomplished with a soap solution. The sample is supported vertically in the center of the column with the top of the specimen 100 mm below the top of the open column. The entire top of the specimen is lighted using a propane torch, and a timer started. The specimen must be allowed to burn for 3 minutes prior to introducing the air/agent mixture and for 2 minutes at each agent concentration. The chimney should be cleaned and cooled between consecutive determinations. A hot chimney will cause extinguishment at a falsely low concentration.

**D. CRITERIA**

A candidate agent's performance in the fire suppression efficiency screen is to be judged relative to the performance of halons 1211 and 1301, the chemicals it is meant to replace. In other words, the screen determines whether the potential replacement is as effective, less effective, or more effective than halons 1211 and 1301.

A sequence to be followed is shown in Figure 11. The concentrations of halons 1211 and 1301 necessary for extinguishment are first determined. The higher of the two values is taken as the present halon extinguishment concentration. Potential replacement chemicals are then evaluated in the screen at this concentration of agent in air. If extinguishment is achieved, demonstrating that the fire suppression efficiency of the candidate agent is as good or better than that of the present halons, a Class 1 rating is given to that candidate. If extinguishment is not achieved, the candidate agent concentration is increased by a factor of two. Time is permitted for the system to achieve dynamic equilibrium. If extinguishment is achieved at this concentration, demonstrating that the fire suppression efficiency of the candidate agent is as effective to one-half as effective as the present halons, that chemical would receive a Class 2 rating. If extinguishment is not achieved, this procedure is repeated one last time, increasing the agent concentration by yet another factor of two (four times the currently used halon concentration). If extinguishment is achieved, a Class 3 rating is assigned to that candidate agent, demonstrating the agent is one-half to one-quarter as effective as the present halons, extinguishment is to a large degree physical. If no extinguishment is achieved, a Class 4 rating is assigned to the candidate agent representing no extinguishment.

This screening procedure embodies speed, simplicity of use, reliability, and minimum quantity of agent. As such, it produces meaningful groupings, rather than precise values, of extinguishment efficiencies. Of course, actual values can be obtained if the other constraints do not pertain. An absolute precision of 0.2 percent reflects the limit of accuracy of the method. About ½ day and 0.5 mole of chemical are needed to perform this test.

Since the toxicity screen (Section 6) relies on this screen for its concentration, it may be useful to further test Class 1 chemicals at one-half and one-quarter of the halon 1301 value.

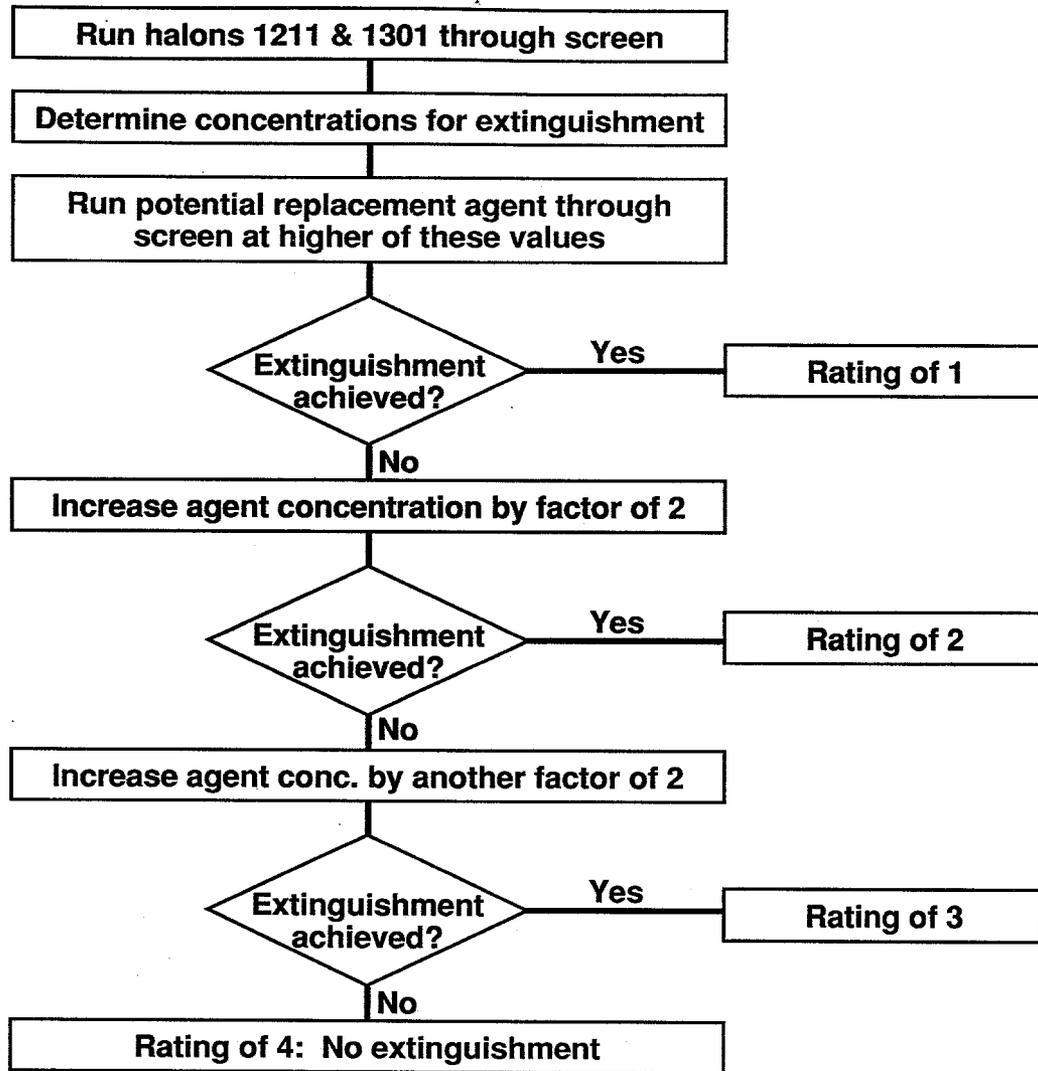


Figure 11. Candidate Agent Test Sequence

## E. PERFORMANCE DATA

### 1. Chemicals Selected

Four gases and two liquids were selected for evaluation in the NIST PMMA burner. Halons 1301 and 1211 were evaluated first to establish their performance in the screening test. Halon 1301 and halon 1211, being known excellent fire suppressants, were expected to perform well in the fire suppression screen. Two other chemicals were thus chosen that were not expected to perform as well, chlorotrifluoromethane ( $\text{CF}_3\text{Cl}$ ), known as halon 131, and tetrafluoromethane ( $\text{CF}_4$ ), known as halon 14.

Halon 131 is a colorless, nonflammable, noncorrosive gas. It is used as a low-temperature refrigerant and is a gas at room temperature. It has a vapor pressure of  $32 \text{ kg/cm}^3$  (458 psig) at  $21^\circ\text{C}$  ( $70^\circ\text{F}$ ) and a boiling point of  $-81.4^\circ\text{C}$  ( $-114.5^\circ\text{F}$ ) at one atm. It produces no toxic effects at concentrations up to 20 percent in air.

Halon 14 an inert, colorless, nonflammable gas. It has a boiling point of  $-92.4^\circ\text{C}$  ( $-198.4^\circ\text{F}$ ) at 1 atm; and is used as a low temperature refrigerant. Tetrafluoromethane has a low order of toxicity, showing no noticeable physiological effects at low concentrations. At high concentrations, it could act as an asphyxiant.

Two chemicals that are liquids at room temperature were then chosen for evaluation in the fire suppression efficiency screen. The purpose of these tests was to demonstrate a procedure useful in vaporizing liquid agents so that they can be evaluated in the NIST PMMA burner. Tests on liquid agents were performed at the Naval Research Laboratory in their cup burner which uses heptane as a fuel. (Halon 1301 was also tested on heptane to relate these results to the PMMA test performed at NIST.) This same procedure for testing liquid agents would be used in the NIST PMMA burner. This procedure is detailed in Section C.2.b. Halon 1202, difluorodibromomethane, a known good fire suppressant, and halon 113, trichlorofluoromethane, a less effective fire suppressant, were tested along with halon 1301. Halon 1202 has a boiling point of  $23^\circ\text{C}$  and halon 113 has a boiling point of  $23.8^\circ\text{C}$ .

### 2. Results

Halon 1301 required 2.5 volume percent concentration in air to extinguish the PMMA fire. Halon 1211 needed a 2.9 volume percent concentration for extinguishment. The higher of the two concentrations was taken as the "present halon concentration," nominally 3.0 percent. Therefore, potential replacement agents are to be tested at 3, 6, and 12 volume percent in air. Halon 131 extinguished the fire at 6 volume percent and, therefore, is rated as Class 2 in accordance with the candidate agent test sequence. Halon 14 extinguished the fire at 12 volume percent and, therefore, is in Class 3, much less effective than halons 1211 and 1301.

As noted above, the liquid agents were tested using heptane as a fuel. For calibration, halon 1301 was also tested on heptane and extinguished the flame at 3.1 percent. This is nominally the same as the 3 percent PMMA-extinguishing concentration used as a reference for defining the Performance Classes. Therefore the same Classes were used. The results for the liquid agents were a Class 1 rating for halon 1202, indicating it is as good or better than halons 1211 and 1301, and a Class 3 rating for halon 113, which extinguished the PMMA at a 12 percent concentration.

## **F. EVALUATION OF SCREENING METHOD**

These results give confidence in the NIST PMMA burner since extinction concentrations were as expected and comparable with previous data reported in the literature for liquid fuels in the cup burner. Halon 1211 and 1301 extinguishment concentrations reported in the literature range from 1.3 to 3.5 percent depending upon fuel type. Reported values for halon 1211 concentrations are slightly higher than for halon 1301 concentrations, for the same fuel. Test results from the NIST PMMA burner are 2.5 percent for halon 1301 and 2.9 percent for halon 1211, consistent with previous test results in both magnitude and relative ranking.

## **G. LABORATORIES/COST**

Equipment needed to run the fire suppression efficiency screen is inexpensive and requires little setup time. Most commercial laboratories experienced in plastics testing have the limiting oxygen index test, which is usable for this screen if the rotameters are calibrated to meter gases other than air, nitrogen, or oxygen. The test can be conducted at any laboratory that can provide skilled people to conduct and analyze test results. Other than the National Institute of Standards and Technology, laboratories already with experience in flame extinguishment testing are the Naval Research Laboratory in Washington, DC, and NMERI at the University of New Mexico. The cost of performing this test ranges between \$100 to \$400, plus the cost of the chemical. About 0.5 mole is required.

## **H. CONCLUSIONS**

1. This is a high quality screening test. It is quick, easy to operate, uses only a small amount of chemical, and gives reliable results. A determination in the NIST PMMA burner takes approximately 10 minutes to run, plus set-up and calibration time. This can add up to a maximum of one-half day, with very little professional time needed. The test requires only approximately 0.5 mole of agent to conduct a single determination, which is an acceptably small amount of chemical.

2. This screen is a reliable method of determining fire suppression efficiency of a candidate agent in relation to halons 1211 and 1301. Concerns relating to reliability center around two potential problems, false negative and false positive results. A false positive result would occur if an agent that is not a good fire suppressant "passed" the screen. A false negative result would occur if an agent that is a good fire suppressant "failed" the screen and was eliminated. For preliminary screening purposes, false negatives are of greater concern than false positives, since a false positive would result in keeping that chemical on the potential list and it would likely be eliminated during second level screening. A false negative result, however, may aid in a decision not to consider that agent for further evaluation. This screen was designed considering this fact so as to avoid false negatives.

3. The results are classification of the potential replacements into one of four classes, providing a good indication of the fire suppression efficiency of a potential replacement agent compared with the current halons.

A summary of the four classes follows:

- Class 1: At least as effective as halons 1211 and 1301; quenches the test flame at 3 percent by volume.
- Class 2: Not as effective as halons 1211 and 1301; quenches the test flame at 3 to 6 percent by volume.
- Class 3: Much less effective than halons 1211 and 1301; quenches the test flame at 6 to 12 percent by volume.
- Class 4: Not a chemical fire suppressant; requires at least 12 percent by volume to quench the test flame.

4. If needed, or if money and agent is available, more information may be obtained from this screen in the form of an exact extinguishment concentration.

5. This method evaluates only the vapor-phase performance of an agent. Halon 1211 is widely used in portable extinguishers and hand-held hose line equipment. To find a chemical to replace halon 1211 in these apparatus, the ability to stream the agent at the fire must be tested. This is a function of the physical properties of the agent. Further research is needed to include this aspect in the screening procedure.

6. A laboratory-scale method for determining effectiveness on deep-seated fires is needed. This is a function of soaking time as well as concentration.

7. This method is not by itself suitable for regulatory use or product specification.

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# SECTION IV

## OZONE DEPLETION POTENTIAL

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## SECTION IV

### OZONE DEPLETION POTENTIAL

#### SECTION SUMMARY

Ozone depletion in the stratosphere may be enhanced as a consequence of chain reactions initiated by the photochemical decomposition of halogen-containing substances. There is no direct measurement method for determining the contribution of a chemical to ozone depletion. At present, such a determination is made using complex atmospheric modeling and specific input data for the chemical under consideration. The pertinent principles are as follows:

- Ozone depletion potential is directly related to the numbers and kinds of halogen atoms contained by a test substance. If a test substance does not contain chlorine, bromine, or iodine, the ozone depletion potential is zero.
- Ozone depletion potential is directly related to the lifetime of a test substance in the atmosphere. The greater the lifetime, particularly within the troposphere, the greater the potential for adverse effects on ozone levels in the stratosphere. Tropospheric lifetime is reduced by physical and chemical processes, the most important of which are the reactivity with respect to OH radicals and absorption of solar radiation in the VIS-UV region of the solar spectrum.

Test methods are provided for determining the tropospheric lifetime of test substances based on the estimation or measurement of reactivity with hydroxyl radicals (OH) and the measurement of absorption cross sections in the VIS-UV region.

On the basis of their estimated lifetimes in the troposphere, candidate fire suppressants may be grouped as follows:

- Class 1: ODP is zero; contains no Cl, Br, or I.
- Class 2: ODP is low; tropospheric lifetime less than 1 year.
- Class 3: ODP is moderate; tropospheric lifetime between 1 and 10 years.
- Class 4: ODP is comparable to current halons; tropospheric lifetime greater than 10 years.

The proposed methods are applied to the halons 1301, 1211, and 1202, and to a selected test compound,  $\text{CH}_2\text{Br}_2$ . The tropospheric lifetimes, as determined using these methods, place the tested halons in Class 4, and the selected test compound,  $\text{CH}_2\text{Br}_2$ , in Class 2.

These methods are research tools and must be performed and interpreted by a senior scientist. An assessment of ODP Class takes about 3 days, uses only about 0.2 mole of chemical, and costs approximately \$3,000-8,000, plus the cost of the chemical. This presumes that the chemical is free of impurities that might affect the results.

It must be emphasized that the interpretation of atmospheric phenomena and the design of screening tests are based on our current knowledge of the properties and processes which control the temporal history and distribution of atmospheric trace species. At some future time, advances in atmospheric science may lead to modifications of the screening tests provided here.

## A. BACKGROUND

### 1. Introduction

The release into the atmosphere of compounds containing halogens can lead to a decrease in the stratospheric levels of ozone and a change in global mean temperature. The effects are closely related, and their quantitative assessment ultimately must be based on detailed modeling studies of the atmosphere.

The problem presented by the currently-used halogenated fire suppressants is essentially the same as that for the chlorofluorocarbons (CFC's) and related gases. Both classes of compounds are covered under the Montreal Protocol.

There is an active program underway to find replacements for the CFC's, the Alternative Fluorocarbon Environmental Acceptability Study (AFEAS), and various test procedures have been developed under that program which have direct application to the halon replacement program [1]. The approach and nomenclature of that program are adopted here.

Although ozone depletion and global warming potentials are being treated separately, the effects are interrelated, and test programs should be carried out in concert. A decision tree is provided to permit testing programs to be executed in a rational and economical manner.

### 2. Chemical Basis for Ozone Depletion in the Stratosphere

Over 90 percent of the column height of atmospheric ozone is located within the stratosphere (Figure 1), the peak concentration lying at about 25 km. Ozone in the stratosphere is formed by the combination of atomic and molecular oxygen:



where M signifies the third body required to carry off the energy released in the combination reaction. Above about 20 km, almost all of the atomic oxygen originates from the photolysis of molecular oxygen by short wavelength solar radiation (wavelength <243 nm):



An additional source of atomic oxygen at lower altitudes (particularly in the troposphere) is the photolysis of  $NO_2$  in the long wavelength ultraviolet:

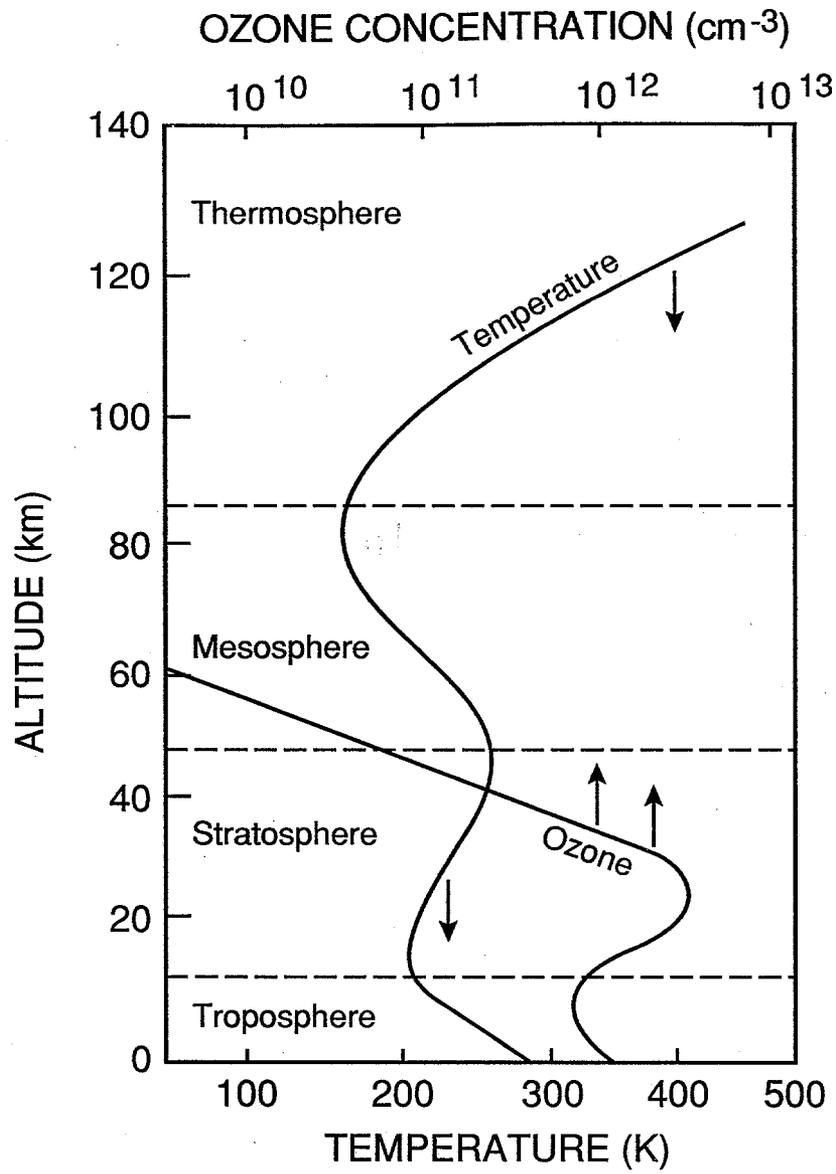


Figure 1. Ozone Concentration as a Function of Altitude. From Reference 27.



The ozone formed in (1) is itself subject to photolysis in the UV and visible portions of the solar spectrum:

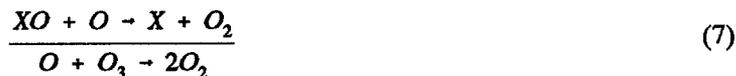


This reaction, along with reaction (1), serves to partition the "odd oxygen" species between O and O<sub>3</sub>.

Reactions (2) and (3) which produce odd oxygen are balanced by physical and chemical loss processes. Although it was originally thought that the only chemical loss process was:



It is now known that the predominant loss processes are catalytic cycles involving free radicals:



where X = H, OH, NO, Cl, and Br. These free radicals are themselves formed in a very complex series of reactions involving the photolysis and reaction of trace atmospheric species of natural or anthropogenic origin [2-6].

When compounds possessing great chemical stability such as CF<sub>2</sub>Cl<sub>2</sub> or CF<sub>3</sub>Br are released into the atmosphere, they pass unchanged through the troposphere and enter the stratosphere. These compounds, although stable in the troposphere where UV radiation capable of being absorbed by them does not penetrate, are photolyzed by UV radiation in the stratosphere. In addition, they are subject to chemical attack by O<sup>1</sup>D which is also generated in the stratosphere by UV photolysis of O<sub>2</sub>. These processes lead to the release of halogen atoms which are able to initiate a chain decomposition of ozone as described by reactions (6) and (7).

Although fluorine atoms may also be formed in these processes, they play only a minor role in ozone destruction, since they are quickly converted to HF, which is chemically and photochemically inert and is eventually washed out of the atmosphere. HCl and HBr are not chemically inert, so that while Cl and Br may be temporarily tied up in the hydrides, they can be released in active form through reactions such as



There are other such temporary reservoir species for Cl and Br that are critical parts of the complex models used to simulate atmospheric chemistry. In the case of the halons, the catalytic destruction cycles based on bromine atom reactions are far more efficient at destroying odd oxygen than the corresponding chlorine atom reactions [7,8].

It should also be emphasized that, on the basis of our current knowledge of atmospheric chemistry, only chlorine, bromine, and iodine atoms are known to have such dramatic effects in destroying ozone. Iodine atoms almost certainly could have an equally or even more harmful effect on ozone levels as do bromine atoms, although there are few data available regarding chemical reactions or atmospheric loading. However, organic iodine compounds absorb solar radiation in the visible to near ultraviolet part of the spectrum [9], and are therefore photolyzed in the troposphere without reaching the stratosphere. In this section, the discussion is based on a consideration of processes known to be important for chlorine- or bromine-containing compounds with the understanding that test methods for iodine-containing compounds, and to a first approximation, the method of grouping test compounds, can be taken as the same as for bromine-containing compounds.

Stratospheric ozone depletion resulting from the release of halocarbons thus depends on two properties of these materials:

- (1) They contain chlorine, bromine, or iodine atoms which provide the means to catalytically destroy ozone.
- (2) They have tropospheric lifetimes sufficiently long to permit the materials to enter the stratosphere.

The desirable characteristics of replacement compounds for CFC's or halons are that they have short tropospheric lifetimes or that they do not release chlorine, bromine, or iodine atoms into the stratosphere.

### 3. Ozone Depletion Potential

The concept of ozone depletion potential (ODP) was introduced to provide a means of scaling the effects of adding fixed amounts of chlorofluorocarbons (CFC's) and hydrochlorofluorocarbons (HCFC's) on the column height of ozone. It is a calculated quantity based on the use of an atmospheric model. The following definitions are taken from Fisher and coworkers [10].

Ozone depletion potential is defined as the ratio of calculated ozone column change for each unit mass of gas emitted into the atmosphere relative to the calculated depletion for the reference gas CFC 11. Column ozone is the total amount of ozone between the earth's surface and space, or mathematically, it is the vertical integral of ozone concentration (molec cm<sup>-3</sup>) through the entire atmosphere.

The definition has been modified by Fisher and coworkers [10] to refer to a depletion of 1 percent in order for the models to make comparisons at a statistically significant level of effect. Thus:

$$\text{ODP} = \frac{\text{calculated steady state O}_3 \text{ depletion due to compound X}}{\text{emission rate of compound X to give depletion of 1\%}}{\text{calculated steady state O}_3 \text{ depletion due to CFC 11}}{\text{emission rate of CFC 11 to give depletion of 1\%}}$$

The calculation requires the use of an atmospheric model with a complete input of chemistry, solar irradiation, and transport. Comparison of the results of various models ranging from the most elaborate three dimensional models to the much simpler one dimensional models indicates that in the case of the halocarbons, simple models give results adequate for use in developing screening tests [10].

It should be emphasized that the atmospheric models, while quite advanced, are approximate and are evolving as new phenomena are added and new computational capabilities are introduced. Moreover, the atmospheric models are only as good as the input data, and if new classes of compounds are to be considered, the existing models may be inadequate to make a quantitative determination of ODP.

Table 1 includes all of the data on ODP reported by Fisher and coworkers [10] as part of the AFEAS program, and is the basis for much of the following discussion. In this discussion, the term ODP is reserved for the quantity calculated using an atmospheric model. We will use "ozone depletion potential" in discussing the basis for developing screening test methods related qualitatively to ODP.

It should also be noted that the effect of any potential ozone-depleting substance is given by the ozone depletion potential scaled to the atmospheric burden of the substance.

The factors which are critical to calculating the ODP of any given compound are the chemical and physical processes that determine its lifetime and vertical distribution. These factors provide a basis for developing screening tests for ozone depletion potential.

#### **4. Atmospheric Lifetime and Ozone Depletion Potential**

The lifetime of a trace atmospheric substituent is controlled almost entirely by three process:

##### **a. Reaction with OH radicals**

This is the principal loss process for most trace pollutants, particularly in the troposphere. If the reaction is very slow, then the substance has such a long tropospheric lifetime that it enters the stratosphere, and its overall lifetime is then determined by processes taking place there. In general, OH reactions are important only if there are abstractable H atoms available or if the test compound has unsaturated C-C bonds (aromatic or aliphatic). Fully halogenated alkanes are unreactive with respect to OH radicals.

##### **b. Photolysis**

For those compounds for which we have data, this is the next most important loss mechanism, and the most important in the stratosphere. This is the mechanism whereby most CFC's and halons are destroyed in the atmosphere by absorption of solar radiation in the 170 to 300 nm region. For replacement substances photolysis in the troposphere also could be important if the test substance absorbs solar radiation in the VIS-UV part of the spectrum (290 to 700 nm). Thus a test substance which was inert to attack by OH radicals could still be destroyed in the troposphere if it contained a chromophore which led to significant absorption in the VIS-UV region of the solar spectrum. Photolysis in the VIS-UV part of the spectrum efficiently removes organic iodine compounds within the troposphere.

##### **c. Reaction with O<sup>1</sup>D**

This is important in the higher regions of the stratosphere only. For substances that have weak absorptions in the VIS-UV, this is a significant loss process. Test compounds for which this is the

TABLE 1. NOMENCLATURE, ODP, GWP, AND ATMOSPHERIC LIFETIME FOR SELECTED HALOCARBONS

Formula	Designation	Lifetime, years	ODP	GWP
CCl <sub>3</sub> F	CFC 11	60	1.0	1.0
CCl <sub>2</sub> F <sub>2</sub>	CFC 12	120	0.97	3.1
CCl <sub>2</sub> FCClF <sub>2</sub>	CFC 113	90	0.85	1.4
CClF <sub>2</sub> CClF <sub>2</sub>	CFC 114	200	0.73	3.9
CClF <sub>2</sub> CF <sub>3</sub>	CFC 115	400	0.41	7.6
CHClF <sub>2</sub>	HCFC 22	15.3	0.051	0.36
CF <sub>3</sub> CHCl <sub>2</sub>	HCFC 123	1.6	0.016	0.19
CF <sub>3</sub> CHClF	HCFC 124	6.6	0.019	0.10
CF <sub>3</sub> CHF <sub>2</sub>	HCFC 125	28.1	0	0.58
CF <sub>3</sub> CH <sub>2</sub> F	HCFC 134a	15.5	0	0.27
CCl <sub>2</sub> FCH <sub>3</sub>	HCFC 141b	7.8	0.080	0.092
CClF <sub>2</sub> CH <sub>3</sub>	HCFC 142b	19.1	0.056	0.37
CF <sub>3</sub> CH <sub>3</sub>	HCFC 143a	41.0	0	0.74
CHF <sub>2</sub> CH <sub>3</sub>	HCFC 152a	1.7	0	0.030
CCl <sub>4</sub>		50	1.1	0.35
CCl <sub>3</sub> CH <sub>3</sub>		6.3	0.11	0.024
The ODP's are averaged values from one dimensional model calculations reported in reference 10. Lifetimes from reference 10. The GWP's are averages from one dimensional models reported in reference 24.				
CF <sub>3</sub> Br	Halon 1301	101	13.2	
CF <sub>2</sub> ClBr	Halon 1211	12.5	2.2	
CF <sub>2</sub> Br <sub>2</sub>	Halon 1202	≈1	0.3	
CF <sub>2</sub> BrCF <sub>2</sub> Br	Halon 2402	≈40	6.2	
ODP from reference 25, using LLNL one dimensional model calculation. Lifetimes of CF <sub>3</sub> Br and CF <sub>2</sub> ClBr from reference 26 also using LLNL one dimensional model calculation. Data on CF <sub>2</sub> Br <sub>2</sub> and CF <sub>2</sub> BrCF <sub>2</sub> Br from reference 20. The latter are tropospheric lifetimes.				
CF <sub>2</sub> BrCF <sub>3</sub>	Halon 2501	≈100		
CH <sub>2</sub> Br <sub>2</sub>		≈6		
CH <sub>3</sub> Br		≈2		
From reference 20. For CF <sub>2</sub> BrCF <sub>3</sub> this is the stratospheric lifetime, and for CH <sub>2</sub> Br <sub>2</sub> and CH <sub>3</sub> Br the lifetimes refer to the troposphere.				

dominant loss mechanism will have very long atmospheric lifetimes, and will be therefore unacceptable as substitutes. This mechanism for destruction of test substances will not be considered further here.

It is clear that compounds having very short atmospheric lifetimes will not contribute significantly to ozone depletion. They will be destroyed in the troposphere before they have a chance to enter the stratosphere and release chlorine or bromine atoms. There is thus a qualitative connection between ozone depletion potential and atmospheric lifetime. Table 1 provides a summary of calculated values of ODP and the corresponding atmospheric lifetimes for selected halocarbons. The data are plotted in Figure 2. It is apparent that compounds with very long atmospheric lifetimes have correspondingly large ODP's. In general, brominated compounds are about 10 times worse in this respect. It can also be seen that in the case of the CFC's, replacement of a halogen atom by a hydrogen atom leads to a marked reduction in ODP. Although no comparable data exist for the halons, a similar effect is expected.

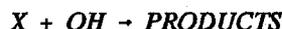
Although there is no simple functional relationship between ODP and atmospheric lifetime, the qualitative connection between these quantities provides a basis for formulating test methods suitable for screening test compounds. Since the most important determining parameter for atmospheric lifetime is the rate constant for reaction with OH radicals, the first screening test proposed is reactivity with respect to reaction with OH radicals. For compounds unreactive with respect to OH radicals, but potentially capable of being photolyzed in the VIS-UV region of the solar spectrum, a second test method, measurement of the absorption coefficient in the VIS-UV is described.

The atmospheric lifetimes shown in Figure 2 refer to the average overall lifetime in the atmosphere. For screening purposes, we are concerned solely with lifetime with respect to processes that destroy test substances within the troposphere. Thus, the test methods described here are designed to provide data on rate constants and lifetimes for removal of test substances from the troposphere with respect to the specific processes of reaction with OH radicals and photolysis. The derived lifetimes are not to be confused with overall atmospheric lifetime. The test methods are interrelated to each other and to test methods for global warming potential. Appendix A provides procedures for carrying out ozone depletion screening tests in the most economical manner. This is illustrated by means of the decision tree shown in Figure 3.

## **B. CHEMICAL FACTORS CONTROLLING TROPOSPHERIC LIFETIME**

### **1. Reaction with OH Radicals**

Hydroxyl radicals transform and remove trace atmospheric substances by abstracting hydrogen atoms or by addition/displacement reactions at unsaturated sites in the molecule. The reaction of any substance, X with OH can be written as:



and the rate of reaction given by:

$$-\frac{d(X)}{dt} = k_{OH}(OH)(X),$$

where  $k_{OH}$  is the rate constant for reaction, (X) the concentration of species X, and (OH) the average tropospheric OH concentration. Since (OH) is essentially constant (concentration independent of the presence of the trace substance X in the atmosphere), the expression can be written as:

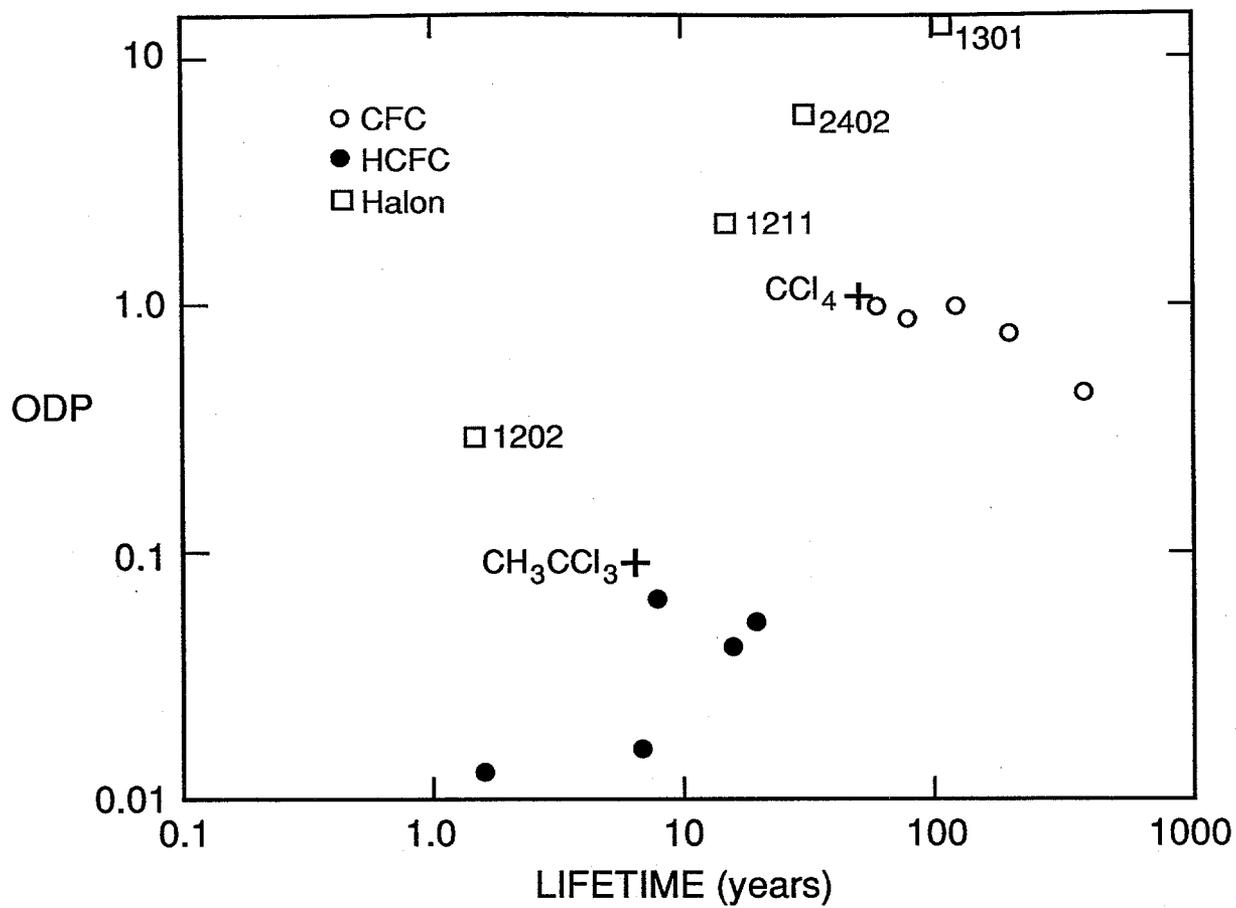


Figure 2. ODP as a Function of Atmospheric Lifetime. Data from Table 1.

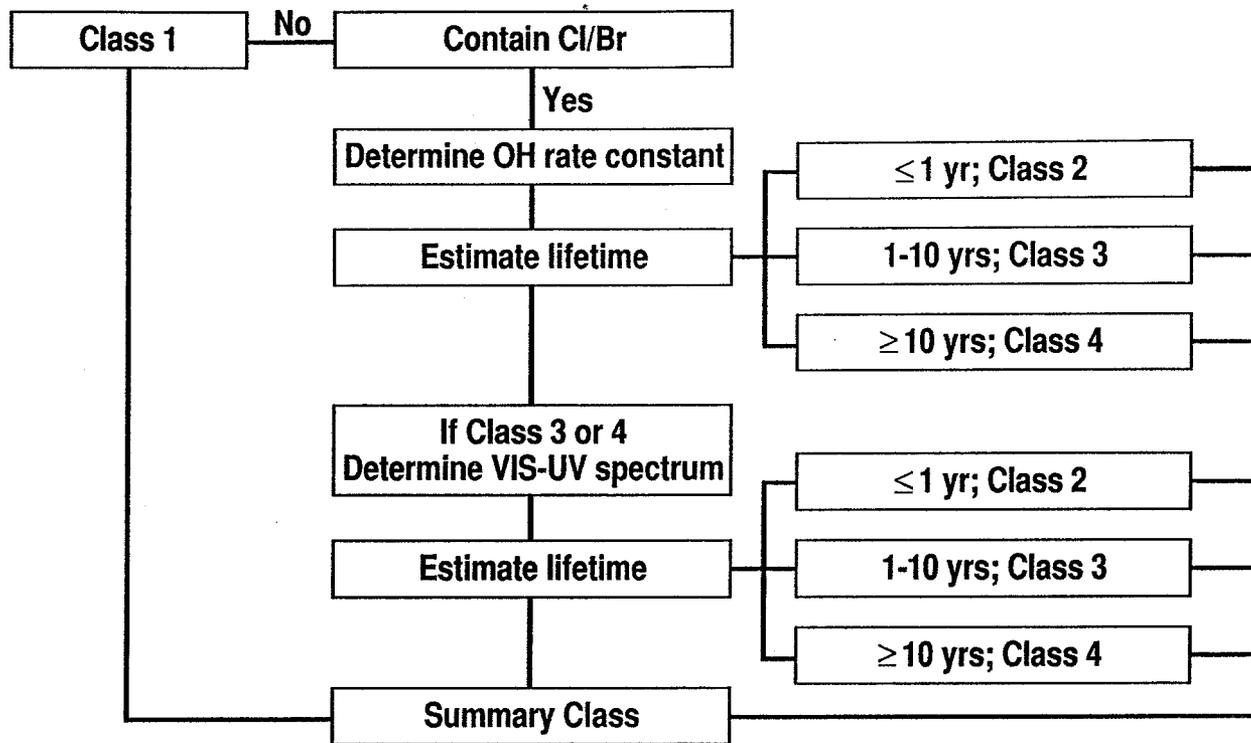


Figure 3. Decision Tree for Ozone Depletion Potential.

$$\frac{-d(X)}{(X)} = k_{OH}(OH)(dt)$$

or:

$$\ln \left( \frac{X_0}{X_t} \right) = k_{OH}(OH) t,$$

where  $X_0$  is the concentration at some zero of time, and  $X_t$  the concentration at time  $t$ . The time for the concentration to decay from  $X_0$  to  $X_t$  is thus given by:

$$t = \frac{\ln \left( \frac{X_0}{X_t} \right)}{k_{OH}(OH)}.$$

Lifetime can be defined as:

$$t = \frac{\ln(2.718)}{k_{OH}(OH)} \quad \text{or} \quad t = \frac{1}{k_{OH}(OH)}.$$

where  $X_0/X_t$  has been set equal to 2.718, the base of natural logarithms. This is the time required for the concentration to fall by a factor of 2.718. Using an average atmospheric hydroxyl radical concentration of  $(OH)=10^6$  molec  $\text{cm}^{-3}$  [11], the tropospheric lifetime is defined as:

$$t_{OH}(trop) = \frac{3 \times 10^{-14}}{k_{OH}},$$

where the units of  $t_{OH}(trop)$  are years (1 year =  $3 \times 10^7$  sec) and of  $k_{OH}$  are  $\text{cm}^3$  molec $^{-1}$  s $^{-1}$ .

## 2. Photolysis

Photolysis is the process whereby a molecule is chemically transformed following the absorption of light. For photolysis to be important in the troposphere, the molecule must be able to absorb photons in the VIS-UV region of the solar spectrum (between about 290 and 700 nm) and the resultant energy-rich molecule must be chemically transformed rather than being physically quenched back to the original state. The rate of photolysis depends upon the flux of solar photons in the VIS-UV region, the absorption cross section of the substance over the same region, and the quantum yield for dissociation as a function of wavelength. The rate of photolysis is:

$$-\frac{dx}{dt} = k_p(X) - f\sigma\phi(X),$$

where  $f$ =flux of solar photons in  $\text{cm}^{-2} \text{s}^{-1}$ ,  $\sigma$ =cross section (base e) in  $\text{cm}^2$ ,  $\phi$ =quantum yield for dissociation,  $k_p$ =the effective first order rate constant in  $\text{s}^{-1}$ , and  $(X)$ =concentration of substance X in  $\text{molec cm}^{-3}$ . Thus:

$$k_p = f\sigma\phi.$$

The rate constant must actually be determined as the integral of this quantity over the whole range of atmospherically-accessible solar radiation. The process is considerably simplified by carrying out the calculation for discrete intervals of the solar spectrum of interest and summing to obtain the total rate constant. The details of the calculational approach are given in Appendix C. Other factors including solar zenith angle, season, latitude, altitude, and surface albedo also enter into the calculation.

The lifetime with respect to photolysis is defined as,

$$t_p (\text{trop}) = \frac{1}{k_p},$$

or

$$t_p (\text{trop}) = 3 \times \frac{10^{-8}}{k_p},$$

where the units of  $t_p(\text{trop})$  are years (1 year= $3 \times 10^7$  sec) and of  $k_p$  are  $\text{s}^{-1}$ .

To determine  $k_p$  it is necessary to know the atmospheric flux of solar photons and their wavelength distribution, the absorption cross section of the compound over the same spectral range, and the quantum yield for dissociation, also as a function of wavelength. The first quantity is tabulated and available [2]. The second quantity is readily measured in the laboratory. The third quantity, however, is not easily obtained. For the purpose of developing a screening test, the quantum yield is conservatively taken to be unity at all wavelengths, and the screening test based on measurement of the absorption cross section. Then,

$$k_p \leq f\sigma \text{ and } t_p (\text{trop}) \geq \frac{1}{k_p} \geq \frac{3 \times 10^{-8}}{k_p}.$$

## C. TEST METHODS

The test methods that follow provide a basis for determining OH radical rate constants and atmospheric photolysis rate constants, and thus for categorizing test compounds.

### 1. Rate Constant for Reaction with OH Radicals

Reactivity with OH may be determined by direct laboratory measurement of the rate constant of reaction, or may be estimated using the structure-activity relationships developed by Atkinson [12]. The latter is preferred for those compounds for which Atkinson provides appropriate data.

The estimation method is based on an analysis of the structure of the molecule and its breakdown into component structural sub-units. The reactivity can be expressed in terms of (a) abstraction of H atoms, (b) addition at double or triple C-C bonds, and (c) addition to aromatic structures. The total rate constant is obtained by summing the contributions of the different groups. In some cases, the reactivity and hence lifetimes of certain classes of compounds can be estimated without going through a detailed estimation calculation or making laboratory measurements. Thus, completely halogenated (with F, Cl, Br, or I) alkanes are essentially inert with respect to reaction with OH radicals, and therefore, belong to Class 4. On the other hand, reactions of OH radicals at unsaturated sites (aliphatic or aromatic in character) are always very much faster than abstraction [12], and therefore, unsaturated substances have short atmospheric lifetimes, and for screening purposes belong in Class 2.

Thus, the estimation methods, are presented only with reference to saturated compounds containing at least one abstractable hydrogen atom. The approach is described in more detail in Appendix B.

Experimental methods are more costly than estimation methods, and should be used only in the event that the structural units in the test compound are not included in the tables of parameters provided by Atkinson.

There are no accepted standard methods for the measurement of OH rate constants, although there are a number of convenient methods available [13]. These include (a) flash-photolysis resonance fluorescence or laser induced fluorescence [14-16], (b) discharge-flow resonance fluorescence [17], (c) discharge-flow laser magnetic resonance [17-19], and (d) steady-state photolysis [12]. Any of these methods can lead to reliable rate constant determinations. The first three methods are based on measurement of the loss of OH under conditions of excess test compound and yield an absolute measurement of the OH rate constant. The last method is based on the loss of test compound in the presence of excess OH, and yields a measure of the rate constant relative to the rate constant for some well known reference compound.

Those methods, based on measurements of OH loss, require that the test compound be free of impurities which are significantly more reactive than the test compound itself. Purity is thus of great importance in executing the test using this approach. In the case of the relative rate measurements, it is necessary to develop the necessary analytical capability to follow the course of the reaction. In addition the relative method is limited to reactions for which the rate constant is greater than about  $10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ , which severely limits its application for the purposes of the screening tests developed here. There are only a limited number of laboratories in this country equipped to do any of these kinds of measurements. The method of choice in terms of availability of equipment and capability to provide rate data over the range of rate constants of interest, is the flash-photolysis resonance fluorescence technique. That is the basis for the test protocol given in Appendix B.

Institutions known to have the capability of applying the flash-photolysis resonance fluorescence technique include:

Harvard University, Cambridge, Massachusetts  
NIST, Gaithersburg, Maryland  
NOAA Environmental Research Laboratories, Boulder, Colorado  
Georgia Institute of Technology, Atlanta, Georgia  
University of Dayton Research Institute, Dayton, Ohio

The approximate costs of these tests are probably in the range of \$2000 to \$5000 per compound depending on the number of test compounds and the assumption that the test samples are free of impurities that can affect the results. These test methods are at the research level, and cannot be carried out without the participation of senior scientific staff.

## 2. VIS-UV Absorption Cross Section

As shown in Section B.2, an upper limit to the rate constant for photolysis is given by:

$$k_p \leq f\sigma$$

and since  $f$  is a tabulated quantity, the test measurement involves measurement of the absorption cross section in the VIS-UV region of the spectrum.

There are no accepted standard methods for the measurement of absorption cross sections. The measurement can be undertaken using a variety of spectrometer configurations. Design options include single pass or multipass for the absorption train, and also single beam or double beam for the detection system. Double beam instruments consist of true double beam configurations employing two identical monochrometers and two detection systems, virtual double beam configurations employing a beam splitter at the exit of the monochromator followed by two detection systems, and broad-band referencing, where the wavelength dispersed signal is referenced to the non-dispersed incident light source. Any of these experimental configurations are acceptable. Of particular relevance are the measurements of Molina and coworkers [20], using a double-beam instrument to measure absorption cross sections for several brominated methanes and ethanes, and those of Gillotay and coworkers [21,22] who measured absorption cross sections for some bromine-containing compounds using both multiple reflection and single pass single-beam instruments.

The choice of instrument is dictated by the requirement that it be able to measure absorption cross sections as low as  $10^{-24}$  cm<sup>2</sup>. Absorption cross section is defined in terms of the fractional absorption of light passing through a defined path length of a given concentration of absorber.

One can define a figure of merit for the measurement system based on the quantity  $\sigma p \ell$  (the optical depth), where  $\sigma$  is the absorption cross section (wavelength dependent),  $p$  the pressure (or concentration) of the test compound, and  $\ell$  the path length. Highest precision cross section measurements are made with an optical depth of about one (30-40 percent absorption). For weak absorbers,  $\sigma p \ell$  will be much smaller. In addition, for a fixed path length, absorption depends on the pressure (or concentration) of the test substance in the optical path. Under nominal conditions of "room" temperature (298 K), absorption may be limited by the available vapor pressure of the test substance. These factors are illustrated in Table 2, where the minimum cross sections for different degrees of absorption at different sample pressures are calculated for a path length of 1 meter.

TABLE 2. MINIMUM MEASUREABLE CROSS SECTIONS FOR DIFFERENT AMOUNTS OF ABSORPTION AND AT DIFFERENT PRESSURES FOR AN OPTICAL PATH LENGTH OF 1 METER

Absorption, %	$\sigma\ell = -\ln(I/I_0)$	Pressure, torr	$\sigma, \text{cm}^2$
1	.01	760	$4 \times 10^{-24}$
		100	$3 \times 10^{-23}$
		10	$3 \times 10^{-22}$
.1	.001	760	$4 \times 10^{-25}$
		100	$3 \times 10^{-24}$
		10	$3 \times 10^{-25}$
.01	.0001	760	$4 \times 10^{-26}$
		100	$3 \times 10^{-25}$
		10	$3 \times 10^{-24}$

To measure the cross section for a weak absorber requires high pressure, and/or long path length, and/or high accuracy in measuring very small amounts of absorption. For screening purposes, the accuracy or reproducibility of the measurements should be about 25 percent, and this should define the smallest possible value of  $\sigma\ell$  suitable for making the measurements.

Although we do not specify a particular instrument configuration for the purpose of this test, we will illustrate the test protocol using a single-beam instrument as described further in Appendix C.

Laboratories known to have the capability to carry out VIS-UV absorption cross section measurements include:

- University of California, Irvine, California
- Jet Propulsion Laboratory, Pasadena, California
- NIST, Gaithersburg, Maryland
- NOAA Environmental Research Laboratories, Boulder, Colorado
- Brookhaven National Laboratory, Upton, New York.

The approximate costs of these tests range from \$1000 to \$3000 per compound, depending on the number of test compounds and the assumption that the test samples are free of impurities that can affect the results. These test methods are at the research level, and cannot be carried out without the participation of senior scientific staff.

#### D. CLASSIFICATION OF HALON SUBSTITUTES BASED ON TROPOSPHERIC LIFETIME

As noted above, the lifetime of a substance in the troposphere can be related to its rate of reaction with OH radicals or to its photolysis rate constant. Rate constants for reaction with OH radicals and photolysis rates corresponding to different tropospheric lifetimes are given in Table 3.

TABLE 3. CORRESPONDENCE BETWEEN TROPOSPHERIC LIFETIME AND THE RATE CONSTANT FOR REACTION WITH OH RADICALS AND FOR THE RATE CONSTANT FOR PHOTOLYSIS

Lifetime, years	$k_{OH}, \text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$	$k_p, \text{s}^{-1}$
.1	$3 \times 10^{-13}$	$3 \times 10^{-7}$
.3	$1 \times 10^{-13}$	$1 \times 10^{-7}$
1	$3 \times 10^{-14}$	$3 \times 10^{-8}$
3	$1 \times 10^{-14}$	$1 \times 10^{-8}$
10	$3 \times 10^{-15}$	$3 \times 10^{-9}$
30	$1 \times 10^{-15}$	$1 \times 10^{-9}$
100	$3 \times 10^{-16}$	$3 \times 10^{-10}$

Based on the qualitative connection between ozone depletion potential and atmospheric lifetime, it is proposed that test compounds be classified into classes on the basis of whether or not they contain Cl, Br, or I, and their tropospheric lifetime. Long lifetimes are less desirable than very short lifetimes with respect to the deleterious effect of a test compound on ozone levels in the stratosphere.

The classification depends on the nature of the halogen substituents. For test compounds which do not contain Cl, Br, or I, the test substance is assigned to Class 1. For chlorine, bromine, or iodine containing test compounds, three classes are used, based on the estimated tropospheric lifetime. The resultant four classes are:

Class 1: ODP is zero; contains no Cl, Br, or I.

Class 2: ODP is low; tropospheric lifetime less than 1 year.

- Class 3: ODP is moderate; tropospheric lifetime between 1 and 10 years.
- Class 4: ODP is comparable to current halons; tropospheric lifetime greater than 10 years.

The classification is based on data given in the AFEAS report [1], and the qualitative observation that ODP is related to atmospheric lifetime as illustrated in Figure 2. The AFEAS program is testing CFC replacements (the hydrochlorofluorocarbons or HCFC's) which have, in general, an ODP of about 0.1 of that of the CFC's they are designed to replace. They would be categorized as Class 3. As seen in Table 1, halon 1301 has a tropospheric lifetime of about 100 years. "Modifying" it to reduce its ODP to the same level would require a reduction by about a factor of 100 in tropospheric lifetime, corresponding to a tropospheric lifetime of less than about 1 year. This would place its replacement chemical in Class 2. If, on the other hand, the goal was to achieve the same degree of reduction as for the proposed CFC's replacements, i. e., a factor of 10, the lifetime would need to be in the range of 1 to 10 years, corresponding to Class 3. It cannot be too strongly emphasized that this classification scheme is designed as part of a screening procedure, and is not meant in any manner to serve as a substitute for a determination of ODP based on an atmospheric model.

Table 4 gives the ranges of OH radical rate constants and of photolysis rate constants corresponding to the different classifications.

TABLE 4. CORRESPONDENCE BETWEEN TEST CLASSES AND THE RATE CONSTANT FOR REACTION WITH OH RADICALS AND FOR THE RATE CONSTANT FOR PHOTOLYSIS

Class	$k_{OH}, \text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$	$k_p, \text{s}^{-1}$
1	NA	NA
2	$>3 \times 10^{-14}$	$>3 \times 10^{-8}$
3	$3 \times 10^{-15} - 3 \times 10^{-14}$	$3 \times 10^{-9} - 3 \times 10^{-8}$
4	$<3 \times 10^{-15}$	$<3 \times 10^{-9}$

#### E. SUMMARY OF SCREENING TESTS AND CLASSIFICATION FOR HALONS 1211, 1301 and 1202, AND FOR TEST COMPOUND $\text{CH}_2\text{Br}_2$

Details of the screening test methods are given in Appendices B and C, while a description of the actual experimental measurements and detailed results are given in Appendix D. The results are summarized in Table 5.

Of the halons and selected test compounds treated in this report, only  $\text{CH}_2\text{Br}_2$  contains an abstractable H atom and is a candidate for using the estimation method for OH rate constant. The estimated rate constant and derived lifetime are given in Table 5. The lifetime corresponds to Class 2.

The experimental rate of decay of OH was measured in the presence of excess concentrations of test substances  $\text{CF}_3\text{Br}$  (halon 1301),  $\text{CF}_2\text{ClBr}$  (halon 1211), and for the selected test compound  $\text{CH}_2\text{Br}_2$ . First

TABLE 5. SUMMARY OF TEST RESULTS FOR RATE CONSTANT FOR REACTION WITH OH RADICALS, RATE CONSTANT FOR PHOTOLYSIS, DERIVED TROPOSPHERIC LIFETIME, AND CLASS ASSIGNMENTS<sup>a</sup>

Test Compound	$k_{OH}$ , est	$k_{OH}$ , meas	$k_a$ , meas	Summary Class
1211 CF <sub>2</sub> ClBr Rate Constant Lifetime Class	NA	(1.2±0.05)×10 <sup>-14</sup> 2.5 3	2.2×10 <sup>-9</sup> 13.6 4	3
1301 CF <sub>3</sub> Br Rate Constant Lifetime Class	NA	(1.8±1.5)×10 <sup>-15</sup> 17 4	<10 <sup>-11</sup> >3000 4	4
1202 CF <sub>2</sub> Br <sub>2</sub> Rate Constant Lifetime Class	NA	Not measured	2.3×10 <sup>-8</sup> 1.4 3	3
1002 CH <sub>2</sub> Br <sub>2</sub> Rate Constant Lifetime Class	7.5×10 <sup>-14</sup> 0.40 2	8.5×10 <sup>-11</sup> 0.36 2	8.5×10 <sup>-11</sup> 353 4	2
a.	Units for OH rate constants, cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup> , and for absorption rate constants, s <sup>-1</sup> . Lifetime in years.			

order hydroxyl radical decay curves were measured under different experimental conditions, first order rate constants derived, and finally, the second order rate constants were determined, as reported in Table 5.

For CF<sub>3</sub>Br (halon 1301) the measured decay rates lead to a second order rate constant, reported in Table 5, close to the minimum decay rate which can be measured using this apparatus. On this basis it would be classified as Class 4.

CF<sub>2</sub>ClBr (halon 1211) appears to be moderately reactive with OH, with a rate constant as reported in Table 5 of (1.2±0.05)×10<sup>-14</sup> cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1</sup>. However, we are certain that this measured value is incorrect, and that the true rate constant is much smaller, certainly less than 10<sup>-15</sup> cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1</sup>. Thus the classification should be Class 4 and not Class 3.

CH<sub>2</sub>Br<sub>2</sub> reacted rapidly with OH as reported in Table 6. The rate constant places CH<sub>2</sub>Br<sub>2</sub> in Class 2.

The results of the measurements of VIS-UV absorption cross section are summarized in Tables 6-8, and the derived lifetimes are summarized in Table 5.

Halon 1301, CF<sub>3</sub>Br, does not absorb strongly in the VIS-UV region and is clearly in Class 4. CH<sub>2</sub>Br<sub>2</sub> absorbs somewhat more strongly, but the rate constant for absorption derived from the absorption measurement is still small and the test compound is categorized as Class 4.

TABLE 6. ESTIMATION OF VIS-UV ABSORPTION RATE CONSTANT FOR DIBROMOMETHANE

Wavelength Interval, nm	Solar Flux, photons $\text{cm}^{-2} \text{s}^{-1}$	Average Absorption Coefficient, $\text{cm}^2 \text{molec}^{-1}$	Rate Constant, $\text{s}^{-1}$
Based on uncorrected data:			
290-295	$0.001 \times 10^{14}$	$1.1 \times 10^{-21}$	$1.1 \times 10^{-10}$
295-300	0.037	$1 \times 10^{-21}$	$3.7 \times 10^{-9}$
300-305	0.362	$1 \times 10^{-21}$	$3.6 \times 10^{-8}$
Total rate constant			$4 \times 10^{-8}$
Total rate constant/3			$1.3 \times 10^{-8}$
Based on extrapolation:			
290-295	$0.001 \times 10^{14}$	$7 \times 10^{-23}$	$7 \times 10^{-12}$
295-300	0.037	$2 \times 10^{-23}$	$7.4 \times 10^{-11}$
300-305	0.362	$3 \times 10^{-24}$	$1.1 \times 10^{-10}$
305-310	1.28	$5 \times 10^{-25}$	$6.4 \times 10^{-11}$
Total rate constant			$2.6 \times 10^{-10}$
Total rate constant/3			$8.5 \times 10^{-11}$

For halon 1211,  $\text{CF}_2\text{ClBr}$ , the absorption cross section is somewhat greater on the edge of the visible part of the solar spectrum, but the calculated lifetime reported in Table 5 indicates Class 4.

Halon 1202,  $\text{CF}_2\text{Br}_2$  absorbs well into the visible region and has an appreciable rate of absorption as shown in Table 5, putting it in Class 3.

The results are summarized in Table 5.

## F. CONCLUSIONS

In designing screening tests for ozone depletion potential, it has been established that the critical factors are the nature of the halogen substituents, if any, and the tropospheric lifetime of the test compound. The key elements for screening a candidate alternative fire suppressant for ozone depletion potential are:

- Grouping compounds in a manner to allow easy comparison of the tropospheric lifetimes of test compounds with those of other known ozone depleting substances such as the chlorofluorocarbons,
- Estimating tropospheric lifetime on the basis of the reactivity of the test compound with OH radicals, or of the rate of photolysis of the test compound in the atmosphere,

TABLE 7. ESTIMATION OF VIS-UV ABSORPTION RATE CONSTANT FOR DIFLUOROCHLOROBROMOMETHANE (HALON 1211)

Wavelength Interval, nm	Solar Flux, photons $\text{cm}^{-2} \text{s}^{-1}$	Average Absorption Coefficient, $\text{cm}^2 \text{molec}^{-1}$	Rate Constant, $\text{s}^{-1}$
Based on uncorrected data:			
290-295	$0.001 \times 10^{14}$	$1.1 \times 10^{-22}$	$1.1 \times 10^{-11}$
295-300	0.037	$8 \times 10^{-22}$	$3 \times 10^{-9}$
300-305	0.362	$5 \times 10^{-23}$	$1.8 \times 10^{-9}$
305-310	1.28	$2.8 \times 10^{-23}$	$3.6 \times 10^{-9}$
310-315	2.85	$1.8 \times 10^{-23}$	$5.1 \times 10^{-9}$
315-320	3.94	$1.5 \times 10^{-23}$	$7.4 \times 10^{-9}$
320-325	4.96	$1.3 \times 10^{-23}$	$6.5 \times 10^{-9}$
Total rate constant			$2.7 \times 10^{-8}$
Total rate constant/3			$9 \times 10^{-9}$
Based on extrapolation:			
290-295	$0.001 \times 10^{14}$	$1.1 \times 10^{-22}$	$1.1 \times 10^{-11}$
295-300	0.037	$6 \times 10^{-22}$	$2.2 \times 10^{-9}$
300-305	0.362	$3 \times 10^{-23}$	$1.1 \times 10^{-9}$
305-310	1.28	$1 \times 10^{-23}$	$1.3 \times 10^{-9}$
310-315	2.85	$4 \times 10^{-24}$	$1.1 \times 10^{-9}$
315-320	3.94	$1.5 \times 10^{-24}$	$6 \times 10^{-10}$
320-325	4.96	$4 \times 10^{-25}$	$2 \times 10^{-10}$
Total rate constant			$6.5 \times 10^{-9}$
Total rate constant/3			$2.2 \times 10^{-9}$

- Performing tests as recommended in Appendix A and in the decision tree of Figure 3, and
- Using the test procedures outlined in Appendices B and C to derive tropospheric lifetimes.

The grouping of compounds based on tropospheric lifetime is not meant to provide a basis for regulation, but rather a basis for comparison with other atmospheric trace gases. The suitability of a test compound is a function both of its ozone depletion potential and some factor related to its atmospheric burden or production rate. Those issues are not treated here.

TABLE 8. ESTIMATION OF VIS-UV ABSORPTION RATE CONSTANT FOR DIFLUORODIBROMOMETHANE (HALON 1202)

Wavelength Interval, nm	Solar Flux, photons $\text{cm}^{-2} \text{s}^{-1}$	Average Absorption Coefficient, $\text{cm}^2 \text{molec}^{-1}$	Rate Constant, $\text{s}^{-1}$
Based on extrapolation:			
290-295	$0.001 \times 10^{14}$	$2 \times 10^{-21}$	$2 \times 10^{-10}$
295-300	0.037	$5 \times 10^{-22}$	$1.8 \times 10^{-9}$
300-305	0.362	$2 \times 10^{-22}$	$7.2 \times 10^{-9}$
305-310	1.28	$2 \times 10^{-22}$	$2.6 \times 10^{-8}$
310-315	2.85	$8 \times 10^{-23}$	$2.3 \times 10^{-8}$
315-320	3.94	$6 \times 10^{-23}$	$4.9 \times 10^{-9}$
320-325	4.96	$1 \times 10^{-23}$	$2.1 \times 10^{-9}$
330-340	$1.5 \times 10^{15}$	$8 \times 10^{-25}$	$1.2 \times 10^{-9}$
Total rate constant			$6.8 \times 10^{-8}$
Total rate constant/3			$2.3 \times 10^{-8}$

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## APPENDIX A

### ORDER OF SCREENING TESTS FOR OZONE DEPLETION POTENTIAL

The order of testing for ozone depletion potential is designed to allow one to proceed in the most direct and economical fashion. The decision tree given in Figure 3, provides a summary of the decision elements discussed in this section.

The first consideration for any test compound is whether or not it contains Cl, Br, or I. If it contains none of these elements, then the compound is classified as Class 1. If the test compound contains Cl, Br or I, then the first quantity to be determined is rate constant with respect to reaction with OH. This should be estimated if possible, and measured only if estimation is impossible. From the rate constant one can estimate the lifetime. If the reaction with OH is slow, then the possibility of photolysis as a consequence of the absorption of VIS-UV solar radiation should be considered. If this is also unimportant, then the compound will have a long atmospheric lifetime.

The procedure to be followed in carrying out ozone-depletion potential screening tests is summarized below.

1. Does not contain Cl, Br, or I: Class 1.
2. Contains Cl, Br, or I: If saturated, containing only F, Cl, Br, or I substituents: unreactive - Class 4.  
If unsaturated C-C bonds (aliphatic or aromatic): very reactive - Class 2.  
If saturated, containing H: Go to 3.
3. If rate constant,  $k_{OH}$ , known: estimate lifetime,  $t_{OH}(\text{trop})$ .  
If not known: can  $k_{OH}$  be estimated?  
If yes: estimate  $k_{OH}$  and  $t_{OH}(\text{trop})$ .  
If no: measure  $k_{OH}$  and estimate  $t_{OH}(\text{trop})$ .
4. If  $t_{OH}(\text{trop}) < 1$  year: Class 2, no further tests.  
If  $t_{OH}(\text{trop}) > 1$  year: Class 3 or 4: Go to 5.
5. If absorbs in VIS-UV region: estimate lifetime,  $t_p(\text{trop})$ .  
If not known: measure absorption cross section and estimate  $t_p(\text{trop})$ .  
If  $t_p(\text{trop}) < 1$  year: Class 2.  
If  $t_p(\text{trop}) > 1$  year: Class 3 or 4.
6. Summary Class is lowest Class resulting from screening tests.

## APPENDIX B

### TEST PROTOCOLS FOR RATE CONSTANT OF REACTION WITH OH RADICALS

#### A. Estimation Using Group Values

The reactions of OH radicals are the most studied of all classes of gas-phase reactions, and as a result, there is a very large body of reliable kinetic data. Atkinson [12] has used this database to develop a group method for estimating OH radical rate constants for hydrogen atom abstraction. He also provides a basis for estimating rate constants for attack at double and triple C-C bonds, and attack at unsaturated aromatic sites. Examination of his database shows that the rate constants for the latter classes of reactions are all very fast compared to those for abstraction reactions, and all test compounds containing these structural units are classified as Class 2. The estimation method will be applied here only to saturated compounds having abstractable hydrogen atoms.

The basis for the Atkinson method is the separation of the molecule into defined structural units. The rate constants for  $-\text{CH}_3$ ,  $-\text{CH}_2-$ , and  $>\text{CH}-$  groups are dependent on the nature of the substituents alpha and beta to the group. In general, rate constants for the groups can be written as:

$$\begin{aligned}k(\text{CH}_3 - \text{X}) &= k'_p F(\text{X}), \\k(\text{Y}-\text{CH}_2 - \text{X}) &= k'_s F(\text{X})F(\text{Y}), \\k(\text{X} - \text{CH}(\text{Z}) - \text{Y}) &= k'_t F(\text{X})F(\text{Y})F(\text{Z}), \text{ and} \\k(\text{X}-\text{OH}) &= k'_{\text{OH}} F(\text{X}),\end{aligned}$$

where  $k'_p$ ,  $k'_s$ ,  $k'_t$ , and  $k'_{\text{OH}}$  refer to the rate constant for abstraction from nominal primary, secondary, tertiary, and hydroxyl groups, respectively, and the factors  $F(\text{X})$ ,  $F(\text{Y})$ , and  $F(\text{Z})$  are correction factors to account for the effects of substituent groups. Using values for group rate constants and correction factors tabulated by Atkinson and given in Table A1, rate constants for test compounds may be derived.

The method is best explained through example, and in Table A2 rate constants are calculated for representative compounds. The choice of groups and calculation of group values are shown.

#### B. Experimental Measurement of OH Rate Constant

In this report we describe one experimental approach to measuring OH rate constants, and in a later section apply the method to selected halons and a test compound. The experimental method is flash-photolysis resonance fluorescence (FPRF) [14,15]. This method is able to provide rate data for reactions of hydroxyl radicals over the range of rate constants of about  $10^{-14}$  to  $10^{-9}$   $\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ . It is an absolute rate measurement based on the rate of decay of OH radicals under first order conditions. It is a very precise, reliable, and commonly used method for the measurement of OH rate constants. Its major drawback is the need for very pure samples, or at least very pure samples with respect to impurities which are significantly more reactive than the test substrate (typical complicating impurities would be unsaturated compounds or compounds with many easily abstracted hydrogen atoms).

The flash-photolysis resonance fluorescence apparatus described here is being used at this time to measure rate constants for reactions of OH radicals with potential CFC replacement compounds under the

TABLE A1. GROUP RATE CONSTANTS AND SUBSTITUENT FACTORS FOR OH RATE CONSTANTS AT 298 K<sup>a</sup>

Group Rate Constants, $10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	
$k'_p=0.144$ $k'_s=0.838$ $k'_t=1.83$ $k'_{OH}=0.13$	
Substituent Group, X	Factor F(X)
-CH <sub>3</sub>	1.00
-CH <sub>2</sub> -	1.29
>CH-	1.29
>C<	1.29
-F	0.099
-Cl	0.38
-Br	≈0.30
-CH <sub>2</sub> Cl	0.57
-CHCl <sub>2</sub>	0.57
-CH <sub>2</sub> Br	≈0.57
-CCl <sub>3</sub>	≈0.083
-CH <sub>2</sub> F	≈0.85
-CHF <sub>2</sub>	≈0.10
-CF <sub>2</sub> Cl	≈0.025
-CF <sub>3</sub>	0.075
=O	8.8
-CHO	0.76
-C(O)-	0.76
-CH <sub>2</sub> C(O)-	4.4
>CHC(O)-	4.4
->CC(O)-	4.4
-C <sub>6</sub> H <sub>5</sub>	≈1.0
-OH	3.6
-O-	8.3
-C(O)OR	≈0.0
-OC(O)R	1.3
-CH <sub>2</sub> ONO <sub>2</sub>	0.34
>CHONO <sub>2</sub>	0.34
->CONO <sub>2</sub>	0.34
-ONO <sub>2</sub>	0.050
>C=C<	≤1
-C≡C-	≤1
-CN	0.14
-CH <sub>2</sub> CN	0.5
3 member ring	0.017
4 member ring	0.22
5 member ring	0.80
6 member ring	1.00
7 member ring	≈1.0

a. Adapted from reference 12.

AFEAS program. The experimental procedures proposed here for screening purposes are identical to those being used in the AFEAS program.

TABLE A2. EXAMPLES OF ESTIMATION OF OH RADICAL RATE CONSTANTS USING GROUP VALUES

Molecule	Groups and Factors	Rate Constant, $10^{-12}$ $\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$	$2k'_p\text{F}(-\text{CH}_2-) + 2k'_s\text{F}(-\text{CH}_3-)\text{F}(-\text{CH}_2-)$	2.5
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	$k'_s\text{F}(-\text{CH}_3-)\text{F}(-\text{CH}_2-) + k'_s\text{F}(-\text{OH})\text{F}(-\text{CH}_2-) + k'_{\text{OH}}\text{F}(-\text{CH}_2-) + k'_p\text{F}(-\text{CH}_2-)$	5.3
$\text{CH}_2\text{BrCH}_2\text{Br}$	$2k'_s\text{F}(-\text{CH}_2\text{Br})\text{F}(-\text{Br})$	0.29
$\text{CHF}_2\text{Br}$	$k'_t\text{F}(-\text{F})^2\text{F}(-\text{Br})$	0.0054
$\text{CHFCIBr}$	$k'_t\text{F}(-\text{F})\text{F}(-\text{Cl})\text{F}(-\text{Br})$	0.021
$\text{CHBr}_3$	$k'_t\text{F}(-\text{Br})^3$	0.049
$\text{CHCl}_2\text{Br}$	$k'_t\text{F}(-\text{Cl})^2\text{F}(-\text{Br})$	0.079

The apparatus, shown in Figure A1, consists of a stainless steel or glass cell (RX) surrounded by an outer wall between which fluid can be circulated to a temperature regulator (RL) to maintain a fixed temperature, measured by means of a thermocouple (TC). The cell has four window ports at 90° positions around the cell, and one additional window port on the base of the cell. The entire cell is mounted within a vacuum housing (VH). Gases can be admitted to the cell through inlets connected to a gas handling system (GHS). A hydroxyl radical resonance lamp (RL), consisting of a microwave powered (MG) discharge in 1 torr of a mixture of Ar saturated with water vapor, and a pulsed N<sub>2</sub> discharge flash lamp (FL), which is powered by discharge capacitors (DC) and a power supply (PS), are located at right angles to each other and to a photomultiplier detector (PM).

Hydroxyl radicals are produced by the flash photolysis of H<sub>2</sub>O. The OH radical resonance lamp was used in cw mode to excite a small fraction of the hydroxyl radicals which then emitted resonance radiation at 308 nm which was detected by the photomultiplier. The signal output was then fed to pulse counting electronics, and ultimately to a computer for signal averaging and subsequent statistical analysis and graphical display. The measurement process was initiated by a photocell (PC) which was triggered by the visible light from the flash lamp. A delay gate (DG) was used to introduce a delay time of 100 to 300 μs to eliminate any scattered light interference from the flash lamp. Fluorescence signal from 50 to 500 flashes were averaged to generate a suitable decay curve.

In a typical experiment, reaction mixtures containing the test compound, argon, and water vapor (prepared manometrically in a 5ℓ bulb before admission to the reaction cell) were flowed slowly through the cell (about 100 cm<sup>3</sup> s<sup>-1</sup>).

The quantity measured in this test is the rate of loss of OH radicals in the presence of a great excess of the test compound. Under these conditions, the rate expression can be written as:

TABLE A3. ESTIMATION OF VIS-UV ABSORPTION RATE CONSTANT<sup>a</sup>

Wavelength Interval, nm	Solar Flux, photons cm <sup>-2</sup> s <sup>-1</sup>	Average Absorption Coefficient, cm <sup>2</sup> molec <sup>-1</sup>	Rate Constant, s <sup>-1</sup>
290-295	0.0001 × 10 <sup>14</sup>		
295-300	0.037		
300-305	0.362		
305-310	1.28		
310-315	2.85		
315-320	3.94		
320-325	4.96		
325-330	7.14		
330-340	1.50 × 10 <sup>15</sup>		
340-350	1.61		
350-360	1.74		
360-370	2.07		
370-380	2.18		
380-390	1.99		
390-400	2.37		
400-410	3.26		
410-420	3.66		
420-440	7.34		
440-460	9.05		
460-480	9.81		
480-500	9.87		
500-520	9.78		
520-540	9.85		
540-560	9.65		
560-580	9.82		
580-600	1.0 × 10 <sup>16</sup>		
600-620	1.01		
620-640	1.01		
640-660	1.01		
660-680	1.01		
680-700	1.01		

a. For a zenith angle of zero, surface albedo zero, uncorrected for latitude or season. The quantum yield is taken as unity at all wavelengths. Adapted from reference 2.

$$-\frac{d(OH)}{dt} = k(OH)(S),$$

where OH is the concentration of OH radicals, S is the concentration of the test substance, k is the rate constant, and t is the reaction time. Under conditions where (OH) << (S), S is essentially constant, and the OH decay is first order, and the rate expression becomes:

where k' the apparent first-order rate constant, is obtained directly from a measurement of the exponential rate of decay of OH. The true rate constant is then:

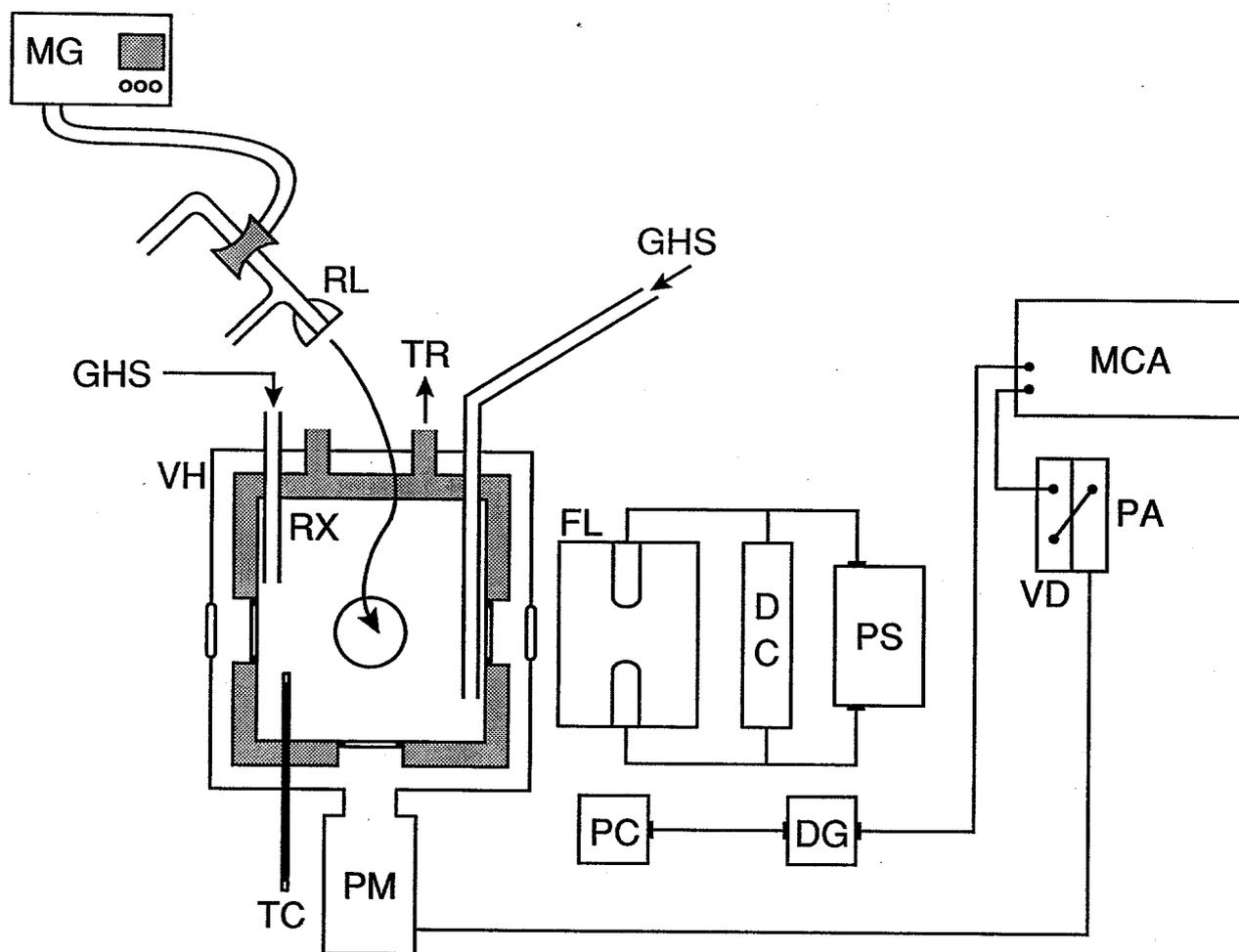


Figure A1. Apparatus for Measurement of OH Rate Constant.

$$\frac{-d(OH)}{(OH)} = k(S)dt = k'dt,$$

$$k = \frac{k'}{(S)}.$$

However, since there are OH diffusional losses from the reaction zone, in practice the first order decay is measured as a function of the concentration of the test compound, and from a plot of first order rate constant against concentration, the second order rate constant is obtained from the slope.

Tests for impurity effects must be included as part of the screening protocol. The effect of reactive impurities on test results can be illustrated by considering a test compound which has a rate constant for reaction with OH radicals of about  $1 \times 10^{-15} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ , corresponding to an atmospheric lifetime of 30 years, placing the compound in Class 4. If the test sample contains a 1 percent impurity in the form of an alkene, which typically may have a rate constant for reaction with OH of about  $1 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ , then the apparent OH rate constant would be about  $1 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ , corresponding to a lifetime of 3 years, placing the compound in Class 3. Purity is thus of great importance in carrying out these tests, and it would be desirable for the test compounds to have impurity levels for alkenes and other unsaturated compounds of less than about 0.1 percent. If the purity is not known, then the following test procedures should be adhered to:

- measure the rate constant
- if  $k < 3 \times 10^{-15} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ , the test results are acceptable
- if  $k > 3 \times 10^{-15} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ , check the test sample for impurities.

This can be done initially by carrying out a trap-to-trap distillation and then remeasuring the rate constant. If the rate constant goes down, the sample was impure, and an analysis is necessary. Only after analysis and, if necessary, purification, should additional measurements be undertaken.

## APPENDIX C

### TEST PROTOCOL FOR VIS-UV ABSORPTION CROSS SECTION

The experimental method described here is based on the use of a single beam monochromator [23]. This method provides an absorption spectrum suitable for estimating the tropospheric lifetime of a test compound with respect to photolysis assuming unit quantum efficiency with respect to dissociation.

The absorption cross section is defined as:

$$\sigma = - \left( \frac{1}{c\ell} \ln \left( \frac{I}{I_0} \right) \right),$$

where  $\sigma$  is the cross section at a given wavelength, (C) the concentration of absorbing test substance in molec  $\text{cm}^{-3}$ ,  $\ell$  the path length in cm, I the intensity of light passing through the cell containing the absorber, and  $I_0$  the intensity of light passing through the empty cell, both in arbitrary units. The test measurement thus involves measuring and ratioing the quantities I and  $I_0$ .

The apparatus is shown in Figure A2. It consists of a 1-meter incidence McPherson vacuum monochromator employing a 600 lines/mm grating blazed at 150 nm. The lamp shown in the figure is a Hamamatsu deuterium lamp with a highly stabilized power supply. This provided a convenient source of radiation over the 290 to 400 nm range. For measurements further into the red region of the spectrum, a tungsten lamp can be used. The detector is a Hamamatsu solar blind side-on multiplier tube. Five absorption cells having a range of path lengths ranging from 0.2 to 20 cm may be chosen by use of the turret assembly. The monochromator wavelength drive is controlled by a stepping motor with 800 steps per revolution. The gear train used is such that 16 pulses are equivalent to 0.1 nm wavelength change. Gas pressure in the cell is monitored with a diaphragm type gauge.

The signal from the photomultiplier tube, which is observed in real time during a measurement, is processed and fed to a controller interface module which is part of an IBM compatible personal computer system. A spectrum is first measured with no gas in the cell, then with an appropriate amount of gas in the cell, and finally with the cell again empty. The deuterium lamp is very stable, and this procedure leads to a very reliable measurement of the adsorption cross section down to about  $10^{-23} \text{ cm}^2$ .

The procedure is to measure the absorption cross section over the range 290 to 700 nm using the definition of absorption cross section given above. The absorption cross section as a function of wavelength is then related to photolysis rate constant using procedures outlined by Finlayson-Pitts and Pitts [2], who also give example calculations. Table A3 provides the required auxiliary data and the format for making the rate constant calculations.

The experimentally measured absorption cross section is averaged over discrete wavelength intervals as specified in Table A3 (which should be copied and used as a worksheet). Over the same intervals, Table A3 provides values of the solar flux, corresponding to a cloudless day, zenith angle of  $0^\circ$ , surface albedo zero, uncorrected for latitude or season. For each discrete spectral region the rate of absorption is calculated as the product of Columns 2 and 3, and the result entered into Column 4. The summation of Column 4 then gives the total rate of absorption. This is an upper limit to the number of photons absorbed. Following Molina and coworkers [20], it is recommended that the maximum rate of absorption be divided by 3 to provide

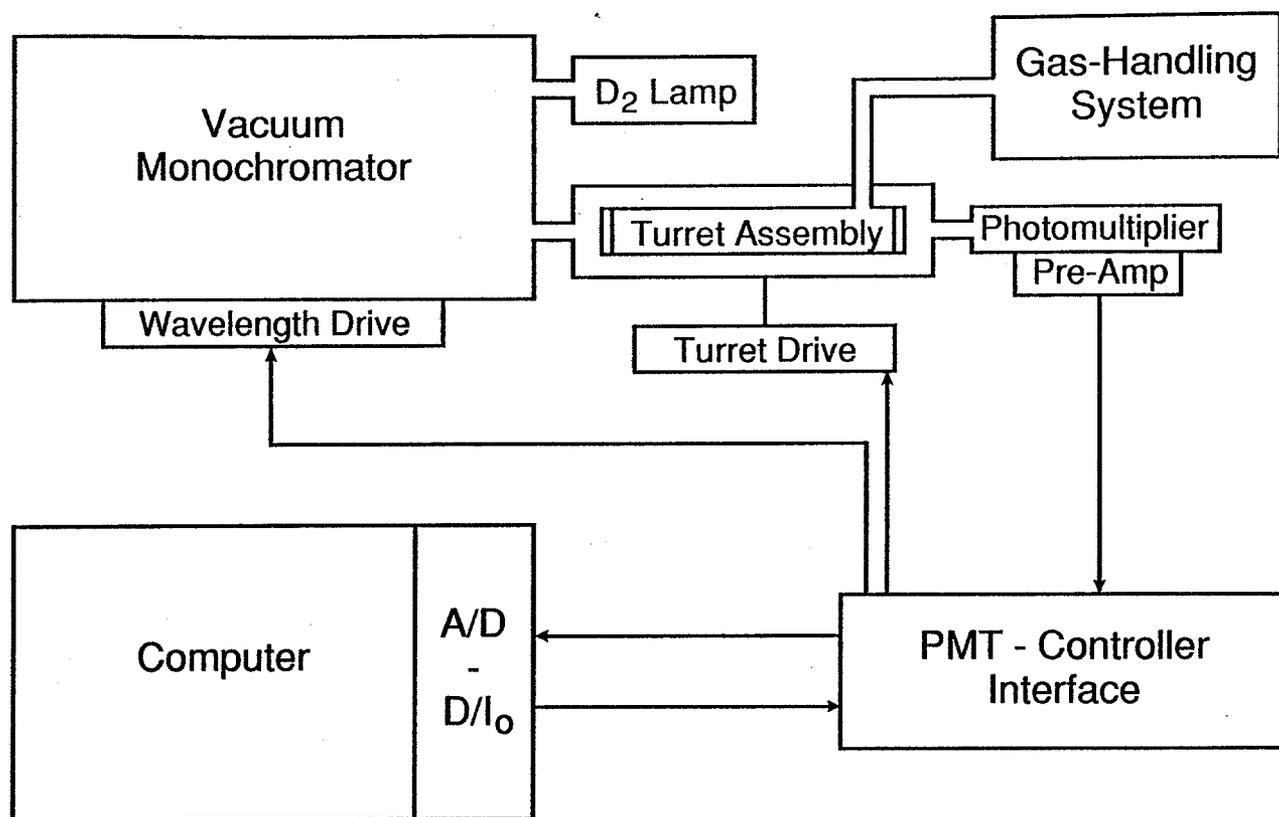


Figure A2. Apparatus for Measurement of Absorption Cross Section.

a more realistic estimate of the average atmospheric absorption rate. This absorption rate constant is an upper limit to the true rate constant for photolysis:

$$k_p \leq k_a.$$

The problem of test sample purity is of concern here as well as with respect to OH reactivity. Low levels of a strongly absorbing impurity will give an incorrect set of cross section results. Therefore, if the purity is not known, the following test procedures should be adhered to:

- measure the absorption cross section as a function of wavelength, and calculate  $k_p$
- if  $k_p < 3 \times 10^{-9} \text{ s}^{-1}$ , the test results are acceptable
- if  $k_p > 3 \times 10^{-9} \text{ s}^{-1}$ , check the test sample for impurities.

This can be done initially by carrying out a trap-to-trap distillation and then remeasuring the absorption cross section. If the absorption cross section changes significantly, the sample was impure, and an analysis is necessary. Only after analysis and if necessary, purification, should additional measurements be undertaken.

Finally, it must be emphasized that the test value derived for lifetime with respect to photolysis provides only a lower limit to the true lifetime, and if the quantum yield is low, the test compound could have a much longer lifetime.

## APPENDIX D

### RESULTS OF SCREENING TESTS FOR HALONS 1211, 1301 AND 1202, AND FOR TEST COMPOUND CH<sub>2</sub>Br<sub>2</sub>

#### A. Estimation of OH Rate Constant

The method is discussed in Appendix B, Part A, and illustrated in Table A1. Of the halons and selected test compounds treated in this report, only CH<sub>2</sub>Br<sub>2</sub> contains an abstractable H atom. The groups, factors, and rate constant calculation are as follows:

$$k = k'_2 \times F(-Br) \times F(-Br) \times 1 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \text{ or}$$
$$k = (0.838) \times (0.3) \times (0.3) \times (1 \times 10^{-12}) = 7.5 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}.$$

This rate constant puts the test compound in Class 2.

#### B. Measurement of OH Rate Constant

The rate of decay of OH was measured in the presence of excess concentrations of test substances CF<sub>3</sub>Br (halon 1301), CF<sub>2</sub>ClBr (halon 1211), and for the selected test compound CH<sub>2</sub>Br<sub>2</sub>. Representative first order hydroxyl radical decay curves are given in Figures A3-A5 for the three test compounds under different experimental conditions as specified in the figure captions. From each decay curve, a first order rate constant is derived as shown in Table A4. These in turn are plotted as shown in Figures A6-A8, and from the slopes of these plots, the second-order rate constants are derived as shown in Table 5.

For CF<sub>3</sub>Br the rate of reaction was essentially the same as the limiting minimum decay rate which can be measured using this apparatus of about  $1 \times 10^{-15} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ , classifying CF<sub>3</sub>Br as Class 4.

In the case of CH<sub>2</sub>Br<sub>2</sub>, there is a measurable decay rate as can be seen from Figures A5 and A8. The rate constants calculated from this decay rate are reported in Tables A4 and 5.

CF<sub>2</sub>ClBr presents a problem, since as can be seen from Table 5, it appears to react at an appreciable rate. The existing data [10] on fully halogenated methanes indicate that this compound should be no more reactive than CF<sub>3</sub>Br, and we attribute the excess rate to impurities in the sample which could be removed with additional purification. The classification of this compound as Class 3, based on the measurements reported here, is almost certainly wrong. The correct Class is 4. This is an excellent illustration of the effect of impurities on test results.

#### C. Measurement of VIS-UV Absorption Cross Section

The results of the measurements of the VIS-UV absorption cross sections are shown in Figures A9-A11. The experimental conditions are specified in the figure captions. These curves illustrate the problems inherent in the measurement of very small absorption cross sections.

TABLE A4. FIRST ORDER RATE CONSTANTS FOR THE REACTIONS OF OH RADICALS WITH DIFLUOROCHLOROBROMOMETHANE (HALON 1211), TRIFLUOROBROMOMETHANE (HALON 1301) AND DIBROMOMETHANE AS FUNCTIONS OF CONCENTRATION AT 298 K

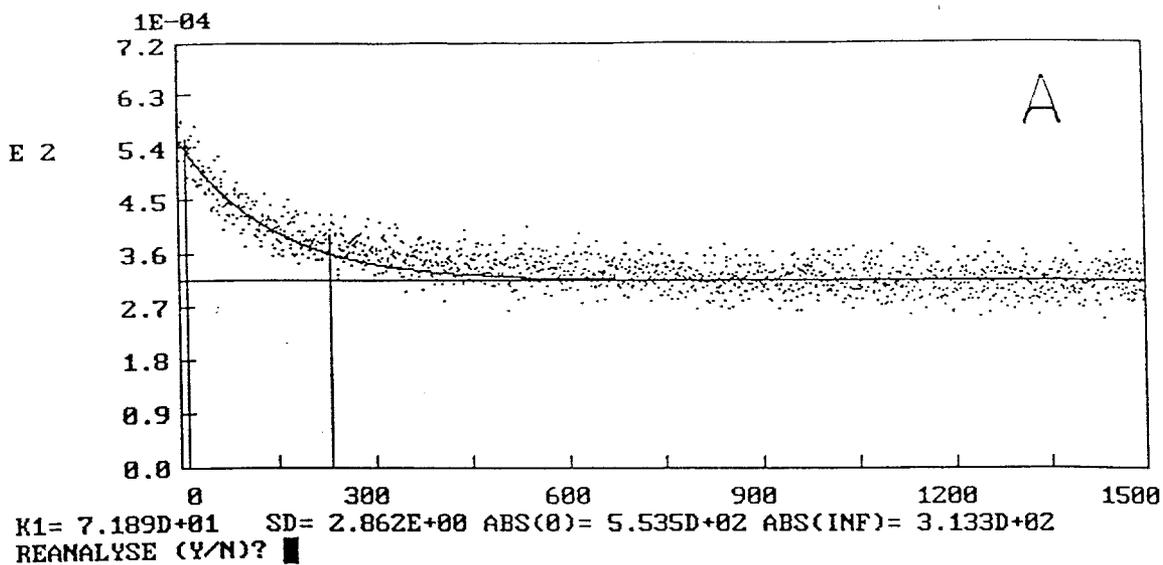
Concentration, mtorr <sup>a</sup>	First order rate constant, s <sup>-1</sup>		
	CF <sub>3</sub> Br	CF <sub>2</sub> ClBr	CH <sub>2</sub> Br <sub>2</sub>
49.7			348
49.7			317
49.7			351
49.7			353
100			490
100			510
100			447
100			473
250	82	166	
250	72	186	
250	64	185	
250		184	
500	79	277	
500	81	281	
500	89	254	
500	93		
No reactant present: 68 and 70 s <sup>-1</sup> .			
a. 1 mtorr=3.2×10 <sup>13</sup> molec cm <sup>-3</sup> at 298 K.			

For halon 1211, CF<sub>2</sub>ClBr, the absorption cross section varies almost exponentially with wavelength as can be seen from Figure A9. This is typical for the halocarbons (and many other classes of compounds). At very low absorbencies, the curve begins to flatten out, suggesting the presence of low levels of some unknown impurity. To gauge the consequences of impurity contamination, we have carried out rate constant calculations using the uncorrected absorption data, and for data obtained by extrapolation of the data as indicated by the dashed curve of Figure A9. The average absorption cross sections taken from the figure for the two possible sets of curves were then used to calculate rate constants for absorption using the format of Table A3. The results of the calculations are given in Table 7. We have not attempted to extend the calculations beyond 325 nm, since the experimental data are in error at this point. The uncorrected data lead to an estimated absorption rate constant a factor of 4 greater than the more correct extrapolated value. The latter value is reported in Table 5.

Halon 1301, CF<sub>3</sub>Br, does not absorb strongly in the VIS-UV region as shown in Figure A9, and the rate of absorption is too small to be of any significance.

Halon 1202, CF<sub>2</sub>Br<sub>2</sub>, for which the absorption curve is shown in Figure A10, absorbs relatively strongly into the visible part of the spectrum. The rate constant for absorption, based on extrapolation of the absorption curve, is calculated in Table 8, and the results given in Table 5.

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AV.OF 200 FLASHES



mcs04-24.006 ORIGINAL FILE = B:0424G2.MCS  
AV.OF 200 FLASHES

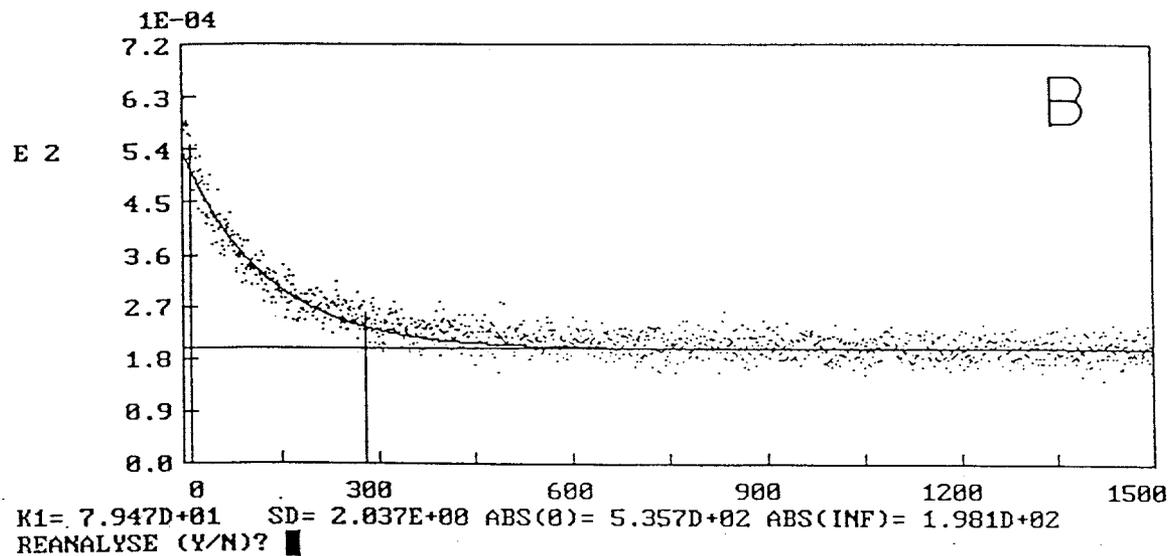
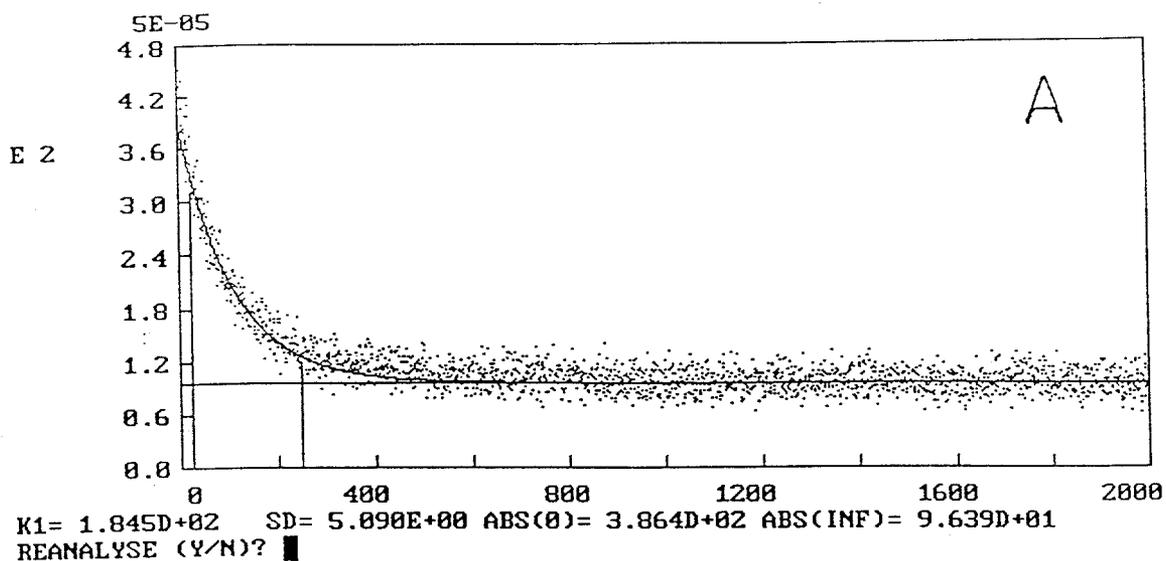


Figure A3. Decay of OH Resonance Fluorescence Signal in the Presence of Trifluorobromomethane (halon 1301). A: 250 mtorr CF<sub>3</sub>Br. B: 500 mtorr CF<sub>3</sub>Br.

mcs04-20.005 ORIGINAL FILE = B:0420C3.MCS  
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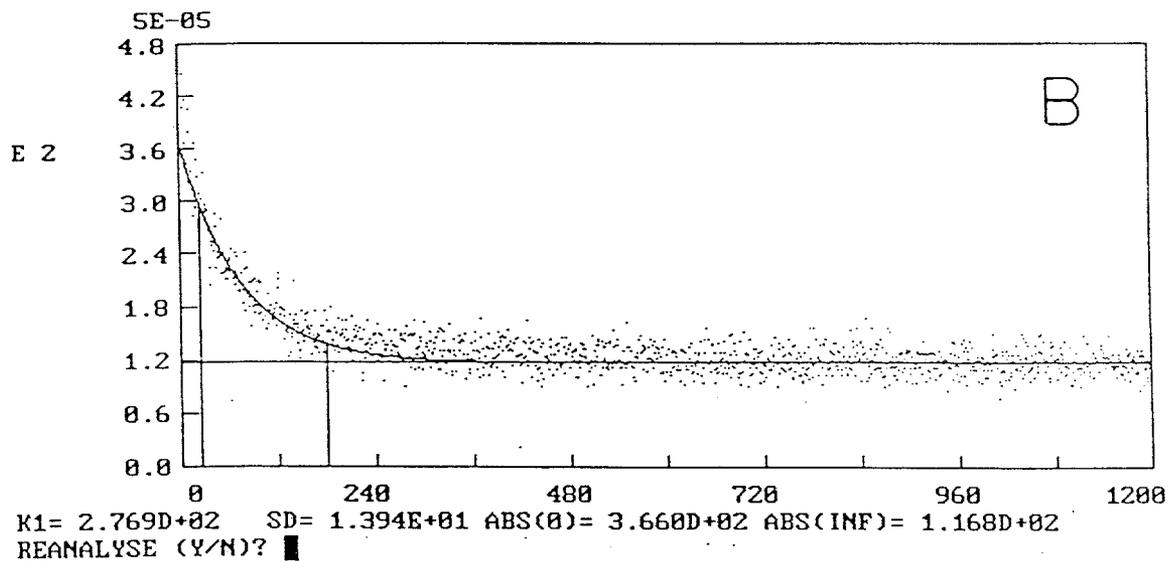
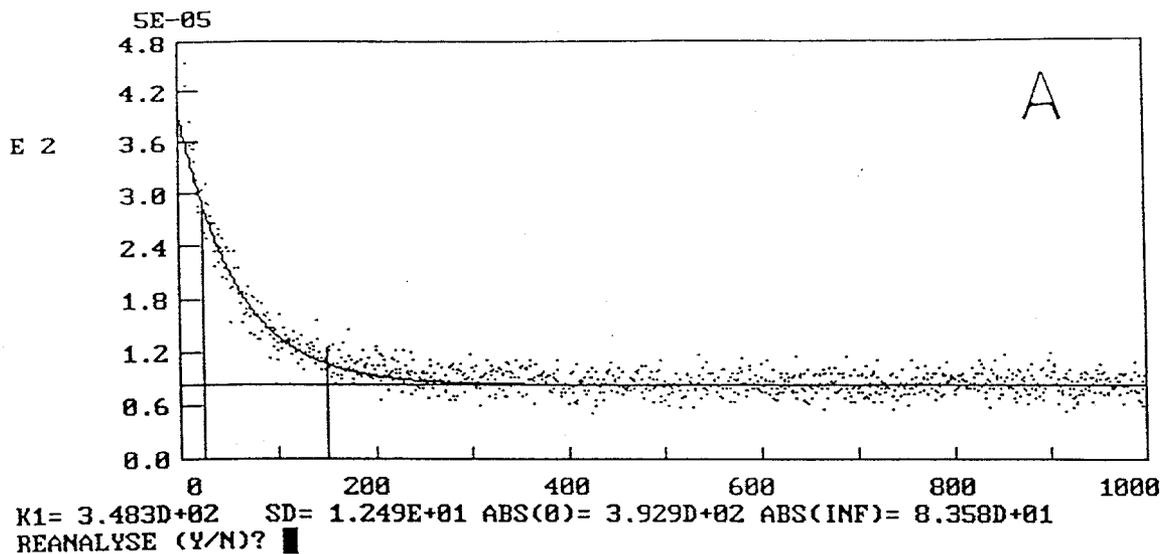


Figure A4. Decay of OH Resonance Fluorescence Signal in the Presence of Difluorochlorobromomethane (halon 1211). A: 250 mtorr  $\text{CF}_2\text{ClBr}$ . B: 500 mtorr  $\text{CF}_2\text{ClBr}$ .

mcs04-25.001 ORIGINAL FILE = B:0425C1.MCS  
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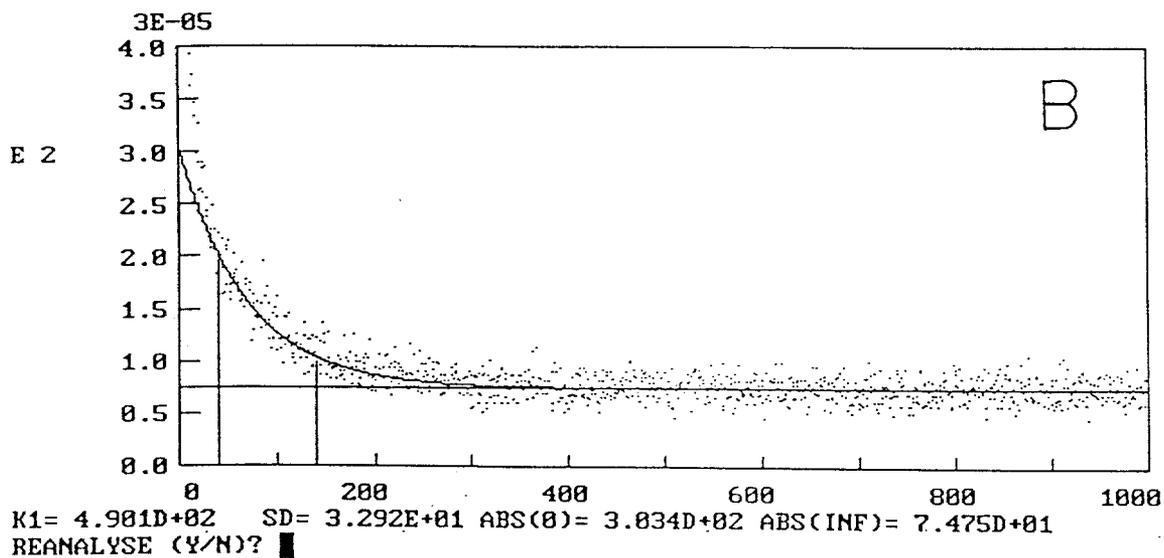


Figure A5. Decay of OH Resonance Fluorescence Signal in the Presence of Dibromomethane. A:  $\text{CH}_2\text{Br}_2$ , 49.7 mtorr. B:  $\text{CH}_2\text{Br}_2$ , 100 mtorr.

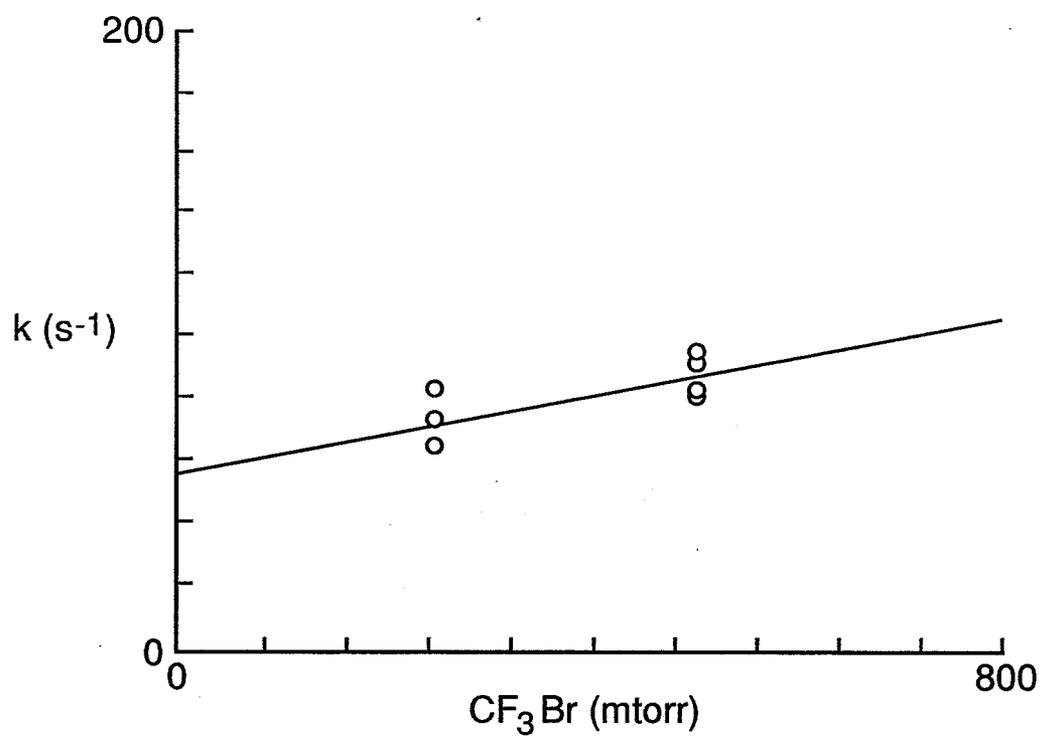


Figure A6. Plot of the First-Order Rate Constant for the Decay of OH Against the Concentration of Trifluorobromomethane (halon 1301)

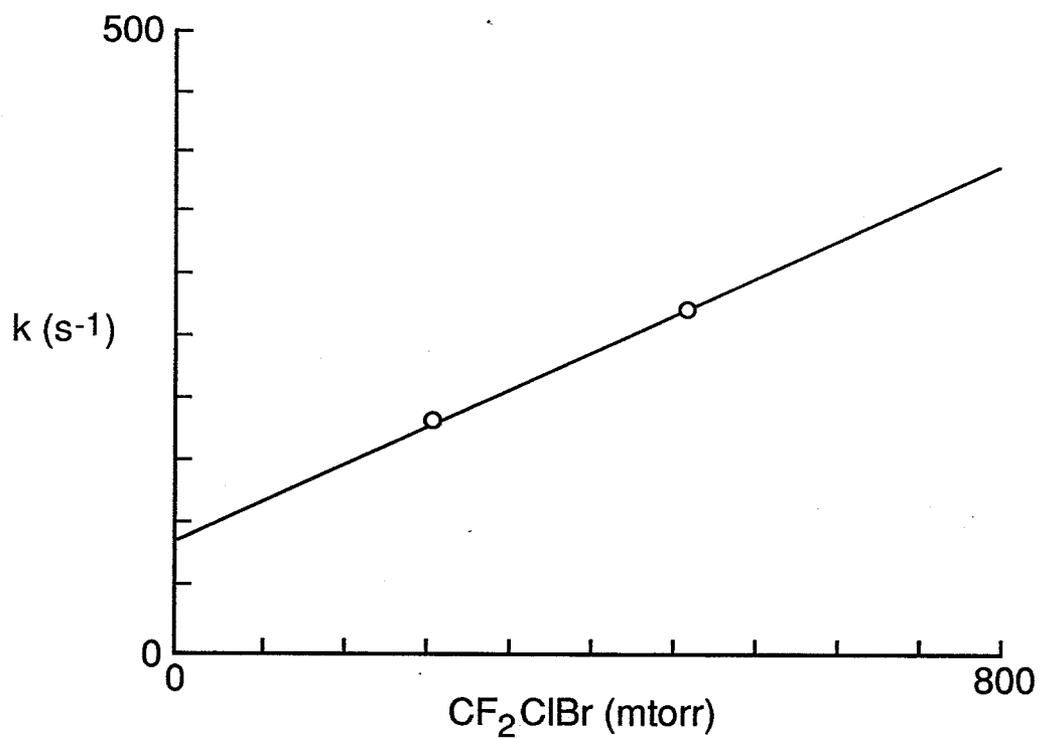


Figure A7. Plot of the First-Order Rate Constant for the Decay of OH Against the Concentration of Difluorochlorobromomethane (halon 1211).

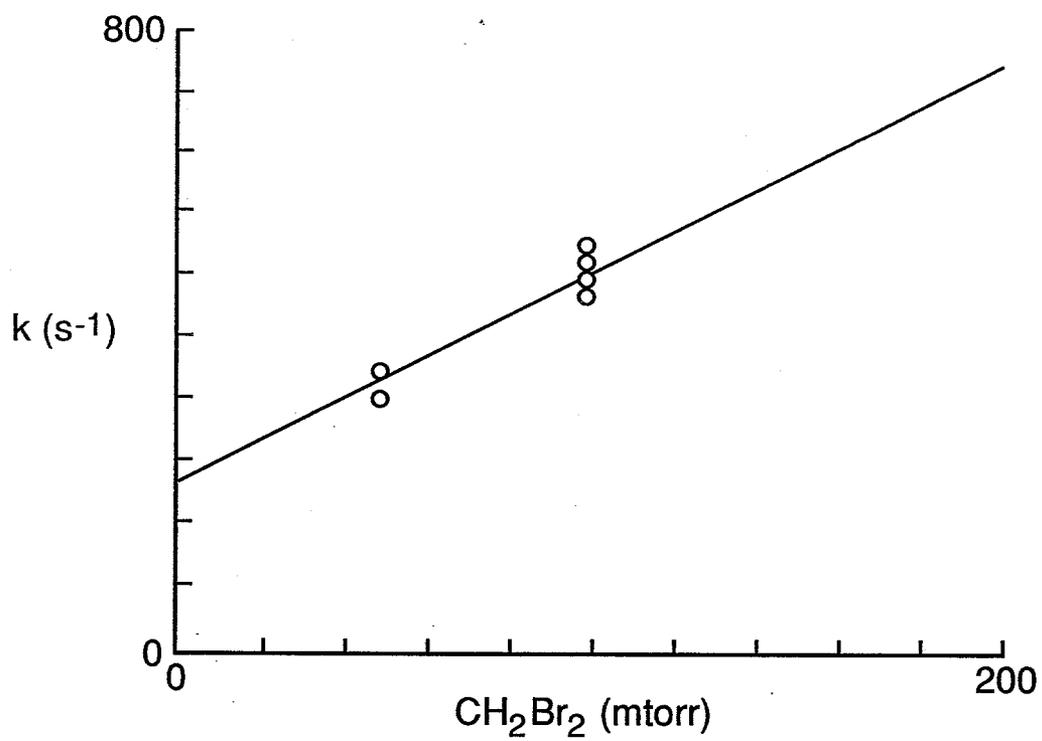


Figure A8. Plot of the First-Order Rate Constant for the Decay of OH Against the Concentration of Dibromomethane.

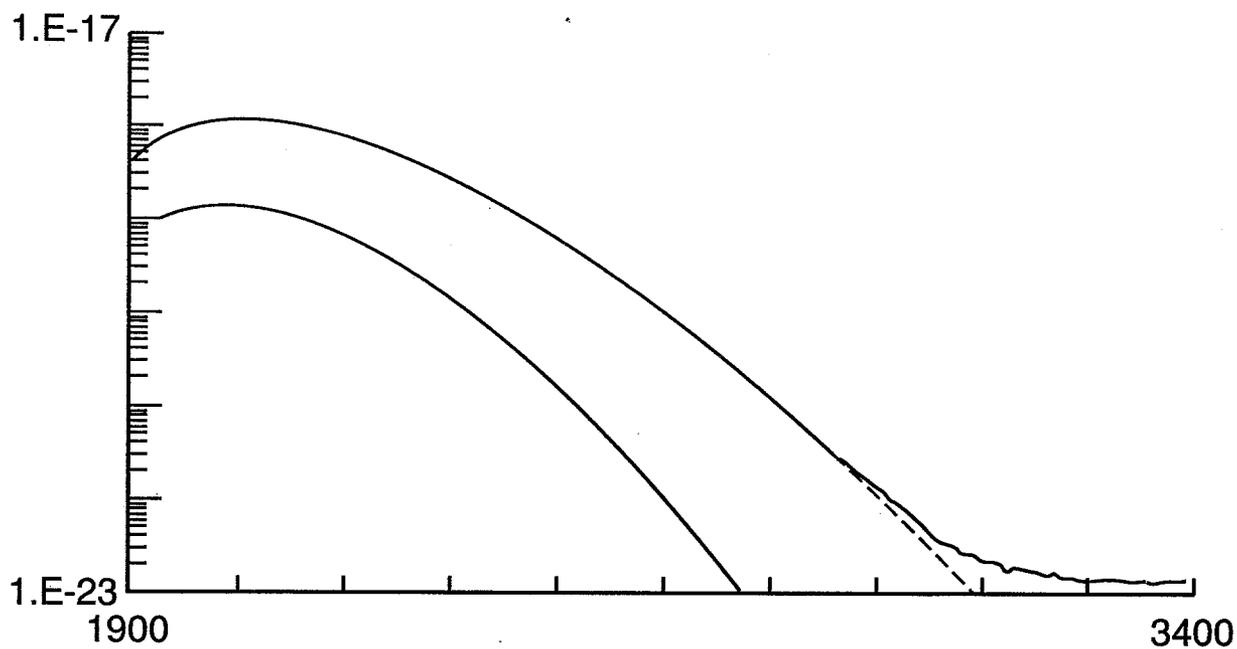


Figure A9. VIS-UV Absorption Cross Section as a Function of Wavelength for Difluorochlorobromomethane, Upper Curve, and Trifluorobromomethane, Lower Curve. For Halon 1211, Path Length 20 cm, Sample Pressure 15-418 Torr.

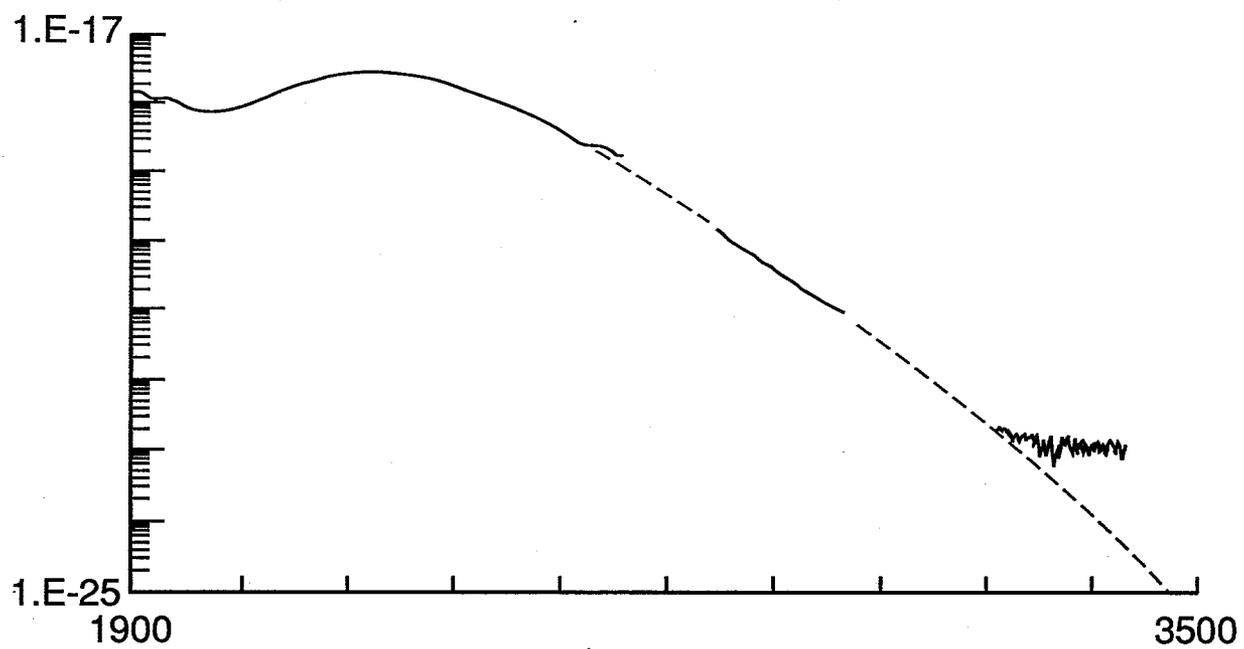


Figure A10. VIS-UV Absorption Cross Section as a Function of Wavelength for Difluorodibromomethane. Path Length 20 cm, Sample Pressure 5-706 torr.

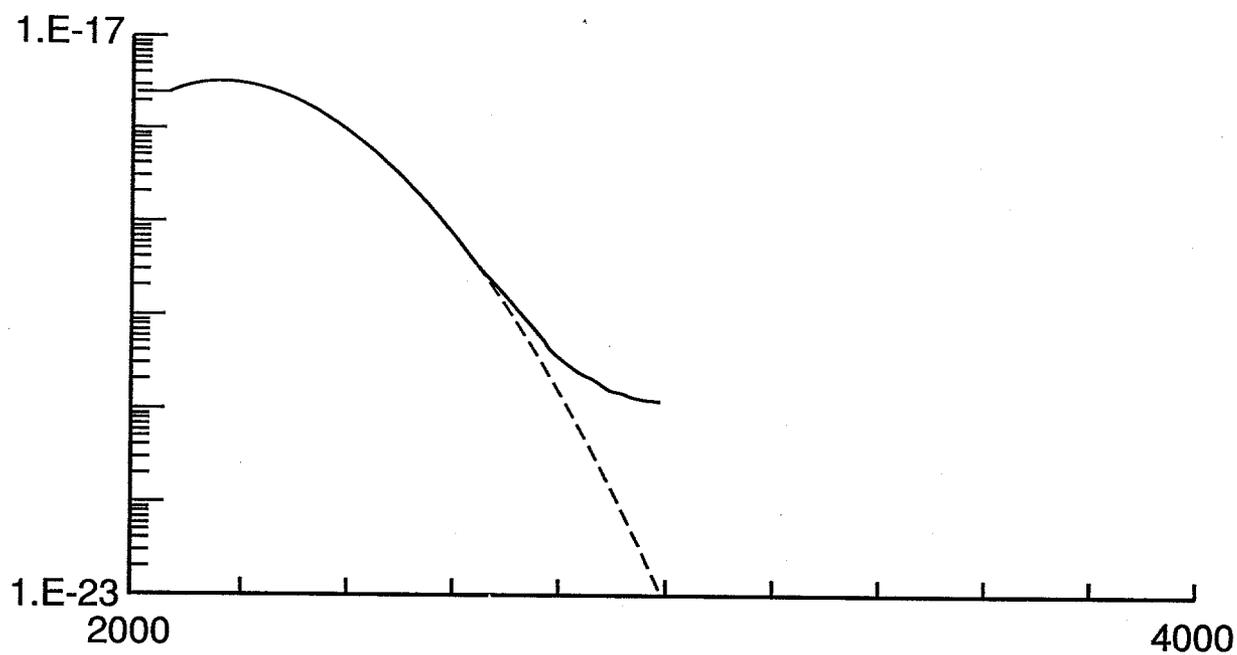


Figure A11. VIS-UV Absorption Cross Section as a Function of Wavelength for Dibromomethane. Path Length 20 cm, Sample Pressure 2-34 torr.

$\text{CH}_2\text{Br}_2$  is similar to  $\text{CF}_2\text{ClBr}$  in displaying an exponential fall-off in absorption with wavelength as shown in Figure A11, with a long tail extending into the visible, suggestive of the presence of an impurity. The data are analyzed in Table 6. The uncorrected data lead to an estimated absorption rate constant a factor of 150 greater than the more correct extrapolated value. The latter value is reported in Table 5.

#### D. Summary of Screening Test Results

The results are summarized in Table 5, where the summary group is based on the shortest lifetime derived from any of the test methods. All of the compounds tested here contained Cl or Br and therefore belonged in Classes 2, 3, or 4. The test results indicate that the halons belong to Class 3 or 4, and the selected test compound,  $\text{CH}_2\text{Br}_2$ , to Class 2. Note, however, the comments in Appendix D.B regarding the OH rate data for  $\text{CF}_2\text{ClBr}$ , which we interpret as a consequence of the presence of reactive impurities in the sample. Thus the classification of this compound as Class 3, should be changed to Class 4.

**SECTION V**  
**GLOBAL WARMING POTENTIAL**

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## SECTION V

### GLOBAL WARMING POTENTIAL

#### SECTION SUMMARY

Global warming may be enhanced by the presence of atmospheric trace gases which are capable of absorbing infrared radiation originating from the earth-atmosphere system. There is no direct measurement method for determining the contribution of a chemical to global warming. At present, such a determination is made using complex atmospheric modeling and specific input data for the chemical under consideration. The pertinent principles are as follows:

- Global warming potential is directly related to the capability of a test compound to absorb radiation in the region of the "atmospheric window" between 7 and 13  $\mu\text{m}$ . Test compounds which are weak absorbers in this region are unimportant with regard to global warming.
- Global warming potential is directly related to the lifetime of a test substance in the atmosphere. The greater the lifetime, particularly within the troposphere, the greater the potential for adverse effects on global temperature. Tropospheric lifetime is determined by physical and chemical factors, the most important of which are the reactivity with respect to OH radicals and absorption of solar radiation in the VIS-UV region of the solar spectrum.

Test methods are provided for determining the tropospheric lifetime of test substances based on the estimation or measurement of reactivity with hydroxyl radicals (OH) and the measurement of absorption cross sections in the VIS-UV region, and for measuring the absorption cross section in the region of the atmospheric window.

On the basis of their estimated lifetimes in the troposphere, and the degree to which they absorb IR in the window region, test compounds may be grouped as follows:

Class 1: Weak absorbers and/or lifetimes less than 30 years.

Class 2: Strong absorbers with lifetimes greater than 30 years.

Since many halogen-containing compounds are expected to be strong absorbers, and the same may be true of other classes of potential replacement compounds, the controlling factor is lifetime.

The proposed test methods are applied to the halons 1301, 1211, and 1202, and to a selected test compound,  $\text{CH}_2\text{Br}_2$ . The test results place halon 1301 in Class 2, and halons 1211, 1201, and the selected test compound,  $\text{CH}_2\text{Br}_2$ , in Class 1.

These methods are research tools and must be performed and interpreted by a senior scientist. After determining the ODP Class, assessment of GWP Class adds less than 1 day, uses only about 0.1 mole of chemical, and costs approximately \$500-2,000 plus the cost of the chemical. This presumes the chemical is free of impurities that might affect the results.

It must be emphasized that the interpretation of atmospheric phenomena and the design of screening tests are based on our current knowledge of the properties and processes which control the temporal history

and distribution of atmospheric trace species. At some future time, advances in atmospheric science may lead to modifications of the screening tests provided here.

## **A. BACKGROUND**

### **1. Introduction**

The release into the atmosphere of compounds containing halogens can lead to a decrease in the stratospheric levels of ozone and a change in global mean temperature. The effects are closely related, and their quantitative assessment ultimately must be based on detailed modeling studies of the atmosphere.

The problem presented by the halon family of fire suppressants is essentially the same as that for the chlorofluorocarbons (CFC's) and related gases. Both classes of compounds are covered under the Montreal Protocol.

An active program is under way to find replacements for the CFC's, the Alternative Fluorocarbon Environmental Acceptability Study (AFEAS), and various test procedures have been developed under that program which have direct application to the halon replacement program [1]. The approach and nomenclature of that program are adopted here.

Although ozone-depletion potential and global-warming potentials are being treated separately, the effects are interrelated, and test programs should be carried out in concert. A decision tree is provided to permit testing programs to be executed rationally and economically.

### **2. The "Greenhouse" Effect**

The greenhouse effect [2-5] can be best described in terms of the radiative balance of the earth-atmosphere system. This is established by comparing the incoming solar radiation in the visible and ultraviolet (UV) portion of the solar spectrum with the outgoing radiation from the earth's surface and atmosphere which is primarily in the infrared (IR) region. This is illustrated in Figure 1. In the simplest terms, it is usually stated that visible solar radiation is absorbed by the earth's surface and re-radiated to space in the infrared, mostly at wavelengths greater than  $4\mu\text{m}$  (longwave infrared). If gases capable of absorbing infrared radiation are present in the atmosphere, then some of this energy is trapped in the atmosphere and leads to an increase in temperature of the earth-atmosphere system. The classic greenhouse gas is  $\text{CO}_2$ , but it is now known that many other trace gases such as the halogen compounds, are even more effective than  $\text{CO}_2$  on a molecule per molecule basis, in promoting the greenhouse effect. The processes which control the heat balance of the system are much more complex than this simple picture indicates, and one must take into account other features such as heating caused by direct absorption of solar radiation in the atmosphere, scattering, convection, overlap of absorption bands, etc. The main point is that the earth radiates as a black body at an average temperature of about 288 K, some of this radiation is absorbed by atmospheric gases, which then re-radiate energy at the lower temperature of the atmosphere. The difference goes into heating the earth-atmosphere system.

The main absorbers of outgoing infrared radiation include  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2\text{O}$ , and  $\text{CH}_4$ . The thermal emission spectrum of the earth above the atmosphere is shown in Figure 2. There is a so-called window region between about 7 to 13  $\mu\text{m}$  ( $800$  to  $1400\text{ cm}^{-1}$ ) in which the atmosphere is relatively transparent to outgoing longwave infrared radiation. However, this corresponds to a region in which many halogen-containing compounds absorb infrared radiation. Any halon or proposed halon replacement which has a long atmospheric lifetime and absorbs in the window region, will contribute to the greenhouse effect.

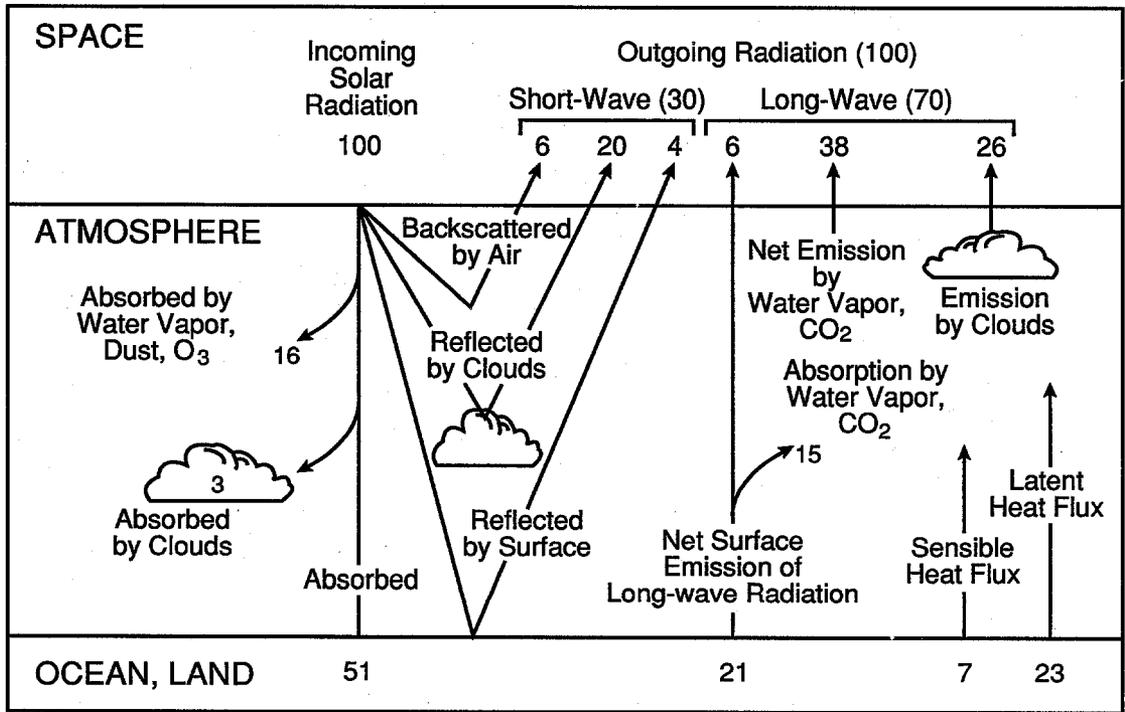


Figure 1. Radiation Budget of the Earth-atmosphere System. From Reference 28.

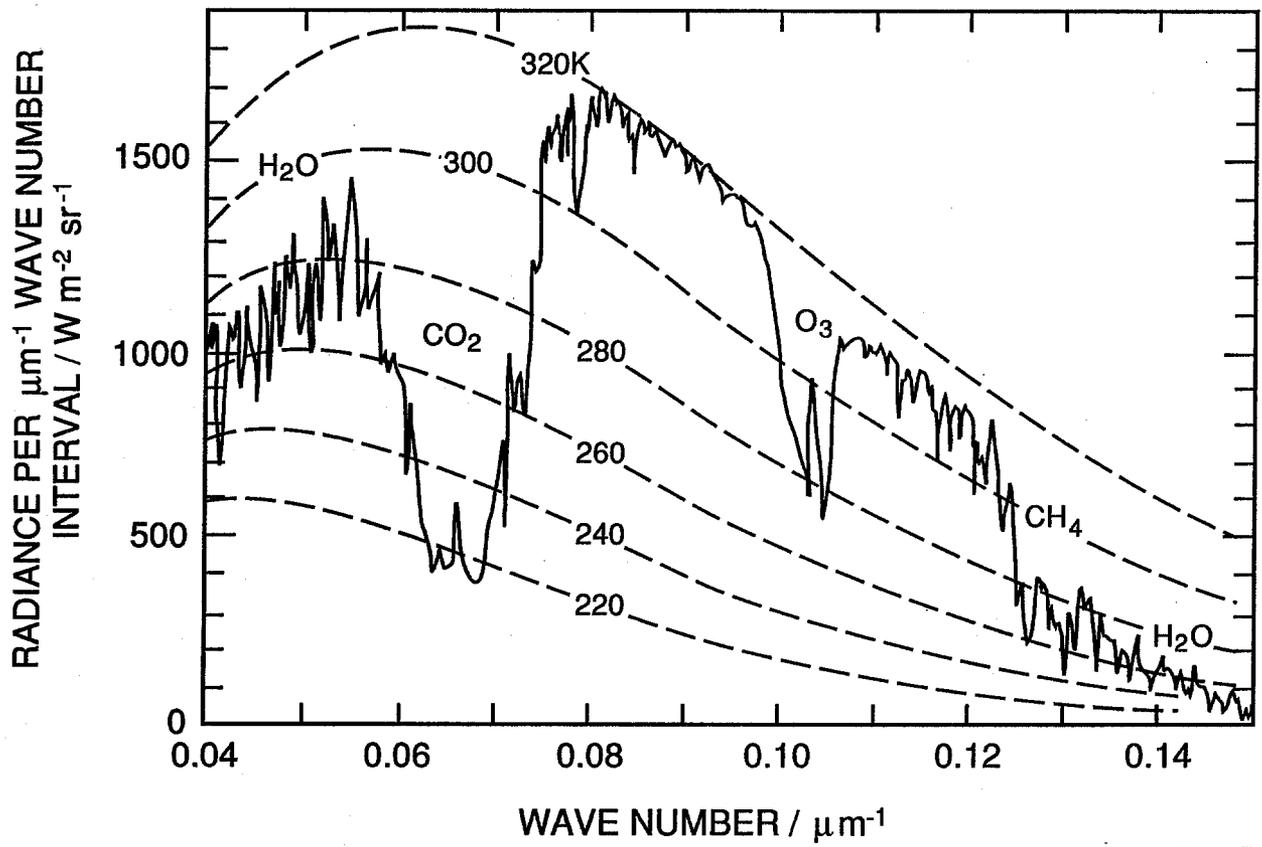


Figure 2. Infrared Emission Spectrum of the Earth. From Reference 29.

### 3. Global Warming Potential

Following Fisher and coworkers [6], global warming potential (which they derived specifically with reference to the halocarbons and designated as HGWP) may be defined as:

"The ratio of calculated warming for each unit mass of a gas emitted into the atmosphere relative to the calculated warming for a mass unit of reference gas CFC 11".

$$\text{GWP} = \frac{\text{calculated IR forcing due to compound X}}{\text{steady state emission rate of compound X}} \div \frac{\text{calculated IR forcing due to CFC 11}}{\text{steady state emission rate of CFC 11}}$$

This is a calculated quantity based on the use of a detailed atmospheric model. Details may be found in the literature. In this chapter, we will describe test methods which allow one to make a qualitative estimate of global warming potential without the use of a full scale modeling calculation.

### 4. Atmospheric Lifetime, Infrared Absorption, and Global Warming Potential

The factors which determine global warming are the lifetime of an atmospheric gas and its absorption cross section in the region of the "atmospheric window." If a substance has a very short lifetime and is a weak absorber in the 7 to 13  $\mu\text{m}$  region, then it does not contribute significantly to global warming. For those compounds which absorb radiation strongly in the window region, GWP is related to atmospheric lifetime. Figure 3 compares calculated values of GWP with calculated atmospheric lifetimes of greenhouse gases. There is a clear and simple correlation between the two quantities. The correlation is not quantitative since it is based on the fact that all of the species for which data are reported in the figure are strong absorbers in the atmospheric window region of the spectrum. Nonetheless, the correlation provides a basis for simple test methods to estimate the potential for climate modification due to proposed halon replacements.

The test methods are designed to provide data which can be used to estimate the lifetime of a test compound in the troposphere, and to evaluate its potential as an absorber of IR radiation in the atmospheric window. Appendix A provides procedures for carrying out the tests in the most economical manner and with particular reference to the corresponding tests for ozone depletion potential. This is further illustrated by means of the decision tree shown in Figure 4.

## B. CHEMICAL FACTORS CONTROLLING TROPOSPHERIC LIFETIME

The lifetime of a trace atmospheric substituent is controlled almost entirely by the rate of reaction with OH radicals, the rate of photolysis, and the rate of reaction with  $\text{O}^1\text{D}$ .

Reaction with OH radicals is the principal loss process for most trace pollutants, particularly in the troposphere. If the reaction is very slow, then the substance has such a long tropospheric lifetime that it enters the stratosphere, and its overall lifetime is then determined by processes taking place there. In general, OH reactions are important only if there are abstractable H atoms available, or the test compound has unsaturated C-C bonds (aromatic or aliphatic). Fully halogenated alkanes are unreactive with respect to OH radicals.

Photolysis is the next most important loss mechanism, and the most important in the stratosphere. This is the mechanism whereby most CFC's and halons are destroyed in the atmosphere by absorption of solar

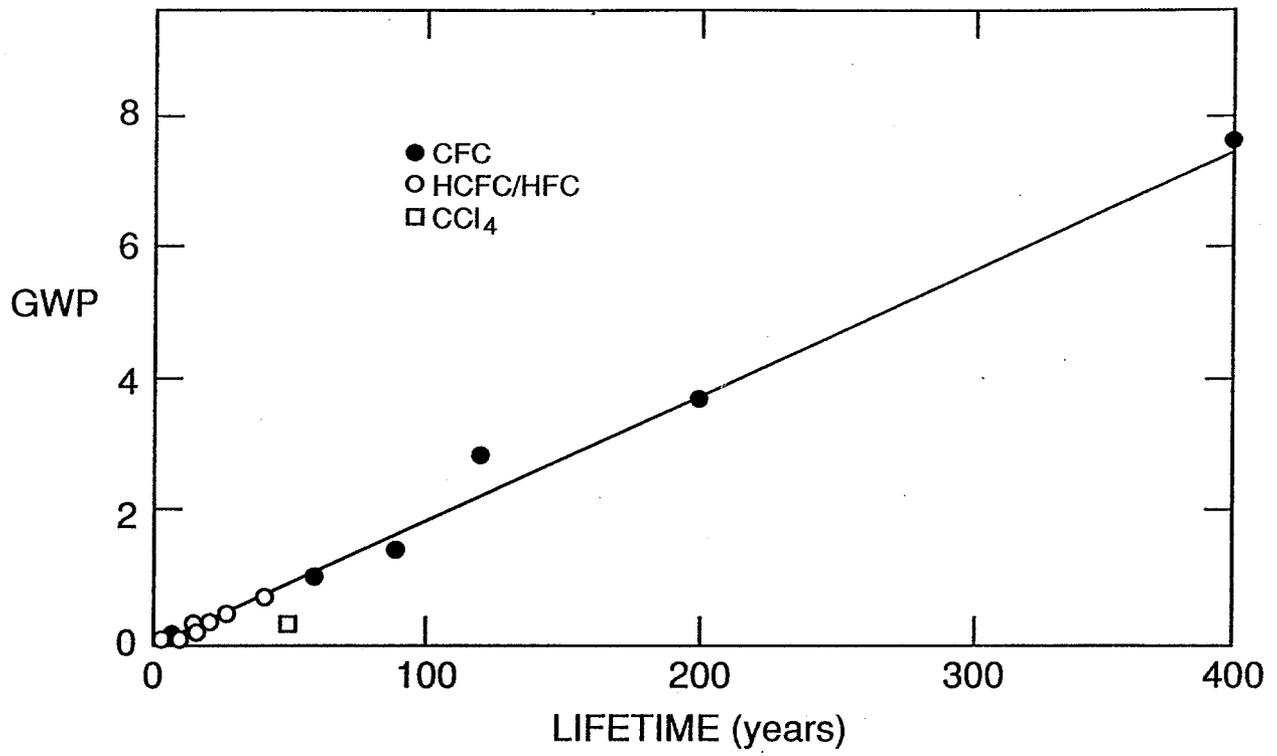


Figure 3. GWP as a Function of Atmospheric Lifetime. Data from Table 1.

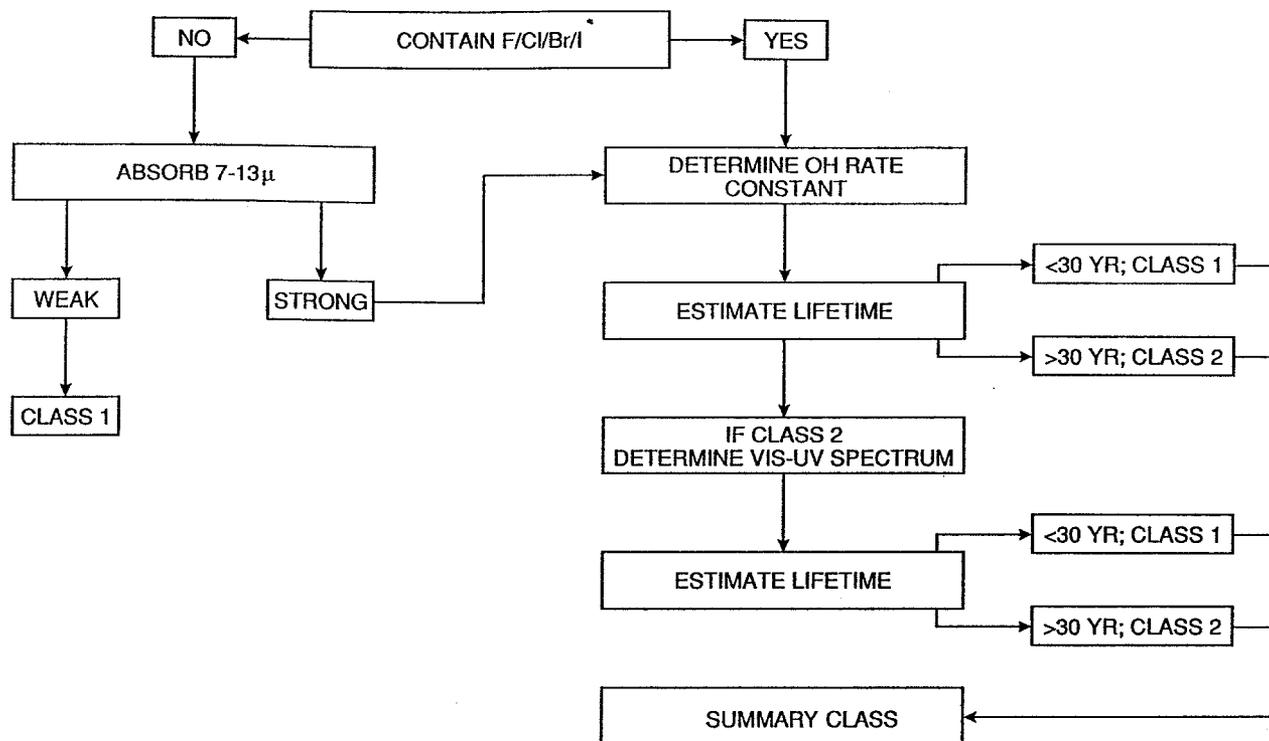


Figure 4. Decision Tree for GWP

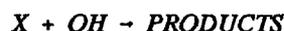
radiation in the 170 to 300 nm region. For replacement substances photolysis in the troposphere also could be important if the test substance absorbs solar radiation in the VIS-UV part of the spectrum (290 to 700 nm). Thus a test substance which was inert to attack by OH radicals could still be destroyed in the troposphere if it contained a chromophore which led to significant absorption in the VIS-UV region of the solar spectrum. Photolysis in the VIS-UV part of the spectrum efficiently removes organic iodine compounds within the troposphere [7].

Reaction with O<sup>1</sup>D is important in the higher regions of the stratosphere only. For substances that have weak absorptions in the VIS-UV, this is a significant loss process. Test compounds for which this is the dominant loss mechanism will have very long atmospheric lifetimes. This mechanism for destruction of test substances will not be considered further here.

It is clear that compounds having very short atmospheric lifetimes will not contribute significantly to global warming. There is thus a qualitative connection between global warming potential and atmospheric lifetime. Table 1 provides a summary of calculated values of GWP and the corresponding atmospheric lifetimes for selected halocarbons. The data are plotted in Figure 3. It is apparent that compounds with very long atmospheric lifetimes have correspondingly large GWP's. Although no comparable data exist for the halons, a similar effect is expected. Note that the atmospheric lifetimes shown in Figure 3 refer to the average overall lifetime in the atmosphere. For screening purposes, we will be concerned solely with lifetime with respect to processes that destroy test substances within the troposphere. These are reaction with OH radicals and photolysis in the VIS-UV region as discussed in more detail in the following sections.

## 1. Reaction with OH Radicals

Hydroxyl radicals transform and remove trace atmospheric substances by abstracting hydrogen atoms or by addition/displacement reactions at unsaturated sites in the molecule. The reaction of any substance, X with OH can be written as:



and the rate of reaction given by:

$$-\frac{d(X)}{dt} = k_{OH}(OH)(X),$$

where  $k_{OH}$  is the rate constant for reaction, (X) the concentration of species X, and (OH) the average tropospheric OH concentration. Since (OH) is essentially constant (concentration independent of the presence of the trace substance X in the atmosphere), the expression can be written as:

$$-\frac{d(X)}{(X)} = k_{OH}(OH)(dt)$$

or

TABLE 1. NOMENCLATURE, ODP, GWP, AND ATMOSPHERIC LIFETIME FOR SELECTED HALOCARBONS

Formula	Designation	Lifetime, years	ODP	GWP
CCl <sub>3</sub> F	CFC 11	60	1.0	1.0
CCl <sub>2</sub> F <sub>2</sub>	CFC 12	120	0.97	3.1
CCl <sub>2</sub> FCClF <sub>2</sub>	CFC 113	90	0.85	1.4
CClF <sub>2</sub> CClF <sub>2</sub>	CFC 114	200	0.73	3.9
CClF <sub>2</sub> CF <sub>3</sub>	CFC 115	400	0.41	7.6
CHClF <sub>2</sub>	HCFC 22	15.3	0.051	0.36
CF <sub>3</sub> CHCl <sub>2</sub>	HCFC 123	1.6	0.016	0.19
CF <sub>3</sub> CHClF	HCFC 124	6.6	0.019	0.10
CF <sub>3</sub> CHF <sub>2</sub>	HCFC 125	28.1	0	0.58
CF <sub>3</sub> CH <sub>2</sub> F	HCFC 134a	15.5	0	0.27
CCl <sub>2</sub> FCH <sub>3</sub>	HCFC 141b	7.8	0.080	0.092
CClF <sub>2</sub> CH <sub>3</sub>	HCFC 142b	19.1	0.056	0.37
CF <sub>3</sub> CH <sub>3</sub>	HCFC 143a	41.0	0	0.74
CHF <sub>2</sub> CH <sub>3</sub>	HCFC 152a	1.7	0	0.030
CCl <sub>4</sub>		50	1.1	0.35
CCl <sub>3</sub> CH <sub>3</sub>		6.3	0.11	0.024
The ODP's are averaged values from one dimensional model calculations reported in reference 25. Lifetimes from reference 25. The GWP's are averages from one dimensional models reported in reference 6.				
CF <sub>3</sub> Br	Halon 1301	101	13.2	
CF <sub>2</sub> ClBr	Halon 1211	12.5	2.2	
CF <sub>2</sub> Br <sub>2</sub>	Halon 1202	≈1	0.3	
CF <sub>2</sub> BrCF <sub>2</sub> Br	Halon 2402	≈40	6.2	
ODP from reference 26, using LLNL one dimensional model calculation. Lifetimes of CF <sub>3</sub> Br and CF <sub>2</sub> ClBr from reference 26 also using LLNL one dimensional model calculation. Data on CF <sub>2</sub> Br <sub>2</sub> and CF <sub>2</sub> BrCF <sub>2</sub> Br from reference 18. The latter are tropospheric lifetimes.				
CF <sub>2</sub> BrCF <sub>3</sub>	Halon 2501	≈100		
CH <sub>2</sub> Br <sub>2</sub>		≈6		
CH <sub>3</sub> Br		≈2		
From reference 18. For CF <sub>2</sub> BrCF <sub>3</sub> this is the stratospheric lifetime, and for CH <sub>2</sub> Br <sub>2</sub> and CH <sub>3</sub> Br the lifetimes refer to the troposphere.				

$$\ln \left( \frac{X_0}{X_t} \right) = k_{OH}(OH) t,$$

where  $X_0$  is the concentration at some zero of time, and  $X_t$  the concentration at time  $t$ . The time for the concentration to decay from  $X_0$  to  $X_t$  is thus given by:

$$t = \frac{\ln \left( \frac{X_0}{X_t} \right)}{k_{OH}(OH)}.$$

Lifetime can be defined as:

$$t = \frac{\ln(2.718)}{k_{OH}(OH)} \quad \text{or} \quad t = \frac{1}{k_{OH}(OH)}.$$

where  $X_0/X_t$  has been set equal to 2.718, the base of natural logarithms. This is the time required for the concentration to fall by a factor of 2.718. Using an average atmospheric hydroxyl radical concentration of  $(OH) = 10^6 \text{ molec cm}^{-3}$  [8], the tropospheric lifetime is defined as:

$$t_{OH}(trop) = \frac{3 \times 10^{-14}}{k_{OH}},$$

where the units of  $t_{OH}(trop)$  are years ( $1 \text{ year} = 3 \times 10^7 \text{ sec}$ ) and of  $k_{OH}$  are  $\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ .

## 2. Photolysis

Photolysis is the process whereby a molecule is chemically transformed following the absorption of light. For photolysis to be important in the troposphere, the molecule must be able to absorb photons in the VIS-UV region of the solar spectrum (between about 290 and 700 nm) and the resultant energy-rich molecule must be chemically transformed rather than being physically quenched back to the original state. The rate of photolysis depends upon the flux of solar photons in the VIS-UV region, the absorption cross section of the substance over the same region, and the quantum yield for dissociation as a function of wavelength. The rate of photolysis is:

$$-\frac{dx}{dt} = k_p(X) = f\sigma\phi(X),$$

where  $f$  = flux of solar photons in  $\text{cm}^{-2} \text{s}^{-1}$ ,  $\sigma$  = cross section (base e) in  $\text{cm}^2$ ,  $\phi$  = quantum yield for dissociation,  $k_p$  = the effective first order rate constant in  $\text{s}^{-1}$ , and  $(X)$  = concentration of substance X in  $\text{molec cm}^{-3}$ . Thus:

$$k_p = f\sigma\phi.$$

The rate constant must actually be determined as the integral of this quantity over the whole range of atmospherically accessible solar radiation. The process is considerably simplified by carrying out the calculation for discrete intervals of the solar spectrum of interest and summing to obtain the total rate constant. The details of the calculational approach are given in Appendix C. Other factors including solar zenith angle, season, latitude, altitude, and surface albedo also enter into the calculation (see Appendix C).

The lifetime with respect to photolysis is defined as

$$t_p (\text{trop}) = \frac{1}{k_p}$$

or

$$t_p (\text{trop}) = 3 \times \frac{10^{-8}}{k_p},$$

where the units of  $t_p(\text{trop})$  are years (1 year =  $3 \times 10^7$  sec) and of  $k_p$  are  $\text{s}^{-1}$ .

To determine  $k_p$ , it is necessary to know the atmospheric flux of solar photons and their wavelength distribution, the absorption cross section of the compound over the same spectral range, and the quantum yield for dissociation, also as a function of wavelength. The first quantity is tabulated and available [9]. The second quantity is readily measured in the laboratory. The third quantity, however, is not easily obtained. For the purpose of developing a screening test, the quantum yield is taken to be unity at all wavelengths, and the screening test based on measurement of the absorption cross section. Then,

$$k_p \leq f\sigma \text{ and } t_p (\text{trop}) \geq \frac{1}{k_p}.$$

### C. INFRARED ABSORPTION IN THE ATMOSPHERIC WINDOW

It is not possible to predict the strength of the absorption bands of the halons or of their potential replacement compounds in the window region. There are data available for the CFC's and HCFC's, and these are shown in Table 2. Clearly, all of the compounds listed here absorb strongly in the window region. There

TABLE 2. INTEGRATED TOTAL ABSORPTION CROSS SECTION IN THE REGION OF THE ATMOSPHERIC WINDOW FOR SELECTED HALOCARBONS<sup>a</sup>

Formula	Designation	AFEAS <sup>b</sup>	Ramanathan, et al. <sup>c</sup>
CCl <sub>3</sub> F	CFC 11	1.00	1.00
CCl <sub>2</sub> F <sub>2</sub>	CFC 12	1.36	
CClF <sub>3</sub>	CFC 13		2.10
CF <sub>4</sub>	CFC 14		1.57
CCl <sub>2</sub> FCClF <sub>2</sub>	CFC 113	1.42	
CClF <sub>2</sub> CClF <sub>2</sub>	CFC 114	1.73	
CClF <sub>2</sub> CF <sub>3</sub>	CFC 115	1.96	
CHClF <sub>2</sub>	HCFC 22	1.07	
CF <sub>3</sub> CHCl <sub>2</sub>	HCFC 123	1.20	
CF <sub>3</sub> CHClF	HCFC 124	1.69	
CF <sub>3</sub> CHF <sub>2</sub>	HCFC 125	1.64	
CF <sub>3</sub> CH <sub>2</sub> F	HCFC 134a	1.37	
CCl <sub>2</sub> FCH <sub>3</sub>	HCFC 141b	0.80	
CClF <sub>2</sub> CH <sub>3</sub>	HCFC 142b	1.08	
CF <sub>3</sub> CH <sub>3</sub>	HCFC 143a	1.42	
CHF <sub>2</sub> CH <sub>3</sub>	HCFC 152a	0.69	
CCl <sub>4</sub>		0.50	0.54
CCl <sub>3</sub> CH <sub>3</sub>		0.51	
CF <sub>3</sub> Br	Halon 1301		1.53
a. Relative to CCl <sub>3</sub> F (CFC 11). b. Reference 6. c. Reference 27.			

are fewer data available for brominated compounds, but they also appear to be strong absorbers. However, there is no simple correlation between strength of the absorption features and GWP. The latter depends on factors other than total absorption cross section in the window region. These include lifetime, the specific location and strengths of the various features in the absorption spectrum, spectral overlap, etc. As a consequence the approach taken here is empirical and comparative and attempts only to draw conclusions as to whether a test compound is or is not of importance as an absorber of IR in the window region.

### D. TEST METHODS

The test methods that follow provide a basis for determining OH radical rate constants, atmospheric photolysis rate constants, and absorption cross sections in the IR window region, and thus for categorizing test compounds.

## 1. Rate Constant for Reaction with OH Radicals

Reactivity with OH may be determined by direct laboratory measurement of the rate constant of reaction, or may be estimated using the structure-activity relationships developed by Atkinson [10]. The latter is preferred for those compounds for which Atkinson provides appropriate data.

The estimation method is based on an analysis of the structure of the molecule and its breakdown into component structural sub-units. The reactivity can be expressed in terms of (a) abstraction of H atoms, (b) addition at double or triple C-C bonds, and (c) addition to aromatic structures. The total rate constant is obtained by summing the contributions of the different groups. In some cases, the reactivity and hence lifetimes of certain classes of compounds can be estimated without going through a detailed estimation calculation or making laboratory measurements. Thus, completely halogenated (with F, Cl, Br, or I) alkanes are essentially inert with respect to reaction with OH radicals, and therefore have very long tropospheric lifetimes. On the other hand, reactions of OH radicals at unsaturated sites (aliphatic or aromatic in character) are always very much faster than abstraction [10] and, therefore, unsaturated substances have short atmospheric lifetimes.

Thus, the estimation methods are presented only with reference to saturated compounds containing at least one abstractable hydrogen atom. The approach is described in more detail in Appendix B.

Experimental methods are more costly than estimation methods, and should be used only in the event that the structural units in the test compound are not included in the tables of parameters provided by Atkinson.

There are no accepted standard methods for the measurement of OH rate constants, although there are a number of convenient methods available [11]. These include (a) flash-photolysis resonance fluorescence or laser induced fluorescence [12-14], (b) discharge-flow resonance fluorescence [15], (c) discharge-flow laser magnetic resonance [15-17], and (d) steady-state photolysis [10]. Any of these methods can lead to reliable rate constant determinations. The first three methods are based on measurement of the loss of OH under conditions of excess test compound and yield an absolute measurement of the OH rate constant. The last method is based on the loss of test compound in the presence of excess OH, and yields a measure of the rate constant relative to the rate constant for some well known reference compound.

Those methods based on measurements of OH loss require that the test compound be free of impurities which are significantly more reactive than the test compound itself. Purity is thus of great importance in executing the test using this approach. In the case of the relative rate measurements, it is necessary to develop the necessary analytical capability to follow the course of the reaction. In addition the relative method is limited to reactions for which the rate constant is greater than about  $10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ , which severely limits its application for the purposes of the screening tests developed here. There are only a limited number of laboratories in this country equipped to do any of these kinds of measurements. The method of choice in terms of availability of equipment and capability to provide rate data over the range of rate constants of interest, is the flash-photolysis resonance fluorescence technique. That is the basis for the test protocol given in Appendix B, which is then applied (Appendix E) to demonstrate the applicability of the method for halons 1211 and 1301, and a test compound,  $\text{CH}_2\text{Br}_2$ , which was chosen in the expectation that it would differ significantly in chemical behavior.

Institutions known to have the capability of applying the flash-photolysis resonance fluorescence technique include:

Harvard University, Cambridge, Massachusetts  
NIST, Gaithersburg, Maryland  
NOAA Environmental Research Laboratories, Boulder, Colorado  
Georgia Institute of Technology, Atlanta, Georgia  
University of Dayton Research Institute, Dayton, Ohio

The approximate costs of these tests are probably in the range of \$2000 to \$5000 per compound depending on the number of test compounds and the assumption that the test samples are free of impurities that can affect the results. It must be emphasized that the test methods are at the research level, and cannot be carried out without the participation of senior scientific staff.

## 2. VIS-UV Absorption Cross Section

As discussed above, an upper limit to the rate constant for photolysis is given by  $k_p \leq f\sigma$  and, since  $f$  is a tabulated quantity, the test measurement involves measurement of the absorption cross section in the VIS-UV region of the spectrum.

There are no accepted standard methods for the measurement of absorption cross sections. The measurement can be undertaken using a variety of spectrometer configurations. Design options include single pass or multipass for the absorption train, and also single beam or double beam for the detection system. Double beam instruments consist of true double beam configurations employing two identical monochrometers and two detection systems, virtual double beam configurations employing a beam splitter at the exit of the monochromator followed by two detection systems, and broad-band referencing, where the wavelength dispersed signal is referenced to the non-dispersed incident light source. Any of these experimental configurations are acceptable. Of particular relevance are the measurements of Molina and coworkers [18] using a double-beam instrument to measure absorption cross sections for several brominated methanes and ethanes, and those of Gillotay and coworkers [19,20], who measured absorption cross sections for bromine containing compounds using both multiple reflection and single pass single beam instruments.

The choice of instrument is dictated by the requirement that it be capable of measuring absorption cross sections as low as  $10^{-24}$  cm<sup>2</sup>. Absorption cross section is defined in terms of the fractional absorption of light passing through a defined path length of a given concentration of absorber.

One can define a figure of merit for the measurement system based on the quantity  $\sigma p \ell$  (the optical depth), where  $\sigma$  is the absorption cross section (wavelength dependent),  $p$  the pressure (or concentration) of the test compound, and  $\ell$  the path length. Highest precision cross section measurements are made with an optical depth of about one (30 to 40 percent absorption). For weak absorbers,  $\sigma p \ell$  will be much smaller. In addition, for a fixed path length, absorption depends on the pressure (or concentration) of the test substance in the optical path. Under nominal conditions of "room" temperature (298 K), absorption may be limited by the available vapor pressure of the test substance. These factors are illustrated in Table 3, where the minimum cross sections for different degrees of absorption at different sample pressures are calculated for a path length of one meter.

To measure the cross section for a weak absorber requires high pressure, and/or long path length, and/or high accuracy in measuring very small amounts of absorption. For screening purposes, the accuracy or reproducibility of the measurements should be about 25 percent, and this should define the smallest possible value of  $\sigma p \ell$  suitable for making the measurements.

Although we do not specify a particular instrument configuration for the purpose of this test, we will illustrate the test protocol using a single-beam instrument [21] as described further in Appendix C.

TABLE 3. MINIMUM MEASURABLE VIS-UV ABSORPTION CROSS SECTIONS FOR DIFFERENT AMOUNTS OF ABSORPTION AND AT DIFFERENT PRESSURES FOR AN OPTICAL PATH LENGTH OF 1 METER

Absorption, %	$\sigma pl = -\ln(I/I_0)$	Pressure, torr	$\sigma, \text{cm}^2$
1	.01	760	$4 \times 10^{-24}$
		100	$3 \times 10^{-23}$
		10	$3 \times 10^{-22}$
.1	.001	760	$4 \times 10^{-25}$
		100	$3 \times 10^{-24}$
		10	$3 \times 10^{-25}$
.01	.0001	760	$4 \times 10^{-26}$
		100	$3 \times 10^{-25}$
		10	$3 \times 10^{-24}$

Laboratories known to have the capability to carry out VIS-UV absorption cross section measurements include:

- University of California, Irvine, California
- Jet Propulsion Laboratory, Pasadena, California
- NIST, Gaithersburg, Maryland
- NOAA Environmental Research Laboratories, Boulder, Colorado
- Brookhaven National Laboratory, Upton, New York.

The approximate costs of these tests range from \$1000 to \$3000 per compound depending on the number of test compounds and the assumption that the test samples are free of impurities that can affect the results. It must be emphasized that the test methods are at the research level, and cannot be carried out without the participation of senior scientific staff.

### 3. Absorption Cross Section in the IR

Absorption cross sections are readily obtained using the now-standard approach of Fourier transform infrared spectroscopy (FTIR). Since this is a widely used analytical instrument available in many commercial configurations, we specify the method without specifying any particular instrument. FTIR spectroscopy has been applied to measuring cross sections for the CFC's and HCFC's [5, 6, 22, 23]. In Appendix D, the specific experimental conditions to be used are described. These include partial pressure of the test compound, total pressure of the measurement, resolution, and sample purity.

Before carrying out a measurement, an effort should be made to determine the absorption characteristics of the test compound using tables of characteristic group frequencies. Socrates [24], for example, provides tables which can be used to establish whether or not a test compound absorbs strongly in

the window region. If the structure of the test compound is known, tables of this type can provide a basis for a determination of the intensity of IR absorption. This is useful only in establishing whether a test compound is a strong absorber. If there are no identifiable strong absorption features, a measurement is necessary to determine whether the test compound is a weak or strong absorber.

Many laboratories are equipped to make FTIR measurements. These include:

NIST, Gaithersburg, Maryland  
E. I. DuPont de Nemours, Inc., Wilmington, Delaware  
General Motors Research Laboratories, Warren, Michigan  
State University of New York at Stony Brook  
Jet Propulsion Laboratory, Pasadena, California  
Air Force Geophysics Laboratory, Hanscom Field, Maine  
NASA Goddard Space Flight Center, Greenbelt, Maryland

The approximate costs of these tests range from \$500 to \$2000 per compound depending on the number of test compounds and the assumption that the test samples are free of impurities that can affect the results. It must be emphasized that the test methods are at the research level, and cannot be carried out without the participation of senior scientific staff.

#### **E. CLASSIFICATION OF HALON SUBSTITUTES BASED ON ATMOSPHERIC LIFETIME AND INFRARED ABSORPTION IN THE ATMOSPHERIC WINDOW**

Whereas bromine-containing compounds are about 10 times more effective than chlorine containing compounds (on a per molecule basis), in catalytically destroying ozone, no such "non-linear" effect is found with respect to global warming. Any substance that absorbs strongly in the region of the atmospheric window, has a significant potential for contributing to global warming. The controlling factor is lifetime.

The classification proposed here is based on the assumption that the linear correlation between GWP and lifetime illustrated in Figure 3 is valid for any compound which is a strong absorber in the window region. It is proposed that test compounds be categorized solely on the basis of their tropospheric lifetime and whether or not they are strong absorbers in the window region. Furthermore, since it is very unlikely that any test compound will absorb significantly more strongly than the compounds listed in Table 2, an estimate of tropospheric lifetime can be used in conjunction with Figure 3 to estimate an upper limit to GWP. This can be done without reference to the IR absorption properties of the test compound.

Test compounds are categorized as follows:

Class 1: Weak absorbers and/or lifetimes less than 30 years.

Class 2: Strong absorbers and lifetimes greater than 30 years.

For screening purposes a strong absorber is defined as one whose integrated total absorption cross section is equal to or greater than 0.1 of the integrated total absorption cross section of CFC 11.

Rate constants for reaction with OH radicals and photolysis rates corresponding to different tropospheric lifetimes are given in Table 4.

The choice of 30 years as the division between the two categories is based on the observation that, with reference to Figure 3, 30 years, corresponding to an ODP of about 0.5, encompasses most of the data on

TABLE 4. CORRESPONDENCE BETWEEN TROPOSPHERIC LIFETIME AND THE RATE CONSTANT FOR REACTION WITH OH RADICALS AND FOR THE RATE CONSTANT FOR PHOTOLYSIS

Lifetime, years	$k_{OH}$ , $\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	$k_p$ , $\text{s}^{-1}$
.1	$3 \times 10^{-13}$	$3 \times 10^{-7}$
.3	$1 \times 10^{-13}$	$1 \times 10^{-7}$
1	$3 \times 10^{-14}$	$3 \times 10^{-8}$
3	$1 \times 10^{-14}$	$1 \times 10^{-8}$
10	$3 \times 10^{-15}$	$3 \times 10^{-9}$
30	$1 \times 10^{-15}$	$1 \times 10^{-9}$
100	$3 \times 10^{-16}$	$3 \times 10^{-10}$

the HCFC's included in the figure, and also corresponds to an OH rate constant of about  $10^{-15} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ , which represents about the limit of measurement using the FPRF method. The classification is thus an indicator of whether a test compound has a greater or less potential for global warming than the HCFC's under consideration.

TABLE 5. SUMMARY OF SCREENING TEST RESULTS FOR GLOBAL WARMING POTENTIAL

Test Compound	Lifetime <sup>a</sup> , years	Relative Total Cross Section <sup>b</sup>	Class
CF <sub>3</sub> Br (halon 1301)	30(101)	1.53	2
CF <sub>2</sub> ClBr (halon 1211)	2.5(12.5)	2.19	1
CF <sub>2</sub> Br <sub>2</sub> (halon 1202)	1.4(1)	2.05	1
CH <sub>2</sub> Br <sub>2</sub>	0.35(6)	0.32	1
<p>a. From Table 6. Figures in parenthesis from Table 1. For CF<sub>3</sub>Br (halon 1301), the correct lifetime is closer to 100 years than the lower value of 30 years reported in Table 6.</p> <p>b. From Table 7.</p>			

**F. SUMMARY OF SCREENING TESTS AND CLASSIFICATION FOR HALONS 1211, 1301 and 1202, AND FOR TEST COMPOUND CH<sub>2</sub>Br<sub>2</sub>**

Details of the screening test methods are given in Appendices B-D, while a description of the actual experimental measurements and detailed results are given in Appendix E. The results are summarized in Table 5.

Of the halons and selected test compounds treated in this report, only CH<sub>2</sub>Br<sub>2</sub> contains an abstractable H atom and is a candidate for using the estimation method for OH rate constant. The estimated rate constant and derived lifetime are given in Table 6. The lifetime corresponds to Class 1.

TABLE 6. SUMMARY OF TEST RESULTS FOR RATE CONSTANT FOR REACTION WITH OH RADICALS, RATE CONSTANT FOR PHOTOLYSIS, DERIVED TROPOSPHERIC LIFETIME, AND SUMMARY LIFETIME<sup>a</sup>

Test Compound	k <sub>OH</sub> , est	k <sub>OH</sub> , meas	k <sub>a</sub> , meas	Summary Lifetime
1211 CF <sub>2</sub> ClBr Rate Constant Lifetime	NA	(1.2±0.05)×10 <sup>-14</sup> 2.5	2.2×10 <sup>-9</sup> 13.6	2.5
1301 CF <sub>3</sub> Br Rate Constant Lifetime	NA	(1.8±1.5)×10 <sup>-15</sup> 17	<10 <sup>-11</sup> >3000	30 <sup>b</sup>
1202 CF <sub>2</sub> Br <sub>2</sub> Rate Constant Lifetime	NA	Not measured	2.3×10 <sup>-8</sup> 1.4	1.4
1002 CH <sub>2</sub> Br <sub>2</sub> Rate Constant Lifetime	7.5×10 <sup>-14</sup> 0.40	8.5×10 <sup>-11</sup> 0.36	8.5×10 <sup>-11</sup> 353	0.35
a.	Units for OH rate constants, cm <sup>3</sup> molec <sup>-1</sup> s <sup>-1</sup> , and for absorption rate constants, s <sup>-1</sup> . Lifetime in years.			
b.	See Appendix E.			

The experimental rate of decay of OH was measured in the presence of excess concentrations of test substances CF<sub>3</sub>Br (halon 1301), CF<sub>2</sub>ClBr (halon 1211), and for the selected test compound CH<sub>2</sub>Br<sub>2</sub>. First-order hydroxyl radical decay curves were measured under different experimental conditions, first-order rate constants derived, and finally, the second order rate constants were determined, as reported in Table 6.

For CF<sub>3</sub>Br (halon 1301) the measured decay rates lead to a second order rate constant close to the minimum decay rate which can be measured using this apparatus, about 1×10<sup>-15</sup> cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1</sup>. The derived lifetime of 17 years reported in Table 6 would classify CF<sub>3</sub>Br as Class 2. However, we are certain that there are impurities in the sample used for this work and that the true rate constant is smaller by at least a factor of 2, leading to a summary value of ≈ 30 years.

CF<sub>2</sub>ClBr (halon 1211) appears to be moderately reactive with OH although we are certain that it can be no more reactive than CF<sub>3</sub>Br, which would classify it as Class 2.

CH<sub>2</sub>Br<sub>2</sub> reacted rapidly with OH as reported in Table 6. The rate constant places CH<sub>2</sub>Br<sub>2</sub> in Class 1.

The results of the measurements of VIS-UV absorption cross section are summarized in Appendix E of this section, and the derived lifetimes are summarized in Table 6.

Halon 1301, CF<sub>3</sub>Br, does not absorb strongly in the VIS-UV region and is clearly in Class 2. CH<sub>2</sub>Br<sub>2</sub> absorbs somewhat more strongly, but the rate constant for absorption derived from the absorption measurement is still small and the test compound is categorized as Class 2.

For halon 1211, CF<sub>2</sub>ClBr, the absorption cross section is relatively strong on the edge of the visible part of the solar spectrum, and the calculated lifetime reported in Table 6 indicates Class 1.

Halon 1202, CF<sub>2</sub>Br<sub>2</sub> absorbs well into the visible region and has an appreciable rate of absorption as shown in Table 6.

All of the compounds tested here absorb strongly in the window region of the IR. The results of the measurements are given in Table 7, and in the absence of other test results would place these compounds in Class 2.

TABLE 7. INTEGRATED TOTAL ABSORPTION CROSS SECTIONS FOR DIFLUOROCHLOROBROMOMETHANE (HALON 1211), TRIFLUOROBROMOMETHANE (HALON 1301), DIFLUORODIBROMOMETHANE (HALON 1202), AND DIBROMOMETHANE IN THE REGION OF THE ATMOSPHERIC WINDOW (7-13 MICRONS)

Compound	Area, arb. units	Pressure, torr	Cross Section Relative to:	
			CF <sub>3</sub> Br	CCl <sub>3</sub> F <sup>a</sup>
CF <sub>3</sub> Br (halon 1301)	192	3.5	1.00	1.53
CF <sub>2</sub> ClBr (halon 1211)	274	3.5	1.43	2.19
CF <sub>2</sub> Br <sub>2</sub> (halon 1202)	169	2.3	1.34	2.05
CH <sub>2</sub> Br <sub>2</sub>	21	1.8	0.21	0.32

a. Based on data given in Table 2.

All of the results are shown in Table 5, where we report the lifetime (always the shortest lifetime derived from any of the test methods), and IR absorption characteristics of the compounds obtained using these test protocols. Clearly, the test compound CH<sub>2</sub>Br<sub>2</sub> is in Class 1 as a consequence of its high degree of reactivity with OH radicals. On the basis of OH reactivity, CF<sub>2</sub>ClBr would belong in Class 2. However, its VIS-UV absorption properties put it in Class 1. The other halons tested are in Class 1 because of their lack of significant OH reactivity and their insignificant absorption cross sections in the VIS-UV region.

## G. CONCLUSIONS

In designing screening tests for global warming potential, it has been established that the critical factors are the cross sections for absorption in the region of the atmospheric window (7 to 13  $\mu\text{m}$  (800 to 1400  $\text{cm}^{-1}$ ) and the tropospheric lifetime of the test compound. The following, then, describe the key elements for screening a candidate alternative fire suppressant for global warming potential:

- Classifying compounds in terms of whether they are relatively more likely or less likely to contribute to global warming than the HCFC's.
- Using tests for evaluating global warming potential following the tests for ozone depletion potential. The role of the halons or their possible replacements in global warming is probably very minor in view of the small amounts of material involved. The order of testing described in Appendix A and in the decision tree of Figure 4 should be followed.
- Using the test methods outlined in Appendices B and C to derive tropospheric lifetime.
- Performing the test methods outlined in Appendix D to determine whether or not a test compound is a strong absorber in the window region of the IR.

The grouping of compounds based on tropospheric lifetime and absorption strength in the window region is not meant to provide a basis for regulation, but rather a basis for comparison with other atmospheric trace gases. The suitability of a test compound is a function both of its global warming potential and some factor related to its atmospheric burden or production rate. Those issues are not treated here.

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## APPENDIX A

### ORDER OF SCREENING TESTS FOR GLOBAL WARMING POTENTIAL

The order of testing for global warming potential is directly related to the order of testing for ozone depletion potential, and is designed to allow one to proceed in the most direct and economical fashion. The decision tree given in Figure 4, provides a summary of the decision elements discussed in this section.

Ozone depletion potential tests should be carried out before global warming tests are undertaken.

If the tropospheric lifetime has already been determined as part of the ozone depletion potential screening tests, or if it can be estimated using the approach given in Appendix B, then the only requirement is to determine whether or not the test compound is a strong absorber in the window region.

If lifetime is not known and cannot be estimated, then it should be determined whether or not the test compound is a strong absorber in the window region. In some cases this can be established by inspection. Thus, all compounds containing C-F bonds are strong absorbers. The same will be true for certain esters, phosphates, and silicon containing compounds (see for example [24]).

If it is not possible to estimate the strength of the absorption bands of a test compound, then it should be measured.

The following is a summary of the test procedure to be followed in carrying out global warming potential screening tests.

1. Lifetime known from ODP tests: If lifetime less than 30 years: Class 1, no further tests.  
If lifetime greater than 30 years: go to 2.
2. Contains C-F or other known strong absorption feature: Class 2, no further tests.
3. Does not contain C-F or other known strong absorption feature:  
Absorption cross section known: integrate over 7 to 13  $\mu\text{m}$ .  
If not: measure and integrate over 7 to 13  $\mu\text{m}$ .
4. Compare integrated cross section with cross section for CFC 11:  
If cross section  $<0.1$  cross section for CFC 11: Class 1.  
If cross section  $>0.1$  cross section for CFC 11: Class 2.

## APPENDIX B

### TEST PROTOCOLS FOR RATE CONSTANT OF REACTION WITH OH RADICALS

#### A. ESTIMATION OF OH RATE CONSTANT

The reactions of OH radicals are the most studied of all classes of gas phase reactions and, as a result, there is a very large body of reliable kinetic data. Atkinson [10] has used this database to develop a group method for estimating OH radical rate constants for hydrogen atom abstraction. He also provides a basis for estimating rate constants for attack at double and triple C-C bonds, and attack at unsaturated aromatic sites. Examination of his database shows that the rate constants for the latter classes of reactions are all very fast compared to those for abstraction reactions, and all test compounds containing these structural units are classified as Class 2. The estimation method will be applied here only to saturated compounds having abstractable hydrogen atoms.

The basis for the Atkinson method is the separation of the molecule into defined structural units. The rate constants for  $-\text{CH}_3$ ,  $-\text{CH}_2-$ , and  $>\text{CH}-$  groups are dependent on the nature of the substituents alpha and beta to the group. In general, rate constants for the groups can be written as:

$$\begin{aligned}k(\text{CH}_3 - \text{X}) &= k'_p F(\text{X}), \\k(\text{Y}-\text{CH}_2 - \text{X}) &= k'_s F(\text{X})F(\text{Y}), \\k(\text{X} - \text{CH}(\text{Z}) - \text{Y}) &= k'_t F(\text{X})F(\text{Y})F(\text{Z}), \text{ and} \\k(\text{X}-\text{OH}) &= k_{\text{OH}} F(\text{X}),\end{aligned}$$

where  $k'_p$ ,  $k'_s$ ,  $k'_t$ , and  $k'_{\text{OH}}$  refer to the rate constant for abstraction from nominal primary, secondary, tertiary, and hydroxyl groups, respectively, and the factors  $F(\text{X})$ ,  $F(\text{Y})$ , and  $F(\text{Z})$  are correction factors to account for the effects of substituent groups. Using values for group rate constants and correction factors tabulated by Atkinson and given in Table A1, rate constants for test compounds may be derived.

The method is best explained through example and, in Table A2, rate constants are calculated for representative compounds. The choice of groups and calculation of group values are shown.

#### B. MEASUREMENT OF OH RATE CONSTANT

This report describes one experimental approach to measuring OH rate constants and, in a latter section, apply the method to selected halons and a test compound. The experimental method is flash-photolysis resonance fluorescence (FPRF) [12,13]. This method is able to provide rate data for reactions of hydroxyl radicals over the range of rate constants of about  $10^{-14}$  to  $10^{-9}$   $\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$ . It is an absolute rate measurement based on the rate of decay of OH radicals under pseudo-first order conditions. It is a very precise, reliable, and commonly used method for the measurement of OH rate constants. Its major drawback is the need for very pure samples, or at least very pure samples with respect to impurities which are significantly more reactive than the test substrate (typical complicating impurities would be unsaturated compounds or compounds with many easily abstracted hydrogen atoms).

The particular FPRF apparatus described here is being used at this time to measure rate constants for reactions of OH radicals for potential CFC replacement compounds under the AFEAS program. The experimental procedures proposed here for screening purposes are the same.

TABLE A1. GROUP RATE CONSTANTS AND SUBSTITUENT FACTORS FOR OH RATE CONSTANTS AT 298 K<sup>a</sup>

Group Rate Constants, $10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	
$k'_p=0.144$ $k'_s=0.838$ $k'_t=1.83$ $k'_{OH}=0.13$	
Substituent Group, X	Factor F(X)
-CH <sub>3</sub>	1.00
-CH <sub>2</sub> -	1.29
>CH-	1.29
>C<	1.29
-F	0.099
-Cl	0.38
-Br	≈0.30
-CH <sub>2</sub> Cl	0.57
-CHCl <sub>2</sub>	0.57
-CH <sub>2</sub> Br	≈0.57
-CCl <sub>3</sub>	≈0.083
-CH <sub>2</sub> F	≈0.85
-CHF <sub>2</sub>	≈0.10
-CF <sub>2</sub> Cl	≈0.025
-CF <sub>3</sub>	0.075
=O	8.8
-CHO	0.76
-C(O)-	0.76
-CH <sub>2</sub> C(O)-	4.4
>CHC(O)-	4.4
->CC(O)-	4.4
-C <sub>6</sub> H <sub>5</sub>	≈1.0
-OH	3.6
-O-	8.3
-C(O)OR	≈0.0
-OC(O)R	1.3
-CH <sub>2</sub> ONO <sub>2</sub>	0.34
>CHONO <sub>2</sub>	0.34
->CONO <sub>2</sub>	0.34
-ONO <sub>2</sub>	0.050
>C=C<	≤1
-C≡C-	≤1
-CN	0.14
-CH <sub>2</sub> CN	0.5
3 member ring	0.017
4 member ring	0.22
5 member ring	0.80
6 member ring	1.00
7 member ring	≈1.0

a. Adapted from reference 10.

The apparatus is shown in Figure A1. It consists of a stainless steel or glass cell (RX) surrounded by an outer wall between which fluid can be circulated to a temperature regulator (RL) to maintain a fixed temperature, measured by means of a thermocouple (TC). The cell has four window ports at 90° positions

TABLE A2. EXAMPLES OF ESTIMATION OF OH RADICAL RATE CONSTANTS USING GROUP VALUES

Molecule	Groups and Factors	Rate Constant, $10^{-12}$ $\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$	$2k'_p\text{F}(-\text{CH}_2-) + 2k'_s\text{F}(-\text{CH}_3-)\text{F}(-\text{CH}_2-)$	2.5
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	$k'_s\text{F}(-\text{CH}_3-)\text{F}(-\text{CH}_2-) + k'_s\text{F}(-\text{OH})\text{F}(-\text{CH}_2-) + k'_{\text{OH}}\text{F}(-\text{CH}_2-) + k'_p\text{F}(-\text{CH}_2-)$	5.3
$\text{CH}_2\text{BrCH}_2\text{Br}$	$2k'_s\text{F}(-\text{CH}_2\text{Br})\text{F}(-\text{Br})$	0.29
$\text{CHF}_2\text{Br}$	$k'_t\text{F}(-\text{F})^2\text{F}(-\text{Br})$	0.0054
$\text{CHFCIBr}$	$k'_t\text{F}(-\text{F})\text{F}(-\text{Cl})\text{F}(-\text{Br})$	0.021
$\text{CHBr}_3$	$k'_t\text{F}(-\text{Br})^3$	0.049
$\text{CHCl}_2\text{Br}$	$k'_t\text{F}(-\text{Cl})^2\text{F}(-\text{Br})$	0.079

around the cell and one additional window port on the base of the cell. The entire cell is mounted within a vacuum housing (VH). Gases are admitted to the cell through two inlets connected to gas handling systems (GHS). A hydroxyl radical resonance lamp (RL), consisting of a microwave powered (MG) discharge in 1 torr of a mixture of Ar saturated with water vapor and a pulsed  $\text{N}_2$  discharge flash lamp (FL), which is powered by discharge capacitors (DC), and a power supply (PS) are located at right angles to each other and to a photomultiplier detector (PM).

Hydroxyl radicals are produced by the flash photolysis of about 0.1 torr  $\text{H}_2\text{O}$ . The OH radical resonance lamp was used in cw mode to excite a small fraction of the hydroxyl radicals which then emitted resonance radiation at 308 nm which was detected by the photomultiplier. The signal output was then fed to pulse counting electronics, and ultimately to a computer for signal averaging and subsequent statistical analysis and graphical display. The measurement process was initiated by a photocell (PC) which was triggered by the visible light from the flash lamp. A delay gate (DG) was used to introduce a delay time of 100 to 300  $\mu\text{s}$  to eliminate any scattered light interference from the flash lamp. Fluorescence signal from 50 to 500 flashes were averaged to generate a suitable decay curve.

In a typical experiment, reaction mixtures containing the test compound, argon, and water vapor (prepared manometrically in a 5ℓ bulb before admission to the reaction cell) were flowed slowly through the cell (about  $100 \text{ cm}^3 \text{ s}^{-1}$ ).

The quantity measured in this test is the rate of loss of OH radicals in the presence of a great excess of the test compound. Under these conditions, the rate expression can be written as:

$$-\frac{d(\text{OH})}{dt} = k(\text{OH})(\text{S}),$$

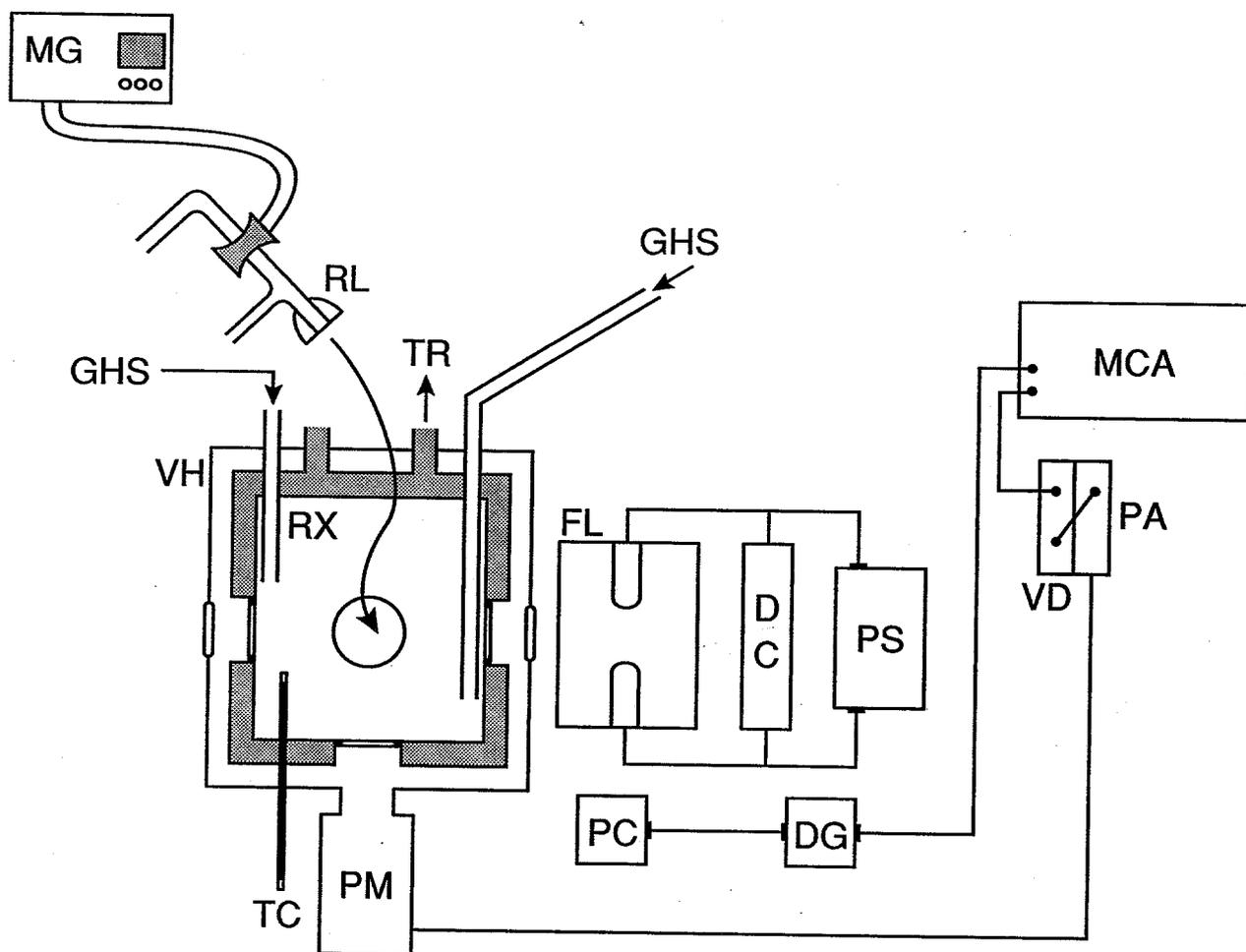


Figure A1. Apparatus for Measurement of OH Rate Constant.

where OH is the concentration of OH radicals, S is the concentration of the test substance, k is the rate constant, and t the reaction time. Under conditions where  $(OH) \ll (S)$ , S is essentially constant, and the OH decay is first order, and the rate expression becomes:

$$\frac{-d(OH)}{(OH)} = k(S)dt = k' dt,$$

where  $k'$ , the apparent first-order rate constant, is obtained directly from a measurement of the exponential rate of decay of OH. The true rate constant is then:

$$k = \frac{k'}{(S)}.$$

However, since there are OH diffusional losses from the reaction zone, in practice the first order decay is measured as a function of the concentration of the test compound, and from a plot of first order rate constant against concentration, the second-order rate constant is obtained from the slope.

Tests for impurity effects must be included as part of the screening protocol. The effect of reactive impurities on test results can be illustrated by considering a test compound which has a rate constant for reaction with OH radicals of about  $1 \times 10^{-15} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ , corresponding to an atmospheric lifetime of 30 years. If the test sample contains a 1 percent impurity in the form of an alkene, which typically may have a rate constant for reaction with OH of about  $1 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ , then the apparent OH rate constant would be about  $1 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ , corresponding to a lifetime of 3 years. Purity is thus of great importance in carrying out these tests, and it would be desirable for the test compounds to have impurity levels for alkenes and other unsaturated compounds of less than about 0.1 percent. If the purity is not known, then the following test procedures should be adhered to:

- measure the rate constant
- if  $k < 10^{-15} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ , the test results are acceptable
- if  $k > 10^{-15} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ , check the test sample for impurities.

This can be done initially by carrying out a trap-to-trap distillation and then remeasuring the rate constant. If the rate constant goes down, the sample was impure, and an analysis is necessary. Only after analysis and, if necessary, purification, should additional measurements be undertaken.

## APPENDIX C

### TEST PROTOCOL FOR VIS-UV ABSORPTION CROSS SECTION

The experimental method described here is based on the use of a single-beam monochromator. This method provides an absorption spectrum suitable for estimating the tropospheric lifetime of a test compound with respect to photolysis assuming unit quantum efficiency with respect to dissociation.

The absorption cross section is defined as:

$$\sigma = - \left( \frac{1}{c \ell} \ln \left( \frac{I}{I_0} \right) \right),$$

where  $\sigma$  is the cross section at a given wavelength, (C) the concentration of absorbing test substance in molec  $\text{cm}^{-3}$ ,  $\ell$  the path length in cm, I the intensity of light passing through the cell containing the absorber, and  $I_0$  the intensity of light passing through the empty cell, both in arbitrary units. The test measurement thus involves measuring and ratioing the quantities I and  $I_0$ .

The apparatus is shown in Figure A2. It consists of a 1-m incidence McPherson vacuum monochromator employing a 600 lines/mm grating blazed at 150 nm. The lamp shown in the figure is a Hamamatsu deuterium lamp with a highly stabilized power supply. This provided a convenient source of radiation over the 290 to 400 nm range. For measurements further into the red region of the spectrum, a tungsten lamp can be used. The detector is a Hamamatsu solar blind side-on multiplier tube. Five absorption cells having a range of path lengths ranging from 0.2 to 20 cm may be chosen by use of the turret assembly. The monochromator wave length drive is controlled by a stepping motor with 800 steps per revolution. The gear train used is such that 16 pulses are equivalent to 0.1 nm wavelength change. Gas pressure in the cell is monitored with a diaphragm type gauge.

The signal from the photomultiplier tube, which is observed in real time during a measurement, is processed and fed to a controller interface module which is part of an IBM- compatible personal computer system. A spectrum is first measured with no gas in the cell, then with an appropriate amount of gas in the cell, and finally with the cell again empty. The deuterium lamp is very stable, and this procedure leads to a very reliable measurement of the adsorption cross section down to about  $10^{-23} \text{ cm}^2$ .

The procedure is to measure the absorption cross section over the range 290 to 700 nm using the definition of absorption cross section given above. The absorption cross section as a function of wavelength is then related to photolysis rate constant using procedures outlined by Finlayson-Pitts and Pitts [9], who also give example calculations. Table A3 provides the required auxiliary data and the format for making the rate constant calculations.

The experimentally measured absorption cross section is averaged over discrete wavelength intervals as specified in Table A3 (which should be copied and used as a worksheet). Over the same intervals, Table A3 provides values of the solar flux, corresponding to a cloudless day, zenith angle of  $0^\circ$ , surface albedo zero, uncorrected for latitude or season. For each discrete spectral region the rate of absorption is calculated as the product of Columns 2 and 3, and the result entered into Column 4. The summation of Column 4 then gives the total rate of absorption. This is an upper limit to the number of photons absorbed. Following Molina and coworkers [18], the maximum rate of absorption should be divided by 3 to provide a more realistic

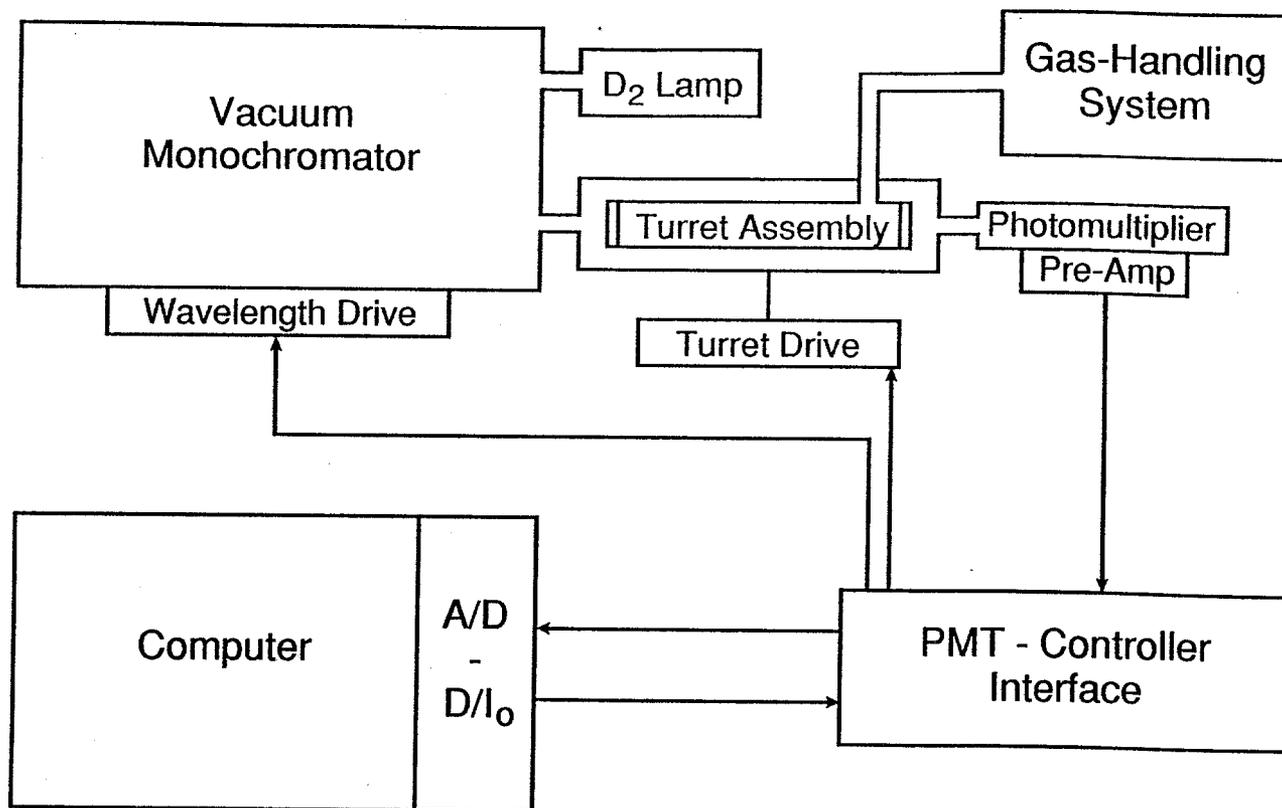


Figure A2. Apparatus for Measurement of VIS-UV Absorption Cross Section.

TABLE A3. ESTIMATION OF VIS-UV ABSORPTION RATE CONSTANT<sup>a</sup>

Wavelength Interval, nm	Solar Flux, photons cm <sup>-2</sup> s <sup>-1</sup>	Average Absorption Coefficient, cm <sup>2</sup> molec <sup>-1</sup>	Rate Constant, s <sup>-1</sup>
290-295	0.0001 × 10 <sup>14</sup>		
295-300	0.037		
300-305	0.362		
305-310	1.28		
310-315	2.85		
315-320	3.94		
320-325	4.96		
325-330	7.14		
330-340	1.50 × 10 <sup>15</sup>		
340-350	1.61		
350-360	1.74		
360-370	2.07		
370-380	2.18		
380-390	1.99		
390-400	2.37		
400-410	3.26		
410-420	3.66		
420-440	7.34		
440-460	9.05		
460-480	9.81		
480-500	9.87		
500-520	9.78		
520-540	9.85		
540-560	9.65		
560-580	9.82		
580-600	1.0 × 10 <sup>16</sup>		
600-620	1.01		
620-640	1.01		
640-660	1.01		
660-680	1.01		
680-700	1.01		

a. For a zenith angle of zero, surface albedo zero, uncorrected for latitude or season. The quantum yield is taken as unity at all wavelengths. Adapted from reference 9.

estimate of the average atmospheric absorption rate. This absorption rate constant is an upper limit to the true rate constant for photolysis:

$$k_p \leq k_a.$$

The problem of test sample purity is of concern here as well as with respect to OH reactivity. Low levels of a strongly absorbing impurity will give an incorrect set of cross-section results. Therefore, if the purity is not known, the following test procedures should be followed:

- measure the absorption cross section as a function of wavelength, and calculate  $k_p$
- if  $k_p < 10^{-9} \text{ s}^{-1}$ , the test results are acceptable
- if  $k_p > 10^{-9} \text{ s}^{-1}$ , check the test sample for impurities.

This can be done initially by carrying out a trap-to-trap distillation and then remeasuring the absorption cross section. If the absorption cross section changes significantly, the sample was impure, and an analysis is necessary. Only after analysis and, if necessary, purification, should additional measurements be undertaken.

Finally, it must be emphasized that the test value derived for lifetime with respect to photolysis provides only a lower limit to the true lifetime, and if the quantum yield is low, the test compound could have a much longer lifetime.

## APPENDIX D

### TEST PROTOCOL FOR IR ABSORPTION CROSS SECTION

Tests for IR absorption cross section are all to be made using an FTIR spectrometer. For development of the test protocol, we have used a Mattson Sirius 100 instrument. Any comparable instrument would be suitable. To maintain comparability of data, all measurements should be carried out with a fixed instrument resolution of  $1\text{-}4\text{ cm}^{-1}$ . This is not the highest resolution available from commercial FTIR instruments, but is attainable with most of these instruments. Total pressure should be 1 atmosphere.

The partial pressure of the test compound should be chosen to prevent band saturation at the resolution of the measurements. Depending on path length this will range from about 1 to 20 torr.

Although impurity effects are not as important in the IR measurements as they would be for the rate measurements, it is important that reasonably pure samples be employed for the tests. The IR spectrum should be examined and bands assigned to the probable absorption features of the test compound. Absorption bands which are not explicable on the basis of the known structure of the compound and the corresponding characteristic group frequencies are indicative of the presence of impurities. The presence of such bands means that the compound should be further purified.

The measurements should be carried out by adding the appropriate amount of test compound, measuring the partial pressure, charging the cell to atmospheric pressure with a non-absorbing gas such as nitrogen or argon, measuring the absorption cross section over a range encompassing the 7 to 13  $\mu\text{m}$  region, and integrating the area of the absorption vs. wavelength plot over the 7 to 13  $\mu\text{m}$  region. The absolute cross section is not required, so that the method of integration is not critical. For comparison, a measurement must be made using halon 1301,  $\text{CF}_3\text{Br}$ .

The data are reported in terms of integrated total cross section, partial pressure, and cross section relative to  $\text{CF}_3\text{Br}$ . The latter is given by:  $(\text{area/partial pressure})$  for test compound/ $(\text{area/partial pressure})$  for  $\text{CF}_3\text{Br}$ . Cross section relative to  $\text{CF}_3\text{Br}$  is then converted to cross section relative to  $\text{CCl}_3\text{F}$  (CFC 11) by multiplying the former by 1.53.

## APPENDIX E

### RESULTS OF SCREENING TESTS FOR HALONS 1211, 1301 AND 1202, AND FOR THE SELECTED TEST COMPOUND CH<sub>2</sub>BR<sub>2</sub>

#### A. ESTIMATION OF OH RATE CONSTANT

The method is discussed in Appendix

. B, Part A, and illustrated in Table A2. Of the halons and selected test compounds treated in this report, only CH<sub>2</sub>Br<sub>2</sub> contains an abstractable H atom. The groups, factors, and rate constant calculation are as follows:

$$k = k_s' \times F(-Br) \times F(-Br) \times 1 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \text{ or}$$
$$k = (0.838) \times (0.3) \times (0.3) \times (1 \times 10^{-12}) = 7.5 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}.$$

#### B. MEASUREMENT OF OH RATE CONSTANT

The rate of decay of OH was measured in the presence of excess concentrations of test substances CF<sub>3</sub>Br (halon 1301), CF<sub>2</sub>ClBr (halon 1211), and for the selected test compound CH<sub>2</sub>Br<sub>2</sub>. Representative first order hydroxyl radical decay curves are given in Figures A3-A5 for the three test compounds under different experimental conditions as specified in the figure captions. From each decay curve, a first-order rate constant is derived as shown in Table A4. These in turn are plotted as shown in Figures A6-A8, and from the slopes of these plots, the second-order rate constants are derived as shown in Table 6.

For CF<sub>3</sub>Br the rate of reaction was essentially the same as the limiting minimum decay rate which can be measured using this apparatus of about  $1 \times 10^{-15} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ , classifying CF<sub>3</sub>Br as Class 1. However, as discussed above, the true lifetime is probably at least 30 years, indicating Class 2. In the case of CH<sub>2</sub>Br<sub>2</sub>, there is a measurable decay rate, as can be seen from Figures A5 and A8. The rate constants calculated from this decay rate are reported in Tables A4 and 6. This would place CH<sub>2</sub>Br<sub>2</sub> in Class 1.

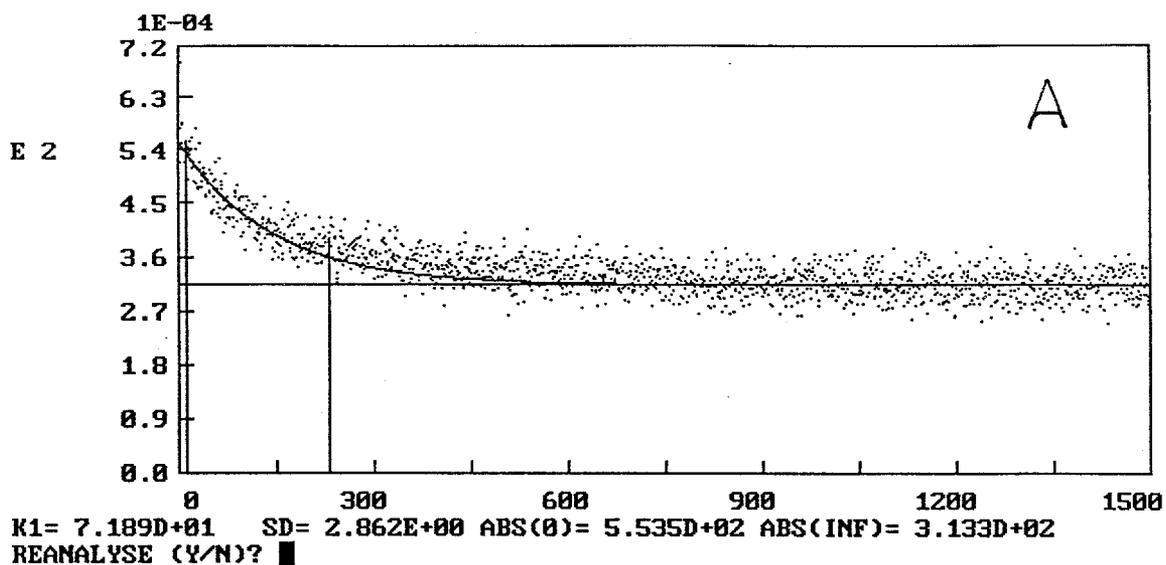
CF<sub>2</sub>ClBr presents a problem, since it appears to react at an appreciable rate (Table 6). The existing data [10] on fully halogenated methanes indicate that this compound should be no more reactive than CF<sub>3</sub>Br, and we attribute the excess rate to impurities in the sample which could be removed with additional purification.

#### C. MEASUREMENT OF VIS-UV ABSORPTION CROSS SECTION

The results of the measurements of the VIS-UV absorption cross sections are shown in Figures A9-A11. The experimental conditions are specified in the figure captions. These curves illustrate the problems inherent in the measurement of very small absorption cross sections.

For halon 1211, CF<sub>2</sub>ClBr, the absorption cross section varies almost exponentially with wavelength as can be seen from Figure A9. This is typical for the halocarbons (and many other classes of compounds). At very low absorbencies, the curve begins to flatten out, suggesting the presence of low levels of some unknown impurity. To gauge the consequences of impurity contamination, we have carried out rate constant

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AU.OF 200 FLASHES



mcs04-24.006 ORIGINAL FILE = B:0424G2.MCS  
AU.OF 200 FLASHES

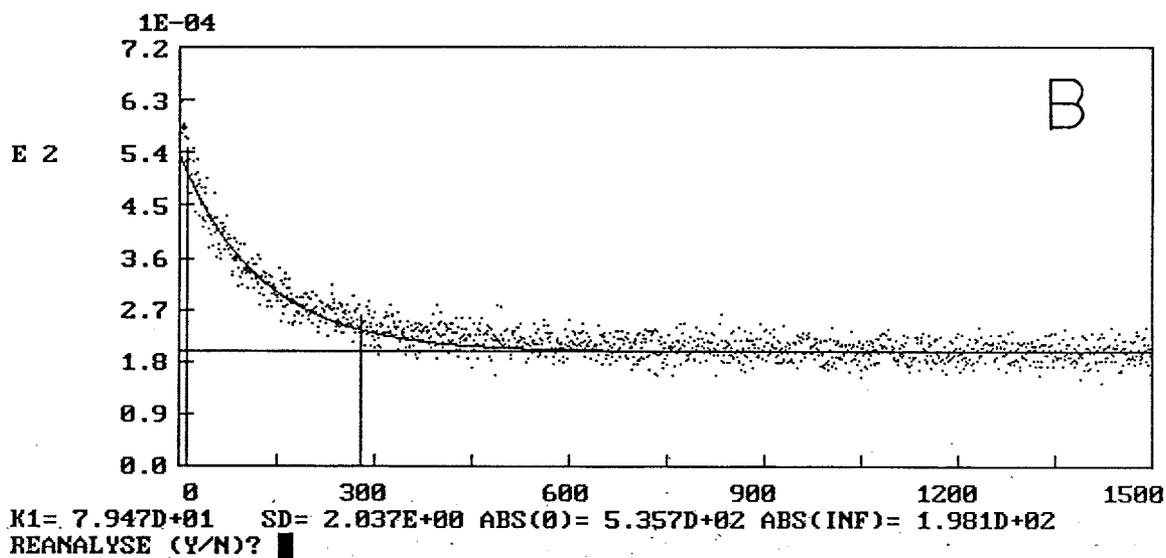
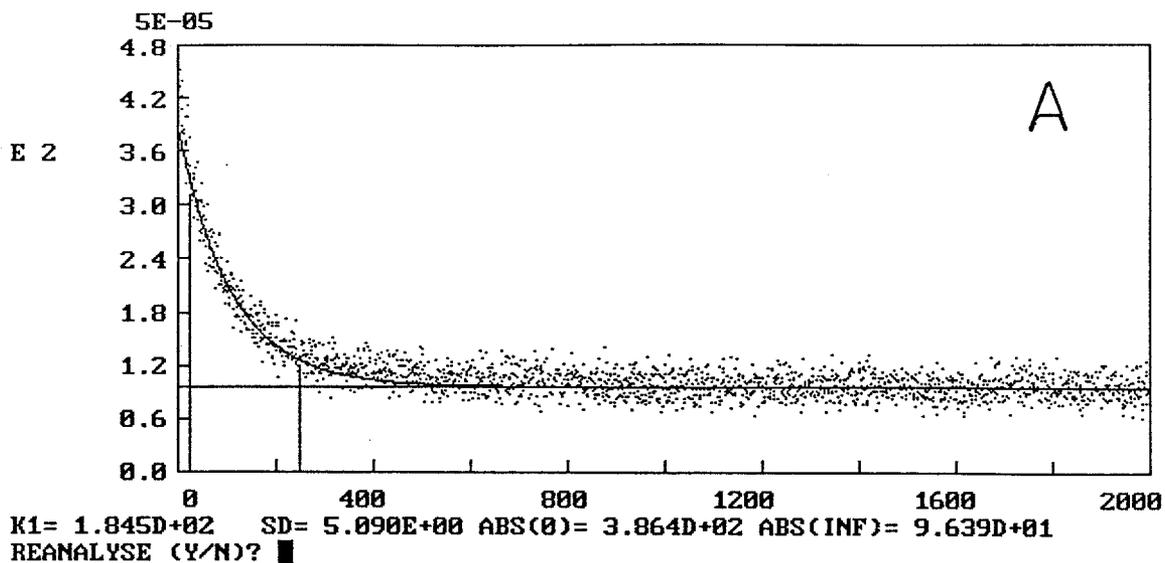


Figure A3. Decay of OH Resonance Fluorescence Signal in the Presence of Trifluorobromomethane (halon 1301). A: 2150 mtorr  $\text{CF}_3\text{Br}$ . B: 500 mtorr  $\text{CF}_3\text{Br}$ .

mcs04-20.005 ORIGINAL FILE = B:0420C3.MCS  
AV.OF 165 FLASHES



mcs04-23.003 ORIGINAL FILE = B:0423F3.MCS  
AV.OF 200 FLASHES

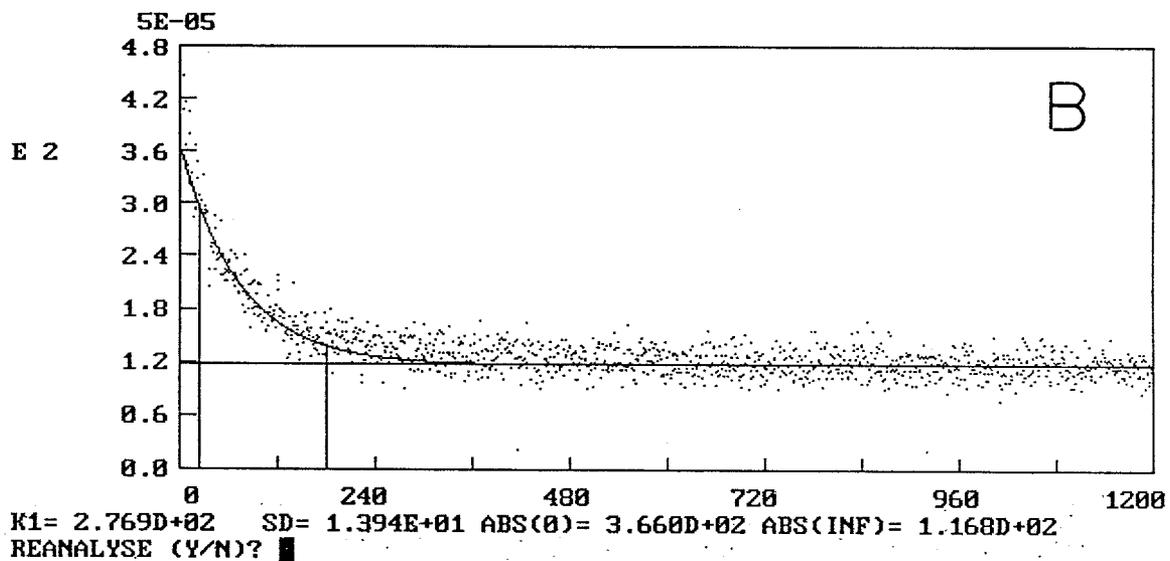
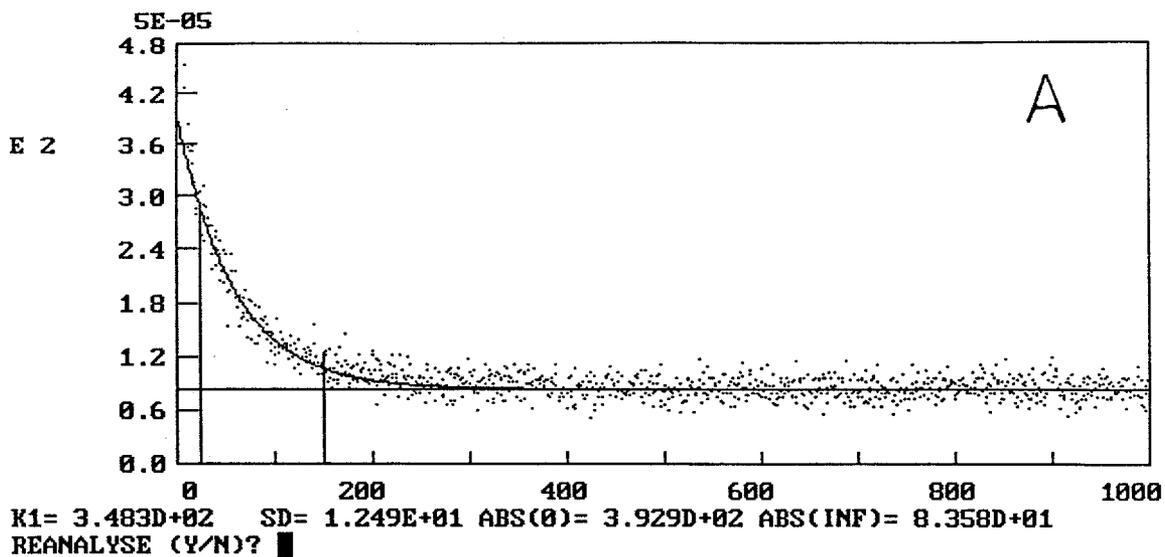


Figure A4. Decay of OH Resonance Fluorescence Signal in the Presence of Difluorochlorobromomethane (halon 1211). A: 250 mtorr  $\text{CF}_2\text{ClBr}$ . B: 500 mtorr  $\text{CF}_2\text{ClBr}$ .

mcs04-25.001 ORIGINAL FILE = B:0425C1.MCS  
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mcs04-25.005 ORIGINAL FILE = B:0425F1.MCS  
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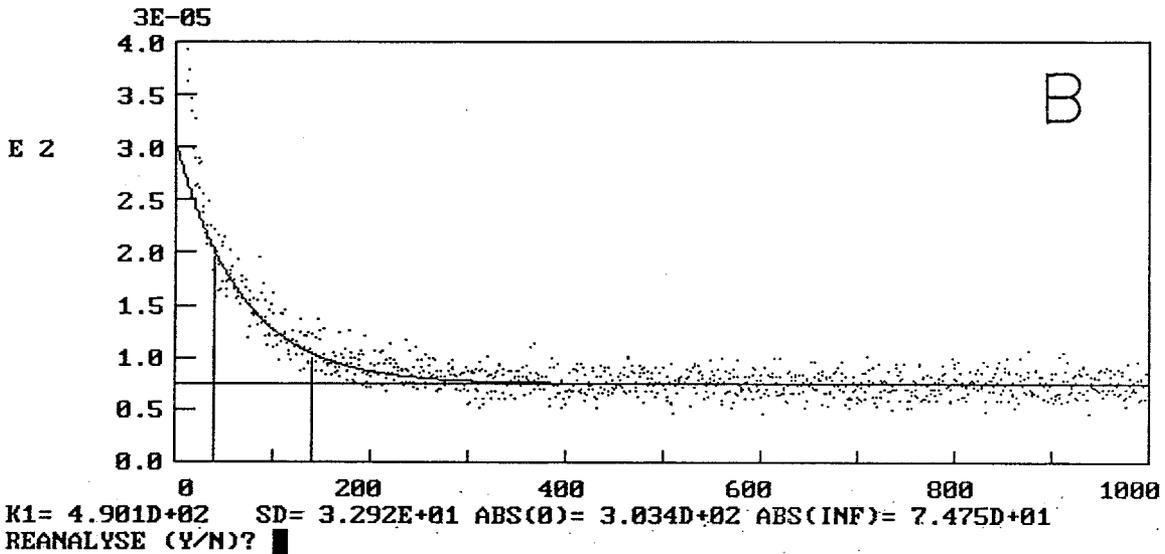


Figure A5. Decay of OH Resonance Fluorescence Signal in the Presence of Dibromomethane (halon 1002). A: 250 mtorr  $\text{CH}_2\text{Br}_2$ . B: 500 mtorr  $\text{CH}_2\text{Br}_2$ .

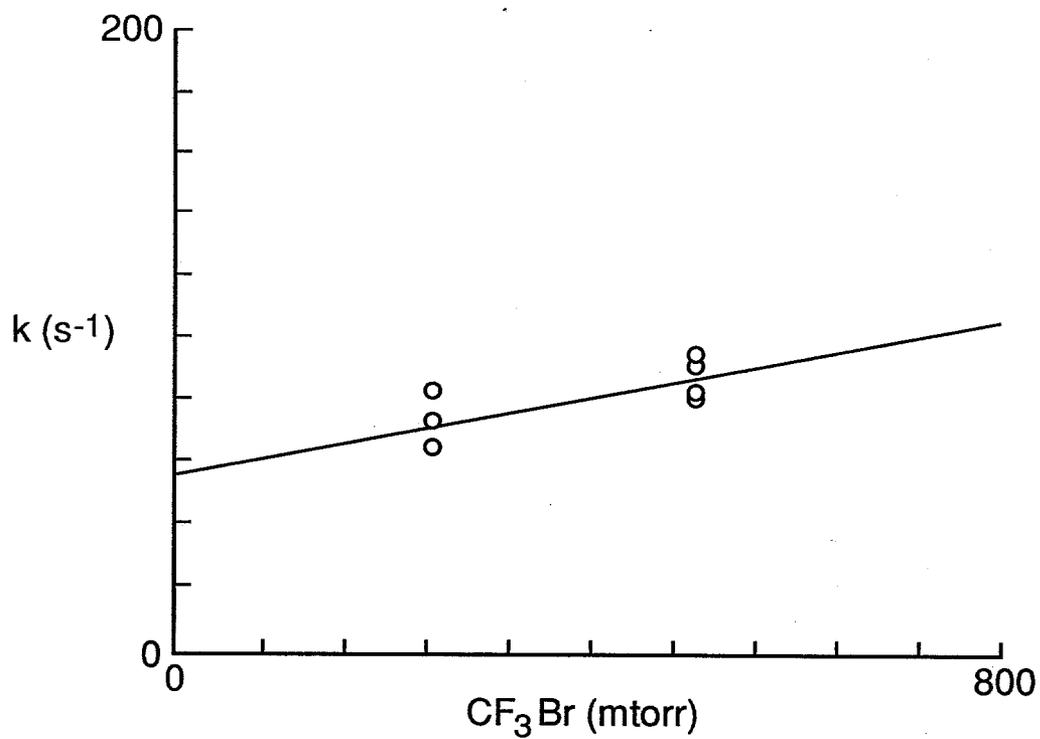


Figure A6. Plot of the First-order Rate Constant for the Decay of OH Against the Concentration of Trifluorobromomethane (halon 1301).

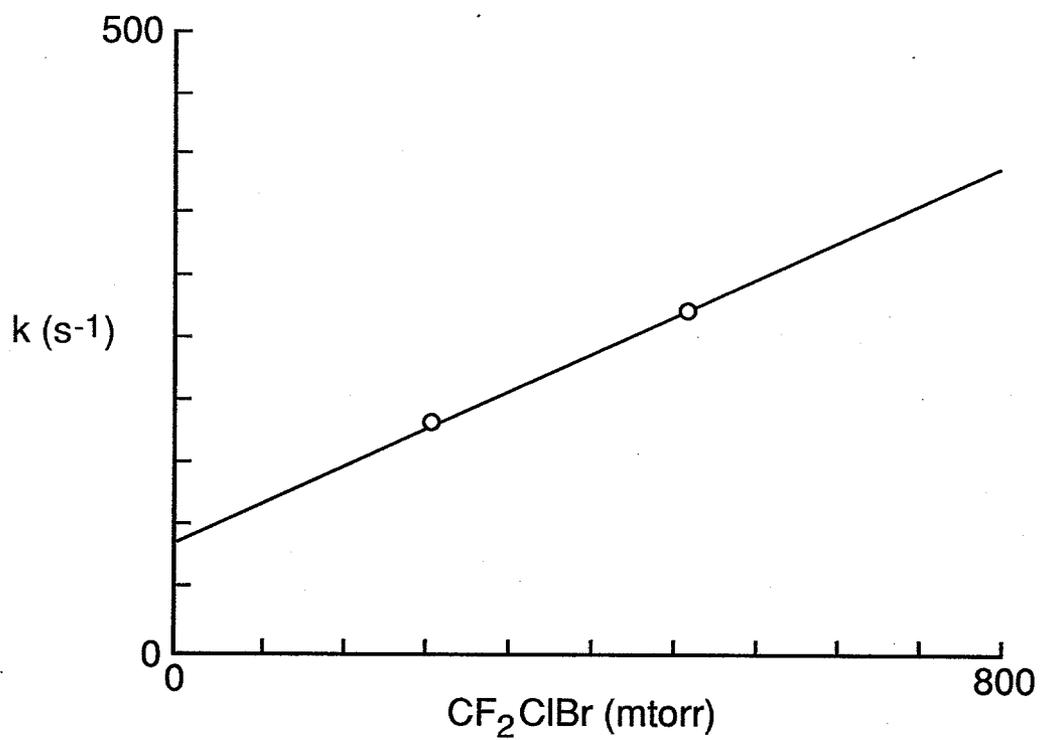


Figure A7. Plot of the First-order Rate Constant for the Decay of OH Against the Concentration of Difluorochlorobromomethane (halon 1211).

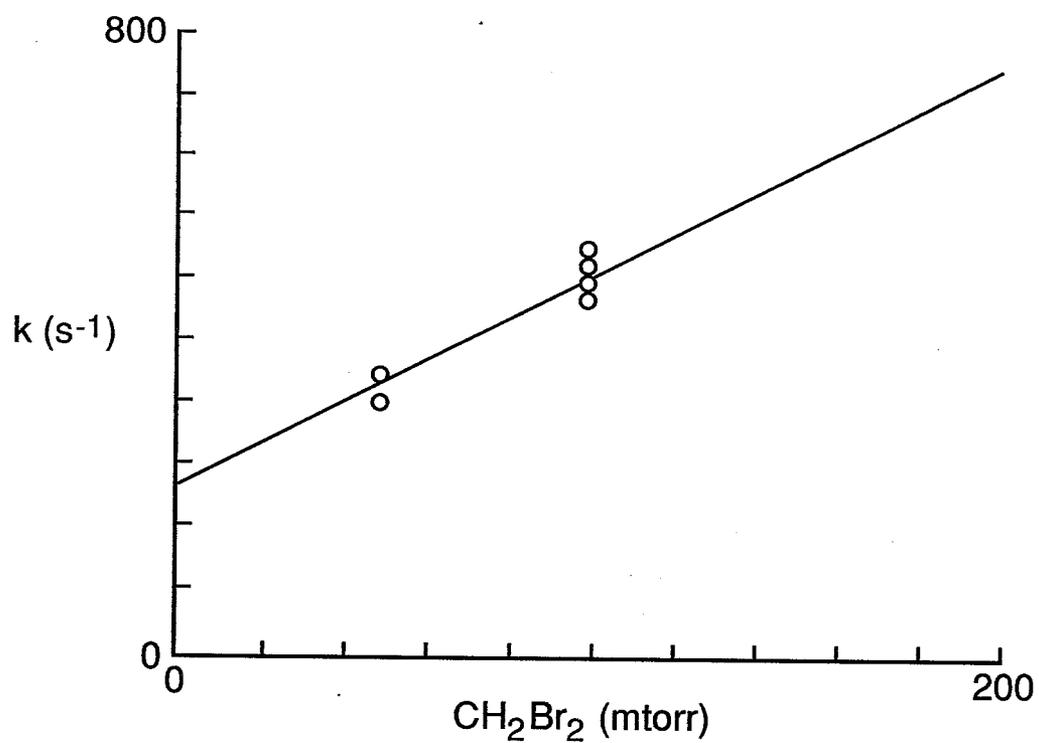


Figure A8. Plot of the First-order Rate Constant for the Decay of OH Against the Concentration of Dibromomethane.

TABLE A4. FIRST ORDER RATE CONSTANTS FOR THE REACTIONS OF OH RADICALS WITH DIFLUOROCHLOROBROMOMETHANE (HALON 1211), TRIFLUOROBROMOMETHANE (HALON 1301) AND DIBROMOMETHANE AS FUNCTIONS OF CONCENTRATION AT 298 K.

Concentration, mtorr <sup>a</sup>	First order rate constant, s <sup>-1</sup>		
	CF <sub>3</sub> Br	CF <sub>2</sub> ClBr	CH <sub>2</sub> Br <sub>2</sub>
49.7			348
49.7			317
49.7			351
49.7			353
100			490
100			510
100			447
100			473
250	82	166	
250	72	186	
250	64	185	
250		184	
500	79	277	
500	81	281	
500	89	254	
500	93		

No reactant present: 68 and 70 s<sup>-1</sup>.

a. 1mtorr=3.2×10<sup>13</sup> molec cm<sup>-3</sup> at 298 K.

calculations using the uncorrected absorption data, and for data obtained by extrapolation of the data as indicated by the dashed curve of Figure A9. The average absorption cross sections taken from the figure for the two possible sets of curves were then used to calculate rate constants for absorption using the format of Table A3. The results of the calculations are given in Table A5. We have not attempted to extend the calculations beyond 325 nm, since the experimental data are clearly in error at this point. The uncorrected data lead to an estimated absorption rate constant a factor of 4 greater than the more correct extrapolated value. The latter value is reported in Table 6.

Halon 1301, CF<sub>3</sub>Br, does not absorb strongly in the VIS-UV region as shown in Figure A9, and the rate of absorption is too small to be of any significance.

Halon 1202, CF<sub>2</sub>Br<sub>2</sub>, for which the absorption curve is shown in Figure A10, absorbs relatively strongly into the visible part of the spectrum. The rate constant for absorption, based on extrapolation of the absorption curve, is calculated in Table A6, and the results given in Table 6.

CH<sub>2</sub>Br<sub>2</sub> is similar to CF<sub>2</sub>ClBr in displaying an exponential fall-off in absorption with wavelength as shown in Figure A11, with a long tail extending into the visible, suggestive of the presence of an impurity. The data are analyzed in Table A7. The uncorrected data lead to an estimated absorption rate constant a factor of 150 greater than the more correct extrapolated value. The latter value is reported in Table 6.

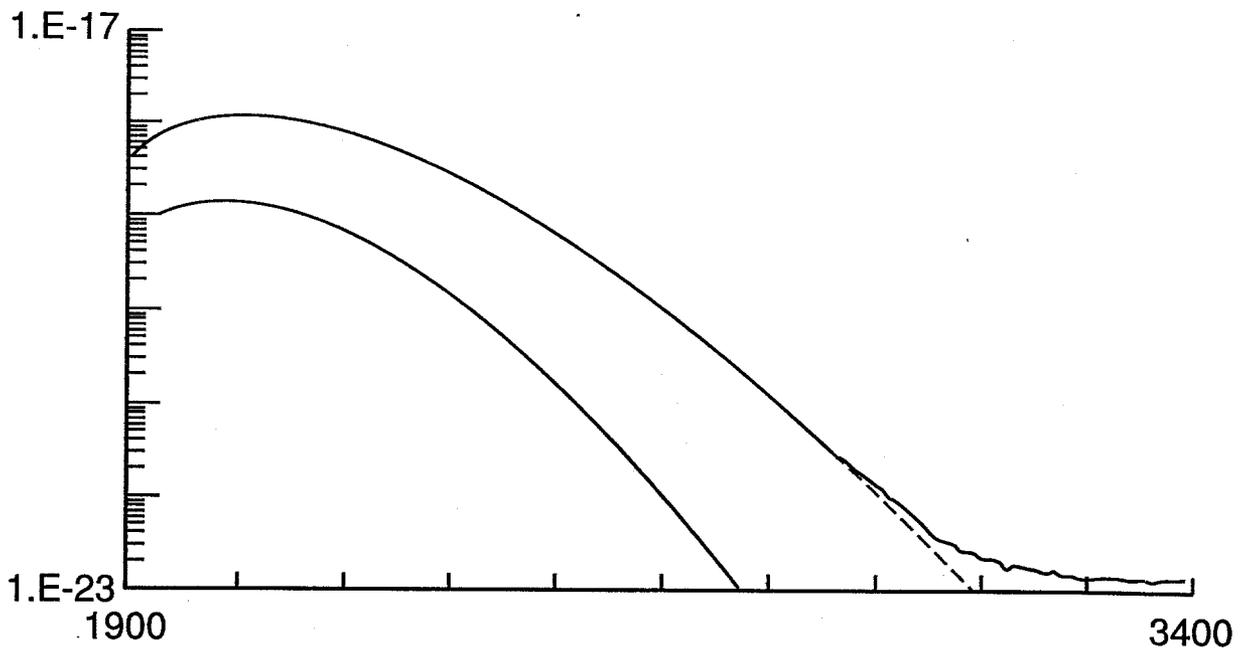


Figure A9. VIS-UV Absorption Cross Section as a Function of Wavelength for halon 1211, Upper Curve, and halon 1301, Lower Curve. For Halon 1211, Path Length 20 cm, Sample Pressure 15-418 torr. Data for halon 1301 from Reference 18.

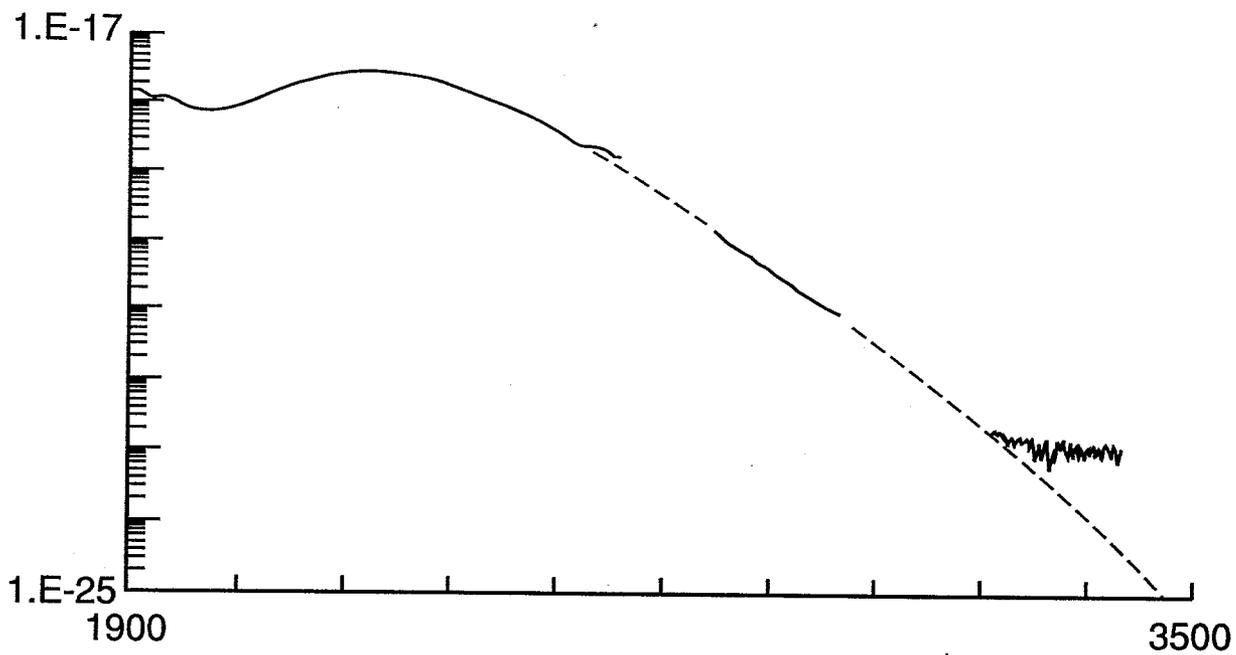


Figure A10. VIS-UV Absorption Cross Section as a Function of Wavelength for Difluorodibromomethane (halon 1202). Path Length 20 cm, Sample Pressure 5-706 torr.

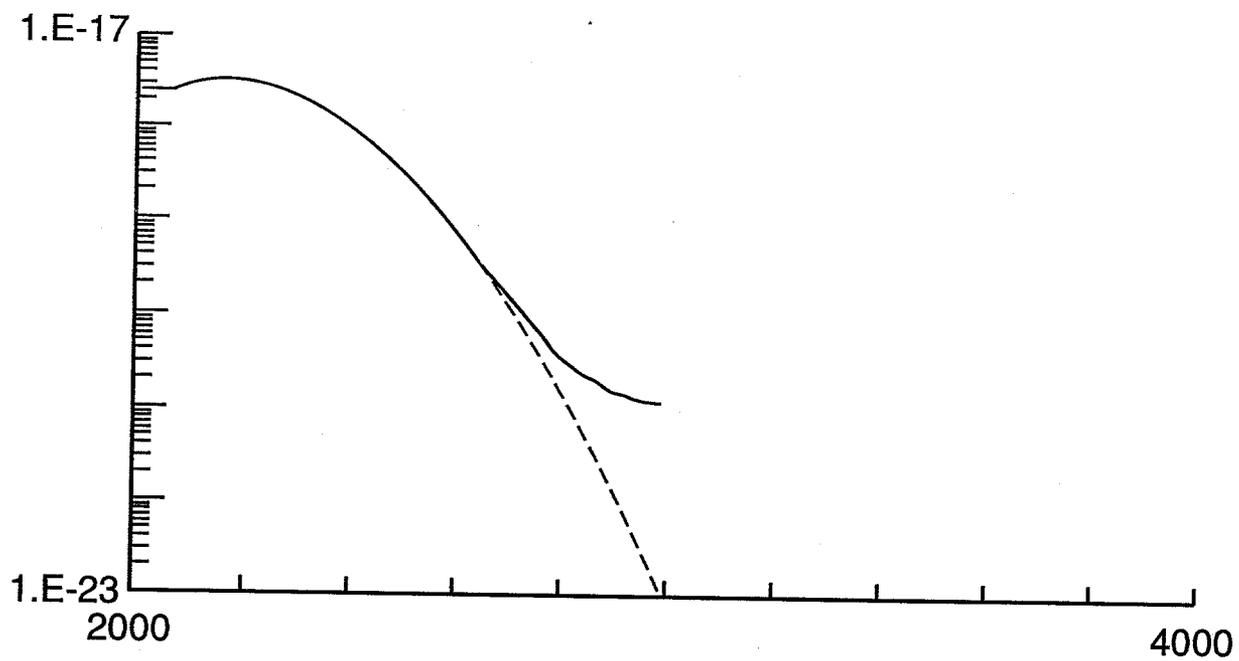


Figure A11. VIS-UV Absorption Cross Section as a Function of Wavelength for Dibromomethane. Path Length 20 cm, Sample Pressure 2-34 torr.

TABLE A5. ESTIMATION OF VIS-UV ABSORPTION RATE CONSTANT FOR DIFLUOROCHLOROBROMOMETHANE (HALON 1211).

Wavelength Interval, nm	Solar Flux, photons $\text{cm}^{-2} \text{s}^{-1}$	Average Absorption Coefficient, $\text{cm}^2 \text{molec}^{-1}$	Rate Constant, $\text{s}^{-1}$
Based on uncorrected data:			
290-295	$0.001 \times 10^{14}$	$1.1 \times 10^{-22}$	$1.1 \times 10^{-11}$
295-300	0.037	$8 \times 10^{-22}$	$3 \times 10^{-9}$
300-305	0.362	$5 \times 10^{-23}$	$1.8 \times 10^{-9}$
305-310	1.28	$2.8 \times 10^{-23}$	$3.6 \times 10^{-9}$
310-315	2.85	$1.8 \times 10^{-23}$	$5.1 \times 10^{-9}$
315-320	3.94	$1.5 \times 10^{-23}$	$7.4 \times 10^{-9}$
320-325	4.96	$1.3 \times 10^{-23}$	$6.5 \times 10^{-9}$
Total rate constant			$2.7 \times 10^{-8}$
Total rate constant/3			$9 \times 10^{-9}$
Based on extrapolation:			
290-295	$1.001 \times 10^{14}$	$1.1 \times 10^{-22}$	$1.1 \times 10^{-11}$
295-300	0.037	$6 \times 10^{-22}$	$2.2 \times 10^{-9}$
300-305	0.362	$3 \times 10^{-23}$	$1.1 \times 10^{-9}$
305-310	1.28	$1 \times 10^{-23}$	$1.3 \times 10^{-9}$
310-315	2.85	$4 \times 10^{-24}$	$1.1 \times 10^{-9}$
315-320	3.94	$1.5 \times 10^{-24}$	$6 \times 10^{-10}$
320-325	4.96	$4 \times 10^{-25}$	$2 \times 10^{-10}$
Total rate constant			$6.5 \times 10^{-9}$
Total rate constant/3			$2.2 \times 10^{-9}$

#### D. MEASUREMENT OF IR ABSORPTION CROSS SECTION

IR absorption cross sections were measured for  $\text{CF}_3\text{Br}$  (halon 1301),  $\text{CF}_2\text{ClBr}$  (halon 1211),  $\text{CF}_2\text{Br}_2$  (halon 1202), and  $\text{CH}_2\text{Br}_2$ . Partial pressures ranged from 1.8 to 3.5 torr. The absorption curves are shown in Figures A12 and A13. Table 7 gives the total integrated cross sections over the 7 to 13  $\mu\text{m}$  range and the cross sections relative to  $\text{CF}_3\text{Br}$  and  $\text{CCl}_3\text{F}$ .

TABLE A6. ESTIMATION OF VIS-UV ABSORPTION RATE CONSTANT FOR DIFLUORODIBROMOMETHANE (HALON 1202)

Wavelength Interval, nm	Solar Flux, photons $\text{cm}^{-2} \text{s}^{-1}$	Average Absorption Coefficient, $\text{cm}^2 \text{molec}^{-1}$	Rate Constant, $\text{s}^{-1}$
Based on extrapolation:			
290-295	$0.001 \times 10^{14}$	$2 \times 10^{-21}$	$2 \times 10^{-10}$
295-300	0.037	$5 \times 10^{-22}$	$1.8 \times 10^{-9}$
300-305	0.362	$2 \times 10^{-22}$	$7.2 \times 10^{-9}$
305-310	1.28	$2 \times 10^{-22}$	$2.6 \times 10^{-8}$
310-315	2.85	$8 \times 10^{-23}$	$2.3 \times 10^{-8}$
315-320	3.94	$6 \times 10^{-23}$	$4.9 \times 10^{-9}$
320-325	4.96	$1 \times 10^{-23}$	$2.1 \times 10^{-9}$
330-340	$1.5 \times 10^{15}$	$8 \times 10^{-25}$	$1.2 \times 10^{-9}$
Total rate constant			$6.8 \times 10^{-8}$
Total rate constant/3			$2.3 \times 10^{-8}$

TABLE A7. ESTIMATION OF VIS-UV ABSORPTION RATE CONSTANT FOR DIBROMOMETHANE

Wavelength Interval, nm	Solar Flux, photons $\text{cm}^{-2} \text{s}^{-1}$	Average Absorption Coefficient, $\text{cm}^2 \text{molec}^{-1}$	Rate Constant, $\text{s}^{-1}$
Based on uncorrected data:			
290-295	$0.001 \times 10^{14}$	$1.1 \times 10^{-21}$	$1.1 \times 10^{-10}$
295-300	0.037	$1 \times 10^{-21}$	$3.7 \times 10^{-9}$
300-305	0.362	$1 \times 10^{-21}$	$3.6 \times 10^{-8}$
Total rate constant			$4 \times 10^{-8}$
Total rate constant/3			$1.3 \times 10^{-8}$
Based on extrapolation:			
290-295	$0.001 \times 10^{14}$	$7 \times 10^{-23}$	$7 \times 10^{-12}$
295-300	0.037	$2 \times 10^{-23}$	$7.4 \times 10^{-11}$
300-305	0.362	$3 \times 10^{-24}$	$1.1 \times 10^{-10}$
305-310	1.28	$5 \times 10^{-25}$	$6.4 \times 10^{-11}$
Total rate constant			$2.6 \times 10^{-10}$
Total rate constant/3			$8.5 \times 10^{-11}$

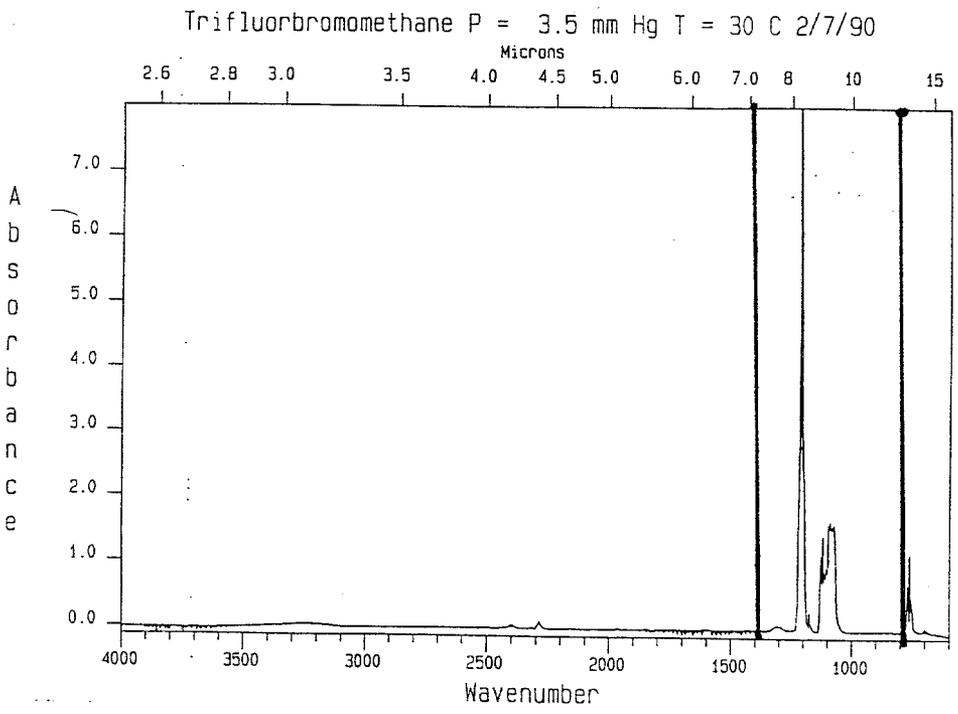
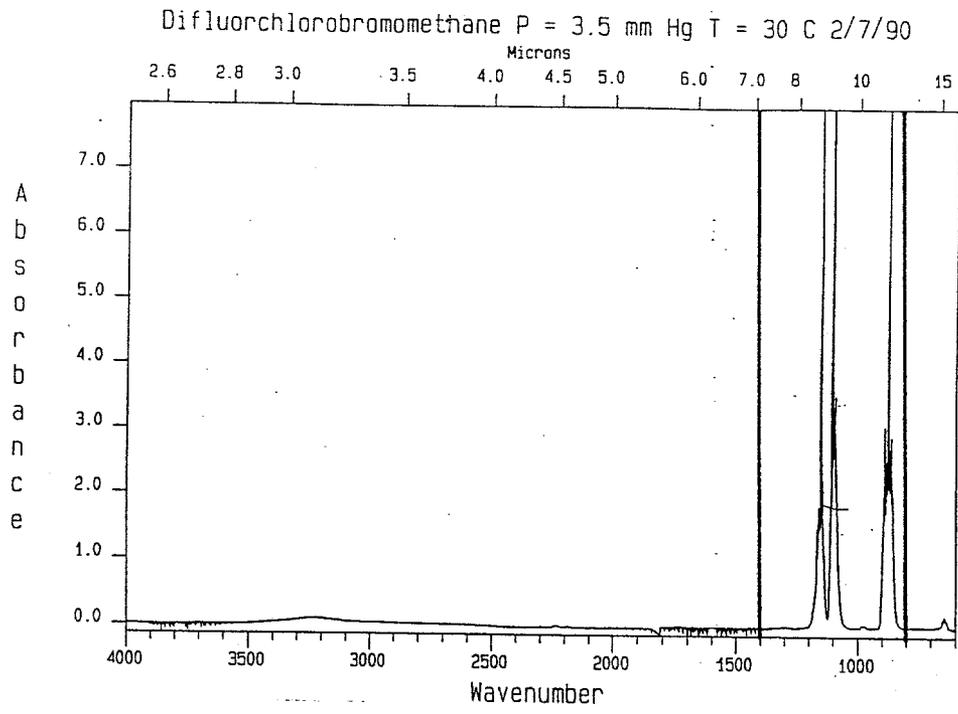


Figure A12. IR Absorption Cross Section as a Function of Wavelength for Trifluorobromomethane (halon 1301) and Difluorochlorobromomethane (halon 1211).

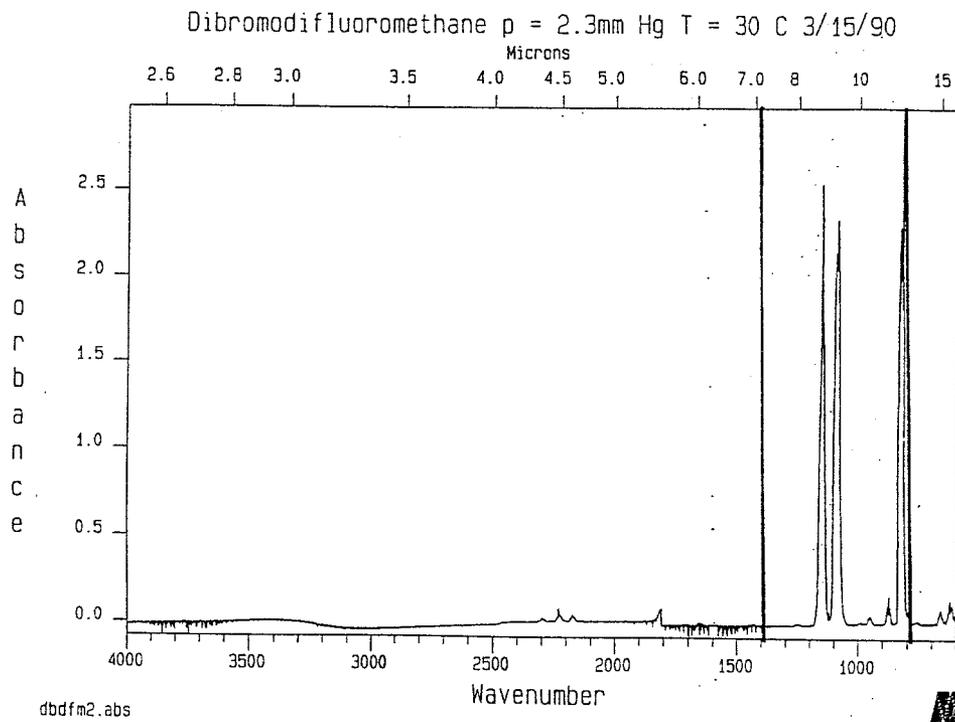
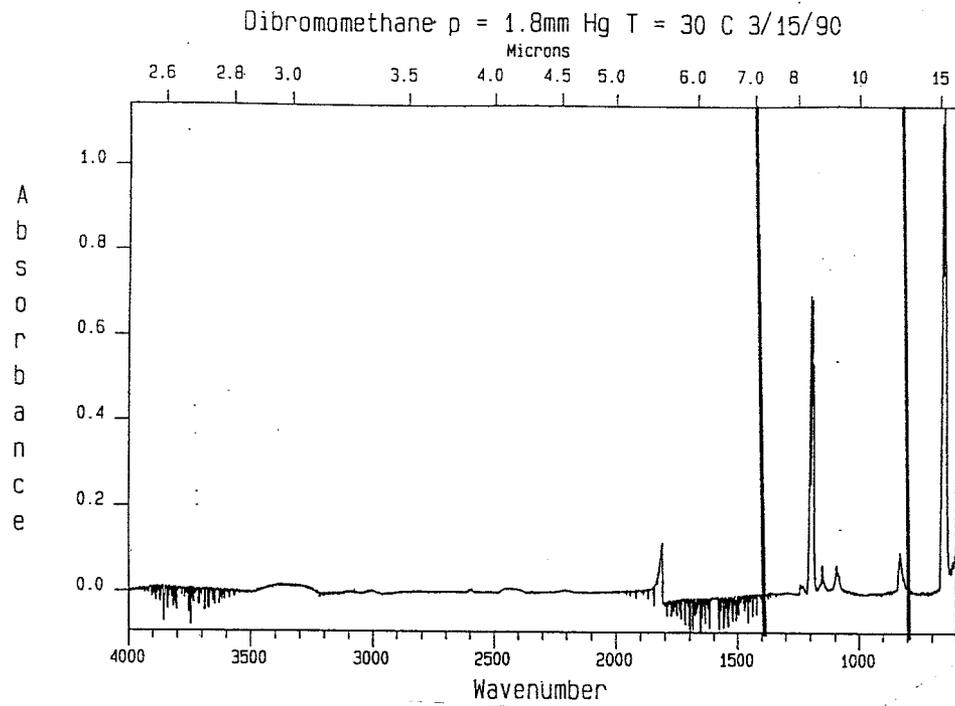


Figure A13. IR Absorption Cross Section as a Function of Wavelength for Dibromomethane and Dibromodifluoromethane (halon 1202).

## E. SUMMARY

Table 5 summarizes the results of the different test procedures applied to global warming. With reference to Table 7, it is clear that all of the halons tested here are strong absorbers in the region of the atmospheric window. Since  $\text{CF}_3\text{Br}$  (halon 1301) also has a long tropospheric lifetime, it falls in Class 2. The other compounds tested had much shorter tropospheric lifetimes. Thus,  $\text{CH}_2\text{Br}_2$ , reacted rapidly with OH, and  $\text{CF}_2\text{ClBr}$  (halon 1211) and  $\text{CF}_2\text{Br}_2$  (halon 1202) both absorbed appreciably in the VIS-UV region. These compounds all fall in Class 1.

## SECTION VI

### INHALATION TOXICITY

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## SECTION VI

### INHALATION TOXICITY

#### SECTION SUMMARY

Alternatives for the current halogenated fire extinguishing agents have to be evaluated for any potentially adverse health effects they might cause. A complete testing series for these is expensive, lengthy, and involves protocols that are still evolving. Whether or not people will die from inhaling a suppressant during a single exposure is identified as the most critical toxicological information needed to enable a decision as to whether to proceed further with the development of a particular chemical. There are no standardized tests for this assessment.

This section describes a screening protocol to assess the acute inhalation toxicity of proposed halon substitutes at their effective use levels. It is based on an apparatus and procedure in widespread use. Chemicals that perform acceptably in this initial toxicity screen and the screens covered in the other sections of this report would then undergo the extensive and expensive additional toxicity testing necessary to assure they do not constitute an undue risk to the public health and safety.

In this screening test, two sets of six rats are exposed for 30 minutes to the test chemical at twice the concentration necessary for fire suppression effectiveness to assure that the compound will not be lethal under severe exposure conditions. These time-concentration exposure conditions are considerably more severe than the potential actual exposures.

The results of the test place a chemical into one of two classes:

- Class 1: All test animals survive both the 30-minute exposure period and a 7-day observation period with no lasting ill effects.
- Class 2: Any of the test animals die during either the 30-minute exposure or the 7-day observation period.

If more time, money and chemical were available, the option of determining a complete  $LC_{50}$  is suggested.

[The chemicals formed when a suppressant is decomposed in a fire are not tested. This is because the smoke from all fires is quite toxic to breathe and it is unlikely that a substitute agent will produce products more toxic than those from the currently-used halons.]

The results from testing 4 halocarbons indicate that the test is capable of distinguishing among compounds whose toxicity is less than or greater than twice the concentration recommended for fire suppression effectiveness.

A team of trained technicians can perform the two tests in about one day. A senior professional is needed to determine the exposure concentration of the chemical, occasionally to observe the animals' demeanor, and to interpret the results at the end of the seven-day post-exposure period. No more than two moles of chemical is needed, with the amount depending on the results of the fire suppression efficiency screen. The estimated cost to test each chemical is \$1500.00. This does not include the cost of the chemical, nor the cost of removing potentially toxic impurities from the chemical.

## **A. BACKGROUND**

### **1. Introduction**

Alternatives for the current halogenated fire extinguishing agents have to be evaluated for any potentially adverse health effects they might cause. A complete test series for these is expensive, lengthy, and involves protocols that are still evolving. It is therefore necessary to identify and measure the most critical toxicological feature to decide whether to proceed further with the evaluation of a candidate suppressant. This section will:

- discuss the breadth of potential health and environmental effects and governmental responsibility to assure public safety,
- review the literature on the toxicity of the halons in current use and some potential alternatives, and
- describe a screening protocol to assess the acute inhalation toxicity of proposed halon substitutes at their effective use levels.

Chemicals that perform acceptably in this initial toxicity screen and the screens covered in the other sections of this report would then undergo the extensive and expensive additional toxicity testing necessary to assure they do not constitute an undue risk to the public health and safety.

### **2. Testing for Health and Environmental Concerns**

The potential toxicological problems include effects of the unheated halons as well as the combustion products formed from these chemicals during and following exposure to fires on:

- individuals that are in the fire vicinity,
- firefighters who may dispense the chemicals,
- workers making or transporting the chemicals, and
- the environment (either air, water, or land) from the disposal of the chemicals or from waste from the manufacturing processes.

The Office of Toxic Substances of the EPA will be evaluating the health and environmental data on proposed CFC and halon substitutes [1]. The Office of Air and Radiation (OAR) will be responsible for the domestic implementation of the Montreal Protocol, and the Office of Water (OW) will be also examining the data [2]. Although the fire suppressants are a much smaller part of the overall problem, alternatives will not likely be placed in the market with any less scrutiny than the CFC substitutes. In fact, since the halon alternatives will be used under combustion conditions, they should be evaluated under both ambient and combustion or heated conditions.

The Program for Alternative Fluorocarbon Toxicity Testing (PAFT) is an international consortium of industrial companies involved in producing CFC's and/or their substitutes. EPA and PAFT are cooperating to determine an acceptable testing program. The Office of Toxic Substances has initiated a new program entitled "CFC Substitutes Human Health and Environmental Effects Program." They will select chemicals for review and assessment and review all proposed CFC substitutes, including new chemicals, those already in use, and those on EPA's list of chemicals, but not in commercial use [2]. PAFT has been testing a number of potential CFC alternatives and has some data, which were presented at a recent meeting of the

American College of Toxicology [3]. Realizing that timeliness will be a problem, EPA has decided that interim assessments will be necessary before all of the data are available. The interim assessments will begin early in 1990 and will allow for tentative approvals to proceed with further testing. The complete assessments, however, will have to wait until all the testing is complete and the data are evaluated.

The discussions between the EPA and PAFT as to the adequacy of the PAFT testing scheme will lead to the establishment of TSCA regulatory requirements for the submission of test results for the fluorocarbon substitutes. However, the precise toxicity test requirements do not yet exist as implementation criteria and the exact methods have not been agreed upon.

For its assessment, the EPA needs information including production levels, use categories, and exposure data from manufacturers and processors of these chemicals [2]. Although the EPA has agreed that the precise data requirements will be decided on a case-by-case basis, they have provided a list of toxicity and safety tests routinely required under Toxic Substances Control Act [TSCA section 4(a)(1)(B)] needed to assess risk. This list includes:

- Acute toxicity (high exposure-short duration studies)
- Combustion Toxicity
- Chronic toxicity
- Subchronic toxicity
- Two-generation reproductive effects
- Developmental toxicity
- Oncogenicity
- Pharmacokinetics (absorption, distribution, metabolism, kinetics, excretion)
- Neurotoxicity (functional observation battery, neuropathology, motor activity, etc.)
- Mutagenicity
- Safety considerations (flammability, volatility, reactivity, etc.)
- Environmental effects (acute and chronic testing on aquatic and terrestrial species, including plants)
- Environmental fate (transport, transformation, bioaccumulation, physical chemical properties, etc.)

The complete toxicity testing could take as long as 5 years and is quite costly. Table 1 provides some approximate costs as of 1986 of various toxicity tests [4].

Under the Significant New Use Regulations (SNUR Criteria), the

"...EPA may determine that the data support a concern about a substance's health or environmental effects if EPA makes any one of the following findings:

1. The substance may cause carcinogenic effects because the substance:
  - a. has been shown by valid test data to cause carcinogenic effects in humans or in at least one species of laboratory animal;
  - b. has been shown to be a possible carcinogen based on the weight of the evidence in short-term tests indicative of the potential to cause carcinogenic effects;
  - c. is closely analogous, based on toxicologically relevant similarities in molecular structure and physical properties, to another substance that has been shown by test data to cause carcinogenic effects in humans or in at least one species of laboratory animal, provided that if there is more than one such analogue, the greatest weight will be given to the relevant data for the most appropriate analogues; and

TABLE 1. TYPICAL COSTS OF DESCRIPTIVE TOXICITY TESTS [5]

Test	Cost (dollars)
Acute toxicity (rat; 2 routes)	6,500
Acute dermal toxicity (rabbit)	3,000
Acute inhalation toxicity (rat)	6,500
Acute dermal irritation (rabbit)	700
Acute eye irritation (rabbit)	500
Skin sensitization (guinea pig)	7,000
Repeated dose toxicity	
14 day exposure (rat)	40,000
90 day exposure (rat)	100,000
1 year (diet; rat)	200,000
1 year (oral gavage; rat)	260,000
2 year (diet; rat)	470,000
2 year (oral gavage; rat)	600,000
Genetic toxicology tests	
Reverse mutation assay ( <i>S. typhimurium</i> )	1,500
Mammalian bone marrow cytogenetics ( <i>in vivo</i> ; rat)	16,000
Micronucleus test (rat)	4,500
Dominant lethal (mouse)	15,000
Host mediated assay (mouse)	6,000
Drosophila	20,000
Reproduction	
Phase I (rat)	30,000
Phase II (rat)	20,000
Phase II (rabbit)	30,000
Phase III (rat)	22,000
Acute toxicity in fish (LC <sub>50</sub> )	1,500
Daphnia reproduction study	1,500
Algae growth inhibition	1,500

- d. is known or can reasonably be anticipated, based on valid scientific data or established scientific principles, to be metabolized in humans or transformed in the environment to a substance which may have the potential to cause carcinogenic effects under the criteria in paragraphs a, b, or c above.
2. The substance has been shown by valid test data to cause acutely toxic effects in at least one species of laboratory animal or is closely analogous, based on toxicologically relevant similarities in molecular structure and physical properties, to another substance that has been shown by valid test data to cause acutely toxic effects in at least one species of laboratory animal, provided that if there is more than one such analogue, the greatest weight will be given to the relevant data for the most appropriate analogues.

3. The substance may cause serious chronic effects, serious acute effects or developmentally toxic effects under reasonably anticipated conditions of exposure because the substance:
  - a. has been shown by valid test data to cause serious chronic effects, serious acute effects, or developmentally toxic effects in humans or in at least one species of laboratory animal at dose levels that could be of concern under reasonably anticipated conditions of exposure;
  - b. is closely analogous, based on toxicologically relevant similarities in molecular structure and physical properties, to another chemical substance that has been shown by valid test data to cause serious chronic effects, serious acute effects, or developmentally toxic effects in humans or in at least one species of laboratory animal at dose levels that could be of concern under reasonably anticipated conditions of exposure, provided that if there is more than one such analogue, the greatest weight will be given to the relevant data for the most appropriate analogues;
  - c. is known or can reasonably be anticipated, based on valid scientific data or established scientific principles, to be metabolized in humans or transformed in the environment to a substance which may have the potential to cause serious chronic effects, serious acute effects, or developmentally toxic effects under the criteria in paragraphs a and b above; and
  - d. has been shown to potentially cause developmentally toxic effects based on the weight of the evidence in short-term test indicative of the potential to cause developmentally toxic effects.
4. The substance may cause significant adverse environmental effects under reasonably anticipated exposures because the substance:
  - a. has been shown by valid test data to cause significant adverse environmental effects at dose levels that could be of concern under reasonably anticipated exposures;
  - b. is closely analogous, based on toxicologically relevant similarities in molecular structure and physical properties, to another substance that has been shown by valid test data to cause significant adverse environmental effects at dose levels that could be of concern under reasonably anticipated conditions of release, provided that if there is more than one such analogue, the greatest weight will be given to the relevant data for the most appropriate analogues;
  - c. has been determined, based on calculations using the substance's physical and chemical properties, to be potentially able to cause significant adverse environmental effects at dose levels that could be of concern under reasonably anticipated exposures; and
  - d. is known or can reasonably be anticipated, based on valid scientific data or established scientific principles, to be environmentally transformed to a substance which may have the potential to cause significant adverse environmental effects under the criteria in paragraphs a, b, or c above.
5. Concern exists about the health or environmental effects of one or more impurities or byproducts of the substance because the impurity or byproduct meets one or more of the criteria discussed above and either:

- a. the impurity or byproduct is a new chemical substance (not on the TSCA section 8(b) inventory) and may be present in concentrations that could cause adverse health or environmental effects under reasonably anticipated exposures; or
- b. reasonably anticipated manufacture, processing, or use activities involving the CFC substitute may result in significantly increased human exposure to or environmental release of the impurity or byproduct compared to exposure or release levels resulting from existing activities involving the impurity or byproduct.

EPA will designate as significant new use only those activities that may be accompanied by changes in exposure or release levels that are significant in relation to the health or environmental concerns identified in 1 through 5 above." [2]

Additional tests have been proposed by the EPA Office of Water if significant amounts of any of the substitutes will be released into the water supplies [2].

### **3. Toxicological Property to be Screened**

For future fire extinguishing agents, an assessment of all of the above health and safety issues has to include consideration of the likelihood of exposure. Thus, an extinguishant of modest toxicity may still be acceptable if the exposure during a fire and its manufacture can be minimized. The toxicity, however, must first be measured to determine the latitude that might be allowed.

As noted above, there are a number of harmful effects that could be caused by exposure to a chemical. For the issue here, the most critical need is survival of a single exposure, such as occurs when a fire is suppressed in an occupied compartment. Therefore, a screening test should measure the acute inhalation lethality of a candidate fire suppressant.

Suppressants are generally decomposed to some degree as they put out the fire. This suggests the need to screen not only the agent itself, but also the products produced when it breaks down. Such a method is not included as a screen for the following reasons:

- The smoke from all fires is quite toxic to breathe. The decomposition products from the suppressant are unlikely to increase that substantially.
- The decomposition products of the currently-used halons include the highly toxic hydrogen bromide (HBr), hydrogen fluoride (HF), and hydrogen chloride (HCl). It is unlikely that a substitute agent will produce compounds that are more toxic.

### **B. TOXICITY OF HALOGENATED HYDROCARBONS**

The acute inhalation toxicity data for halons 1301, 1211, 2402, 1202, and a few other halogenated hydrocarbons which have been used as fire extinguishing agents are presented in Table 2 and discussed below. This discussion is extended to some potential alternative suppressants, the data for which were used as a basis for selecting exposure conditions appropriate for a screening test method.

TABLE 2. TOXICITY OF HALOGENATED HYDROCARBONS<sup>a</sup>

Compound	Atoms in molecule					15 minute ALC (ppm)		Maximum safe exposure to man for one minute (%)	Fire extinguishment V/V agent in heptane (%)	F factor <sup>c</sup>
	C	F	Cl	Br	I	Agent	Dec. Products <sup>b</sup>			
CBrF <sub>3</sub>	1	3	0	1	0	832,000	14,000	7-10	3.5	0.8
CBrClF <sub>2</sub>	1	2	1	1	0	324,000	7,650	5	3.8	4.5
C <sub>2</sub> Br <sub>2</sub> F <sub>4</sub>	2	4	0	2	0	126,000	1,600		2.1	14.0
CBr <sub>2</sub> F <sub>2</sub>	1	2	0	2	0	54,000	1,850		2.4	
CH <sub>2</sub> BrCl	1	0	1	1	0	65,000	4,000		4.5	64
CCl <sub>4</sub>	1	0	4	0	0	28,000	300			129
CH <sub>3</sub> I	1	0	0	0	1	5,900	9,600		5.1	
CO <sub>2</sub>						658,000	658,000		20.5	6

a. Data from reference [5].  
 b. Thermal decomposition products.  
 c. The F factor is the ratio of the concentration required to extinguish a fire divided by the concentration which will give rise to the early symptoms of narcosis [5,6].  
 ALC. Approximate lethal concentration.

### 1. Halon 1301 [7,8]

Halon 1301 seems to be the least toxic of all of the halogenated fire extinguishing agents that have been used. However, limits have been promulgated for exposing people to it.

- Based on the results of toxicological tests, the National Fire Protection Association has recommended that the length of time of human exposure not be longer than 15 minutes if the concentration is 7 percent or lower, not be longer than 1 minute for concentrations between 7 and 10 percent, and not be longer than 30 seconds if the concentration is 10 to 15 percent. Above 15 percent, there should be no human exposure [9].
- OSHA 1910.162(b)(6) has more stringent regulations [10]. They recommend egress in one minute from environments with 7 percent, 30 second egress from areas up to 10 percent, and no concentrations greater than 10 percent if the area is normally occupied and cannot be evacuated in less than 30 seconds.

The primary toxicological effects of high concentrations of halon 1301 are on the cardiovascular system and the central nervous system (CNS). Heart arrhythmias and ventricular fibrillation have been noted, especially in conjunction with high levels of epinephrine (adrenaline). Such cardiac sensitization has been observed in animals which have received injected epinephrine and been exposed to concentrations of halon 1301 of 7.5 percent or higher. Mullin et al. [11] were able to produce serious cardiac arrhythmias in dogs exposed to concentrations of 7.5 percent or greater if also given intravenous injections of

epinephrine of 8 to 10  $\mu\text{g}/\text{kg}$ . Two dogs exposed to 80 percent halon 1301 plus 10  $\mu\text{g}/\text{kg}$  of epinephrine experienced ventricular fibrillation and cardiac arrest [12]. Some alteration of cardiovascular function was seen in all dogs exposed to 20 percent or greater concentrations of halon 1301. The first symptom was an irregular increase in heart rate. At higher concentrations (50 to 80 percent), hypotension was also noted. Monkeys and baboons exposed to 80 percent halon 1301 plus 10  $\mu\text{g}/\text{kg}$  of epinephrine only showed brief periods of ventricular fibrillation and no deaths. In all cases, the cardiovascular effects were reversed when the animals were returned to room air. Depending on the concentration of halon 1301 and species of animal tested, this halon can either stimulate or depress the CNS to produce effects ranging from tremors and convulsions to lethargy and unconsciousness. Some dogs had epileptiform convulsions after a 12 minute exposure to 50 percent halon 1301. Twenty percent halon 1301 caused visible agitation and tremors. The central nervous system responses of the monkeys were different from the dogs. The monkeys showed cortical depression rather than the agitation seen in the dogs.

Humans exposed to concentrations of halon 1301 greater than 10 percent have experienced dizziness and reduced physical and mental dexterity [13]. With concentrations from 7 to 10 percent, they experienced tingling in their extremities and dizziness. Less than 7 percent had little effect. Like the animal experiments, removal of the halon eliminated all symptoms.

The decomposition products of halon 1301, when exposed to flames or hot surfaces (above  $950^{\circ}\text{C}$ ), include HBr, HF, and perhaps trace quantities of bromine ( $\text{Br}_2$ ), carbonyl fluoride ( $\text{COF}_2$ ), and carbonyl bromide ( $\text{COBr}_2$ ). The most noticeable effect of exposure to the decomposition products is sensory irritation. This irritation becomes severe well in advance of the hazardous levels [13].

## 2. Halon 1211 [14-16]

The maximum safe exposure for humans reported in the literature is 4 to 5 percent for one minute. Exposure to lower levels is probably safe for several minutes. However, prolonged exposures to concentrations higher than 4 percent is likely to cause unconsciousness and even death. The effects of the exposures disappear upon removal from the area. For these reasons, total flooding systems are allowed only in areas that are not normally occupied or can be evacuated in less than 30 seconds.

Experiments conducted by Underwriters' Laboratories indicated that halon 1211 was more toxic than halon 1301, but less toxic than halon 2402. Rats and guinea pigs have been exposed to various concentrations of halon 1211. The lethal concentrations found in rats were 22 percent for 140 minutes, 23 percent for 30 minutes, 30 to 32 percent for 15 minutes (Table 2). Guinea pigs died in 15 to 30 minutes from exposures of 23 percent. All animals experienced a severe depression of the central nervous system prior to death and all survivors recovered promptly following the exposures. Halon 1211 can first stimulate, then depress the CNS to give first muscular tremors and then narcosis. Rats, mice, guinea pigs, rabbits, cats, dogs, and a monkey all experienced tremors when exposed to concentrations of 10 percent or higher. (In Section E, it will be noted that rats exposed to 10 percent halon 1211 in our laboratory also experienced tremors throughout the 30 minute exposures but recovered fully when returned to normal conditions.) Convulsions were also noted. If the exposures were stopped, the animals recovered. If the experiments continued, then the animals would become comatose and their breathing would become slower and shallower until death occurred. Concentrations lower than 10 percent showed little or no effects. Rats exposed to 1 percent for six hours/day for three weeks showed only a slight lethargy and no histopathology. Like halon 1301, cardiac sensitization was also noted with halon 1211. Dogs were especially sensitive and cardiac arrhythmias were noted during exposures to 1 to 2 percent halon 1211 when the animals also received epinephrine.

Humans exposed to 4 to 5 percent halon 1211 became dizzy and light-headed after 30 to 40 seconds. After one minute, the dizziness was quite pronounced and tingling of the fingers and toes occurred. Further exposure indicated that the CNS would be affected and even a transient disorder of the heart beat was

noted after 2 minutes. Recovery was rapid when removed from the test atmosphere. There were no subsequent effects.

Thermal decomposition of halon 1211 will occur if the compound is exposed to a flame or a surface above 500°C. The decomposition products are mainly HF, HCl, HBr, Cl<sub>2</sub>, Br<sub>2</sub>, and traces of the carbonyl halides - COF<sub>2</sub>, COCl<sub>2</sub>, and COBr<sub>2</sub>.

### 3. Halon 2402 [17-19]

Although halon 2402 is a more efficient fire extinguishing agent, it is more toxic than halons 1301 and 1211 (Table 2) and has not been used extensively in this country. Many experiments have been conducted to determine its toxicity. Some of these data are presented in Table 3. A few experiments with humans indicate that concentrations as low as 0.2 percent for 2 minutes can cause disorientation and dizziness. Like halons 1301 and 1211, the pyrolysis products are significantly more toxic than the undecomposed compound.

TABLE 3. TOXICOLOGICAL DATA ON HALON 2402<sup>a</sup>

Temperature	Species	Concentration (ppm)	Exposure time	Effects
Ambient	human	1000	4 hrs	slight dizziness
	human	2200	2 min	disorientation, dizziness, unable to maintain balance
	rats	260000	15 min	no deaths
	rats	260000	30 min	2/4 deaths
	rats	125000	15 min	lowest concentration causing death
	rats	125000	15 min	pulmonary irritation
	rats	120000	60 min	8/8 deaths
	rats	60000	60 min	no deaths
	rats	10000	7 hrs	no deaths
	guinea pigs	120000	60 min	1/8 deaths
	guinea pigs	60000	60 min	no deaths
	guinea pigs	10000	7 hrs	no deaths
	mice	40000	2 hrs	fatal
	mice	28000	2 hrs	50% fatal
	mice	18000	2 hrs	lowest concentration causing death
	mice	14000	2 hrs	maximum tolerated concentration
	rabbits	50000	---	convulsive movements
	rabbits	1300	---	interfered with unconditioned reflex response
	rats and mice	43000	10 min	changes in enzymatic activities in mitochondria
	dogs	2500	---	marked cardiac arrhythmias, deaths from ventricular fibrillation
800°C	rats	1600	15 min	lowest concentration causing deaths
	rats	1600	15 min	pulmonary edema, occluded lumen of trachea and alveoli

a. References: 18-20.

### 4. Potential Alternatives

At the present time, other groups (in particular, PAFT) have been examining potential CFC alternatives. Since a non-flammable CFC substitute may also be suitable as a halon alternative, it is worth

TABLE 4. CFC ALTERNATIVES UNDER REVIEW

Designation	Structure	Flammability	Alternative for	Structure
22	CHClF <sub>2</sub>		115	C <sub>2</sub> ClF <sub>5</sub>
123	CHCl <sub>2</sub> CF <sub>3</sub>	NF	11, 113	CCl <sub>3</sub> F, C <sub>2</sub> Cl <sub>3</sub> F <sub>3</sub>
124	CHClFCF <sub>3</sub>	NF	114	C <sub>2</sub> Cl <sub>2</sub> F <sub>4</sub>
125	C <sub>2</sub> HF <sub>5</sub>		115	C <sub>2</sub> ClF <sub>5</sub>
134a	CH <sub>2</sub> FCF <sub>3</sub>	NF	114	C <sub>2</sub> Cl <sub>2</sub> F <sub>4</sub>
141b	CH <sub>3</sub> CCl <sub>2</sub> F	F	113	C <sub>2</sub> Cl <sub>3</sub> F <sub>3</sub>
142b	CH <sub>3</sub> CClF <sub>2</sub>	F	114	C <sub>2</sub> Cl <sub>2</sub> F <sub>4</sub>
152a	CH <sub>3</sub> CHF <sub>2</sub>	F	114	C <sub>2</sub> Cl <sub>2</sub> F <sub>4</sub>

examining the CFC data that have been collected. There are eight chemicals that are already being examined as potential CFC alternatives (Table 4).

The potential replacements are HCFC 22, HCFC 123, HCFC 124, HCFC 125, HCFC 134a, HCFC 141b, HCFC 142b, and HCFC 152a. PAFT has started the toxicological examination of five of these chemicals (123, 124, 125, 134a, and 141b). The other three are chemicals in current use; therefore, human health and environmental data are already available for EPA to examine. Only the nonflammable alternatives - HCFC 123, HCFC 124, and HCFC 134a - could be considered as possible halon replacements.

The initial toxicological data on HCFC 123 and HCFC 134a were presented at a recent meeting of the American College of Toxicology held in Williamsburg, VA, in October, 1989. Results for HCFC 123 (2,2-dichloro-1,1,1-trifluoroethane) [20] indicated a low order of toxicity in both acute and chronic tests. Rat studies showed an oral ALD of 9000 mg/kg, a 4 hour LC<sub>50</sub> of 32000 ppm, and non-significant skin absorption (LD<sub>50</sub> > 2000 mg/kg). Rabbit tests also showed similar skin absorption, no indication of dermal irritation potential, but some mild-to-moderate eye irritation. In dogs, cardiac sensitization was induced by injections of adrenalin and exposure to HCFC 123. The EC<sub>50</sub> for cardiac sensitization was 19000 ppm. Chronic exposures of 6 hours/day, 5 days/week for 4 weeks at concentrations  $\geq$  20000 ppm showed CNS depression, slight decreases in weight gain and slight liver damage. Pregnant rabbits and rats were exposed to concentrations of 5000 and 10000 ppm, respectively, during a critical part of their gestation and showed no evidence of teratogenicity or embryotoxicity. There was only slight maternal toxicity. No mutagenic potential was observed following *in vitro* and *in vivo* testing. The 2-year carcinogenic studies were started in January, 1989. Rats are being exposed to concentrations of 0, 300, 1000, and 5000 ppm for 6 hours/day, 5 days/week.

The toxicity of 134a also appears to be low [21]. The 4 hour LC<sub>50</sub> in the rat is greater than 500000 ppm. Acute symptoms indicate a CNS depression and anesthetic effects at sub-lethal levels. Cardiac sensitization in dogs was seen at concentrations above 75000 ppm. A 90 day study in which rats were exposed for 6 hours/day, 5 days/week showed the no effect level was 50000 ppm. Inhalation teratogenicity studies in rats and rabbits did not disclose any teratogenic effects, although some minimal maternal toxicity was apparent at 40000 ppm in rabbits and some maternal and embryo-fetal toxicity was noted in rats at 100000 ppm. *In vitro* and *in vivo* short-term tests indicated that 134a is not genotoxic. After 125 weeks, no carcinogenicity has been noted in rats receiving daily oral doses of 300 mg/kg body weight (in corn oil). A two year inhalation combined chronic toxicity/carcinogenicity study in rats is currently being conducted. Exposure levels are 0,

5000, 15000, and 50000 ppm for 6 hours/day, 5 days/week for 104 weeks. A radio-labelled material study has shown that 134a is not transformed in the body, does not accumulate in any organ and is quickly eliminated via respiration.

### C. SCREENING METHOD DEVELOPED

While a number of measurements of acute inhalation toxicity have been reported, there are no standard tests. It is thus necessary to design a method for this program, combining the essence of prior work with the exposures likely to be experienced in the vicinity of a fire. The design of the new method was based on the following guidance:

- An animal test is necessary. It is, of course, desirable to make use of structure-activity relationships, but these do not exist in reliable, readily-available form for the expected diversity of chemicals to be screened.
- Small rodents are reasonable subjects. They have been used extensively in similar tests, and they are more genetically homogeneous and less expensive than higher-order mammals.
- The screen exposure should be at least several minutes. This is longer than is needed to leave a burning room, but handicapped or injured people will need more time. Also workers manufacturing the suppressant and firefighters dispensing it could be exposed for longer times.
- The screen exposure should be to a constant concentration of suppressant. This enables comparison with the currently-used suppressants and among candidate replacements.
- The exposure concentration should be based on the amount of chemical needed to suppress the fire. The concentration should thus be higher for a less efficient fire suppressant.

The procedure we developed measures the survival of rats exposed for 30 minutes to the test compound at a concentration twice the concentration estimated for fire extinguishment from Section III. The apparatus is essentially that designed for the National Bureau of Standards (NBS) Toxicity Test Method (Figures 1 and 2) [22]. Further information about the procedure is as follows:

- Two experiments, each with six rats, are conducted.
- The tested concentration is twice that necessary for fire extinguishment since, in many cases, the engineering specifications require a backup system in case of failure of the first flooding system. Also the installed amount of chemical could be higher than required if the standard-size container holds more suppressant than that needed for the room at hand. Another factor to consider is that individuals near the dispensing nozzle(s) may be exposed to higher concentrations during the early part of the extinguishment process.
- The animals are exposed for 30 minutes to introduce a safety factor into the screen.
- The toxicological endpoint is death.

A full description of the test procedure appears in the appendix to this section. If more time, money and chemical were available, the option of determining the complete LC<sub>50</sub> is suggested.

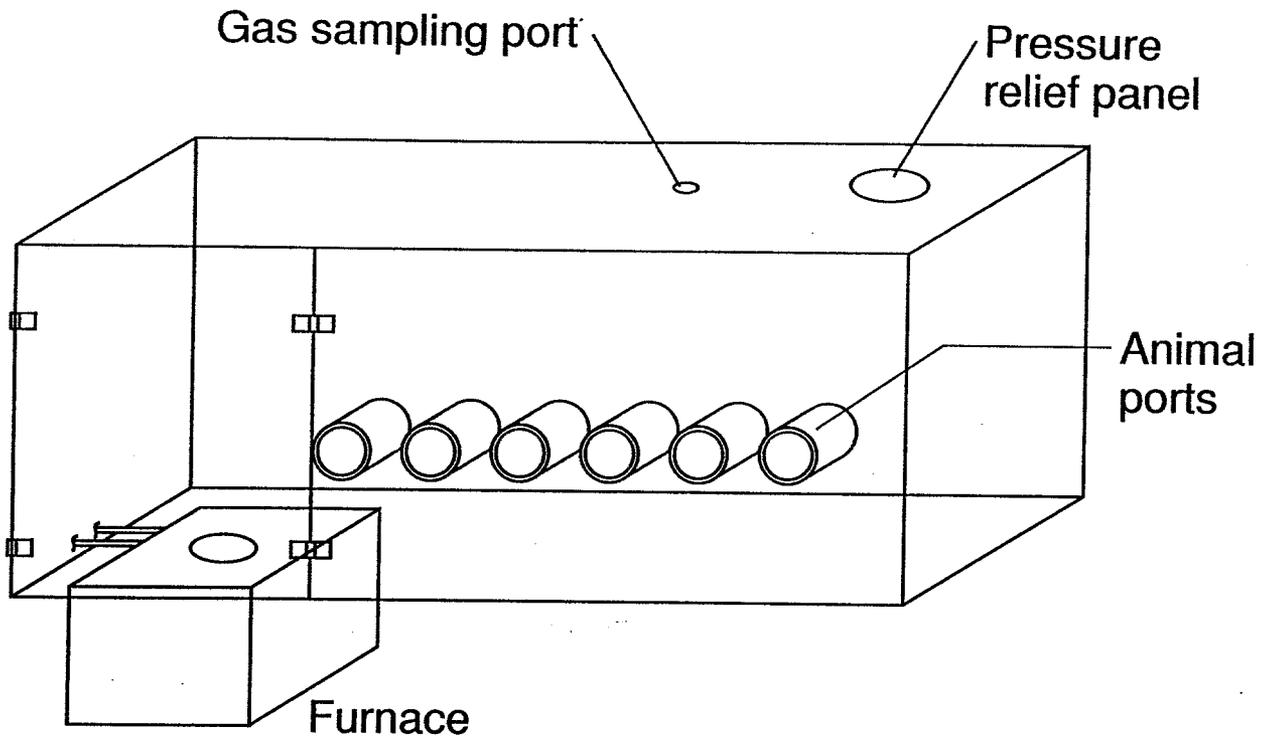


Figure 1. Animal Exposure Chamber

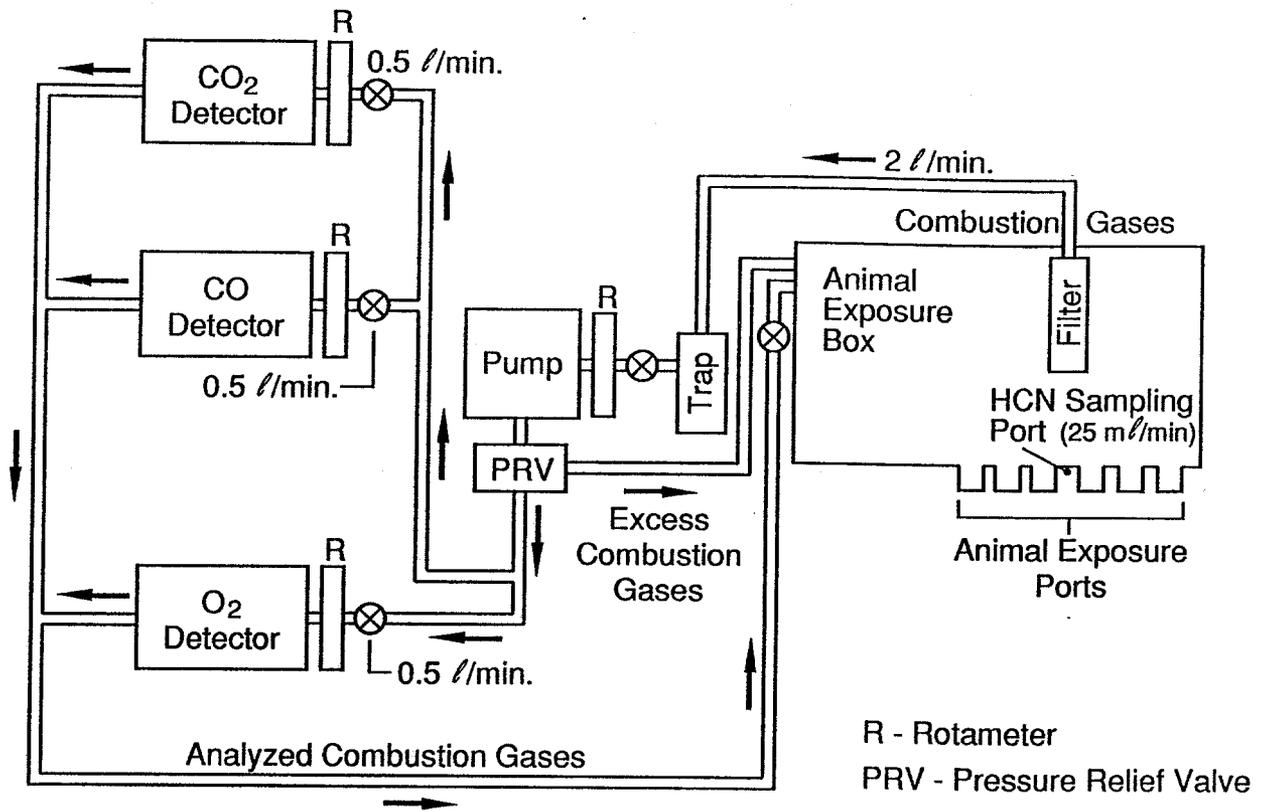


Figure 2. Schematic of NBS Toxicity Test Method

## D. CRITERIA

The results of the test place a chemical into one of two classes:

- Class 1: All test animals survive both the 30-minute exposure period and a 7-day observation period with no lasting ill effects.
- Class 2: Any of the test animals die during either the 30-minute exposure or the 7-day observation period.

A single rat dying during only one of the two tests may well be because the rat was unhealthy from the start. If this happens, a third exposure of six animals should be performed. If no animals die, then the chemical should be placed into Class 1; if any die, then the chemical should be placed into Class 2.

## E. PERFORMANCE DATA

For this series of experiments, halons 1301, 1211, and 1202 and methyl chloride (halon 101) were all obtained from commercial sources.

The National Fire Protection Association (NFPA) has published standards on halons 1301 and 1211 [9,17]. Those standards indicate that the minimum design concentration necessary for flame extinguishment of a number of fuels is 5 percent (Tables 5 and 6), even though the results in Section III showed that only 3

TABLE 5. HALON 1301 DESIGN CONCENTRATIONS FOR FLAME EXTINGUISHMENT<sup>a,b</sup>

Fuel	Minimum design concentration (% by volume)
Acetone	5.0
Benzene	5.0
Ethanol	5.0
Ethylene	8.2
Methane	5.0
n-Heptane	5.0
Propane	5.2

a. Data from reference [9]  
b. Conditions of tests were 25°C and 1 atmosphere pressure

percent was needed to extinguish the small flame. Based on this information, the concentration tested for 1301, 1211, and 1202 was 10 percent. [NFPA does not have a halon 1202 standard. However, in the results in Section III, it was determined to be in Class 1 for fire suppression efficiency. Therefore, the same concentration was used as for halon 1301 and 1211.] In the case of methyl chloride, the concentration tested was 5.9 percent, since the explosive limits of this material are 7 to 19 percent. The gases were metered into

TABLE 6. HALON 1211 DESIGN CONCENTRATIONS FOR FLAME EXTINGUISHMENT<sup>a,b</sup>

Fuel	Minimum Design Concentration (% by volume)
Acetone	5.0
Benzene	5.0
Ethanol	5.0
Ethylene	8.6
Methane	5.0
n-Heptane	5.0
Propane	5.8

a. Data from Reference [16]  
b. Conditions of tests were 25°C and 1 atmosphere pressure

the exposure chamber through a rotameter at a rate of about 2 liters/minute. All given gas concentrations are the average exposure values which were calculated by integrating the area under the instrument response curve and dividing by the exposure time.

Fischer 344 male rats weighing 200 to 300 grams were obtained from Taconic Farms (Germantown, NY). They were allowed to acclimate to our laboratory conditions for at least 7 days prior to experimentation. Animal care and maintenance were performed in accordance with the procedures outlined in the National Institutes of Health's "Guide for the Care and Use of Laboratory Animals." Each rat was housed individually in suspended stainless steel cages and provided with food and water *ad libitum*. Twelve hours of fluorescent lighting per day were provided using an automatic timer.

The results of the two animal exposures to these halons at these concentrations are presented in Table 7. All animals that survived the exposures recovered, gained weight normally during a 14-day post-exposure observation period (Figures 3-8), and appeared to have suffered no ill effects. We did note that the animals exposed to halons 1211 and 1202 experienced tremors throughout the exposures, but no tremors following the tests.

The lethality data would place halons 1301, 1211, and methyl chloride in Class 1. Halon 1202 would fall into Class 2.

## F. EVALUATION OF SCREENING METHOD

These results indicate that the test is capable of distinguishing between compounds whose toxicity is less than or greater than twice the concentration recommended for fire suppression effectiveness. As described, this toxicity screening test:

TABLE 7. ANIMAL LETHALITY RESULTS FROM EXPOSURES TO HALOGENATED HYDROCARBONS

Material	Predicted LC <sub>50</sub> <sup>a</sup> (%)	Test Concentration (%)	Average O <sub>2</sub> Concentration (%)	<u>No. died</u> No. tested
Halon 1301	83.2	10.0	18.5	0/6
		10.0	18.5	0/6
Halon 1211*	32.4	10.0	18.6	0/6
		10.1	18.5	0/6
Methyl Chloride	7.3	5.9 <sup>b</sup>	19.4	0/6
Halon 1202*	5.5	10.0	NM	3/6
		10.0	NM	6/6

a. Data from References [5, 24]  
b. Tested at 5.9% since upper and lower explosive limits were 19 and 7%  
NM. Not measured  
\*. Animals exhibited tremors throughout the exposures, but not following the exposures.

- is rapid,
- can be performed by an experienced technician,
- uses the least amount of sample possible (unlikely to exceed 2 moles),
- uses a minimum number of animals, and
- has a definitive toxicological endpoint for comparison of the many candidates.

#### G. LABORATORIES/COST

This toxicity screening test uses the heating system, the chemical analysis system, and the animal exposure system that was designed for the NBS Toxicity Test Method [22]. Therefore a number of industrial, government, and independent testing laboratories in the U.S. can now perform this test. These include:

Consumer Product Safety Commission  
Arthur D. Little, Inc.  
Haskell Laboratories, Du Pont  
Mobay Company  
Southwest Research Institute  
Wright-Patterson Air Force Base  
U.S. Testing Company  
Weyerhaeuser Company  
National Institute of Standards and Technology.

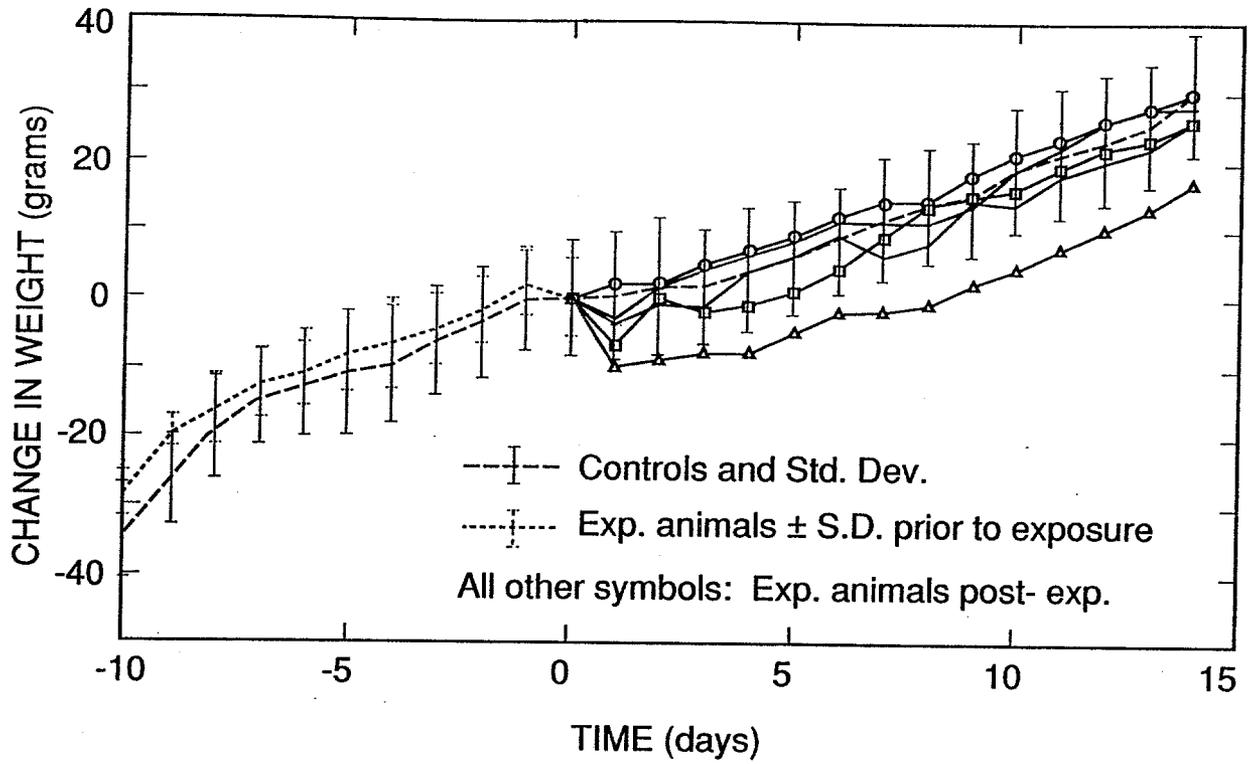


Figure 3. Change in Weight Prior to and Following Exposure to 10% Halon 1301. Animals Were Exposed for 30 Minutes on Day 0. All Exposed Animals Lived 14 Days

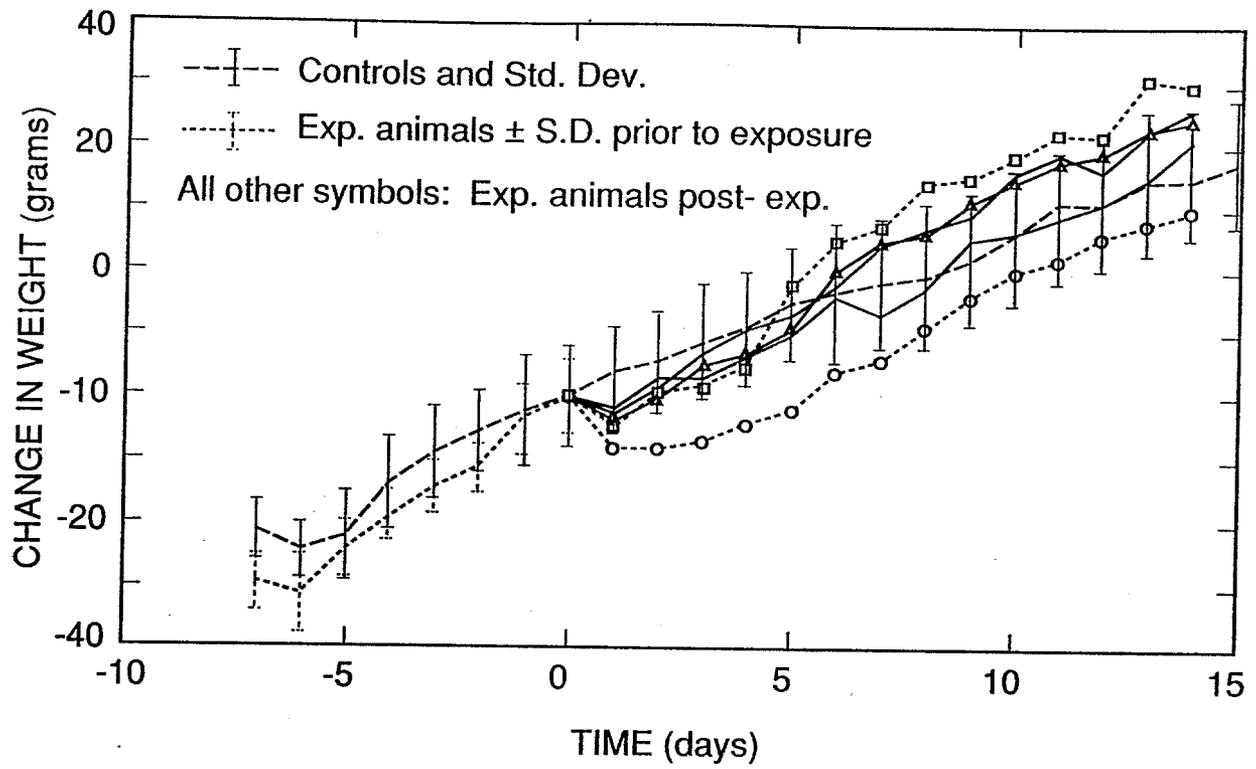


Figure 4. Change in Weight Prior To and Following Exposure to 10% Halon 1301. Animals Were Exposed for 30 Minutes on Day 0. All Exposed Animals Lived 14 Days.

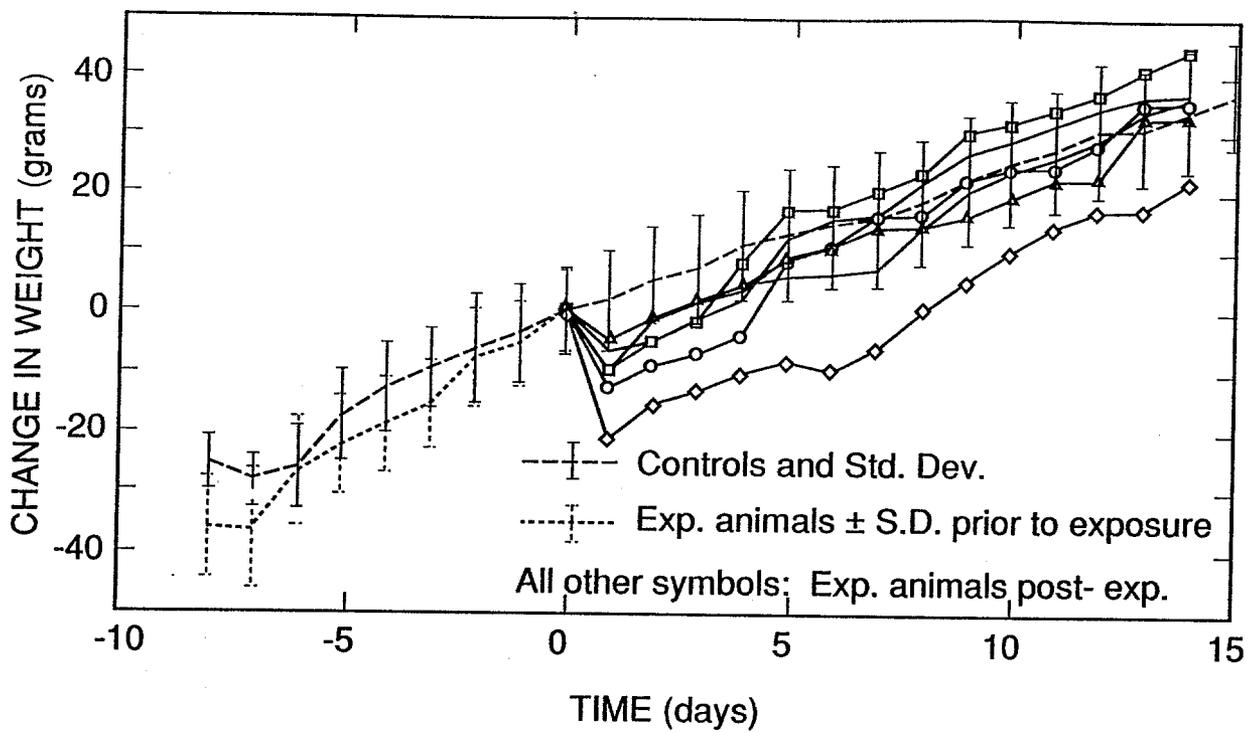


Figure 5. Change in Weight Prior To and Following Exposure to 10% Halon 1211. Animals Were Exposed for 30 Minutes on Day 0. All Exposed Animals Lived 14 Days

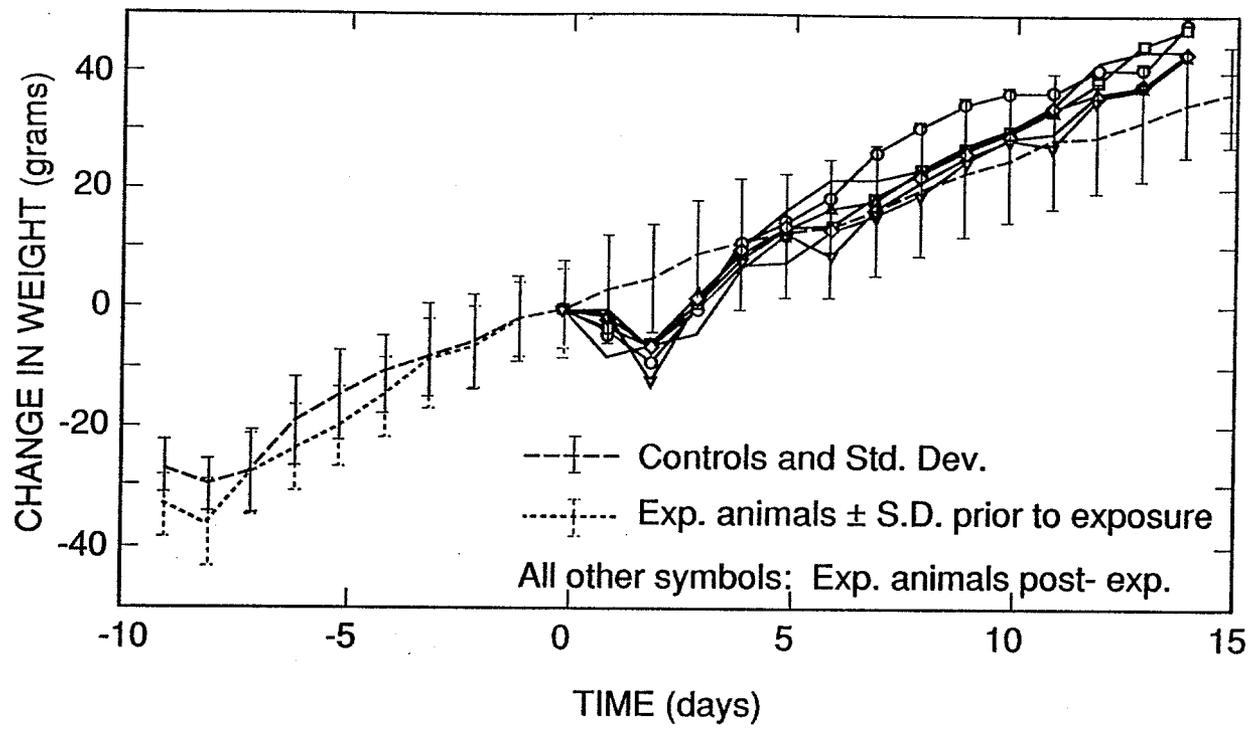


Figure 6. Change in Weight Prior To and Following Exposure to 10% Halon 1211. Animals Were Exposed for 30 Minutes on Day 0. All Exposed Animals Lived 14 Days.

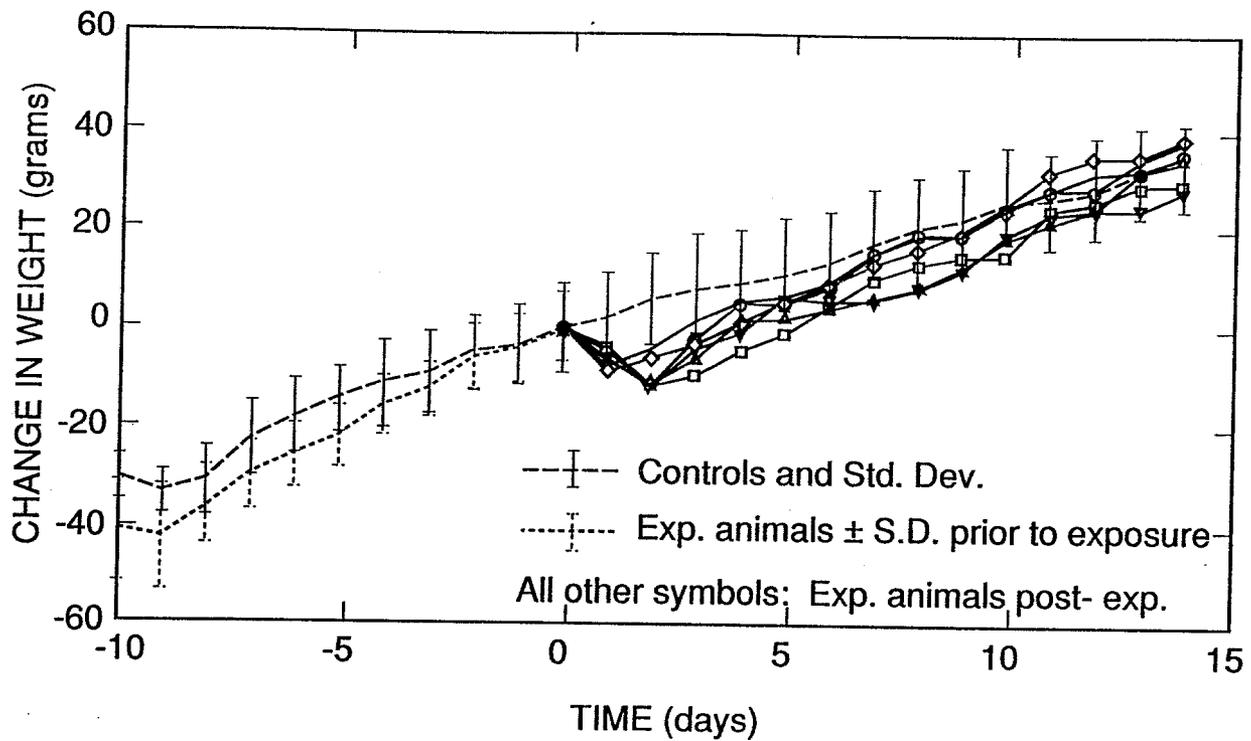


Figure 7. Change in Weight Prior To and Following Exposure to 5.9% Methyl Chloride. Animals Were Exposed for 30 Minutes on Day 0. All Exposed Animals Lived 14 Days.

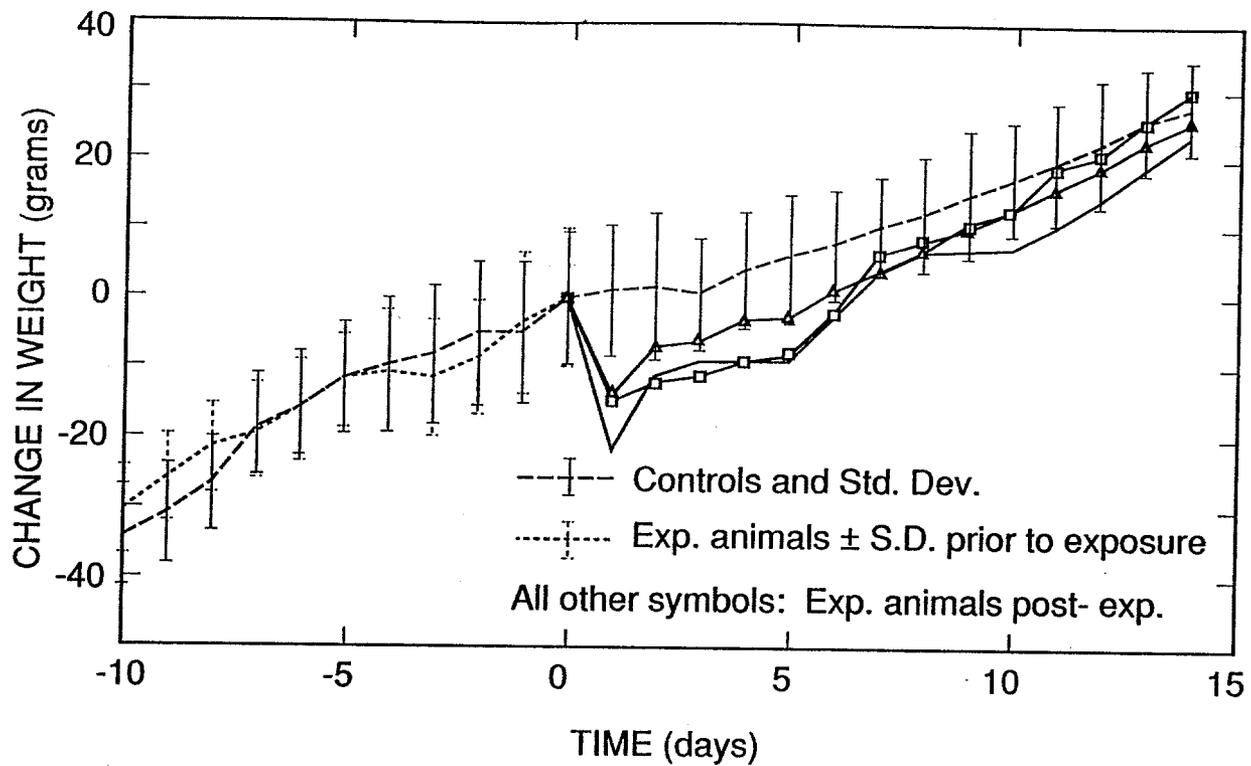


Figure 8. Change in Weight Prior To and Following a 30 Min. Exposure to 10% Halon 1202. 3/6 Exposed Animals Died During the 30 Min. Exposure. The Other 3 Lived 14 Days. In a Duplicate Test (not shown), All 6 Animals Died During the 30 Min. Exposure.

Performing the two tests should require a team of trained technicians about 1 day. A senior professional is needed to determine the exposure concentration of the chemical, occasionally to observe the animals' demeanor, and to interpret the results at the end of the post-exposure period. No more than 2 moles of chemical are needed, with the amount depending on the results of the fire suppression efficiency screen. The estimated cost to test each chemical is \$1500.00. This does not include the cost of the chemical, nor the cost of removing potentially toxic impurities from the chemical.

## H. CONCLUSIONS

- We have developed a screening method that is easy to use, requires a modest amount of material, and can be performed by a variety of laboratories.
- The designed screening procedure determines whether rats will survive a 30-minute inhalation of a candidate compound at twice the concentration (in air) recommended for fire suppression. Unusually toxic effects are also to be noted during and following the exposures.
- If more time, money and chemical were available, determination of the complete  $LC_{50}$  is a good alternate possibility.
- The results of the test place a chemical into one of two classes:
  - Class 1: All test animals survive both the 30-minute exposure period and a 7-day observation period with no ill effects.
  - Class 2: Any of the test animals die during either the 30-minute exposure or the 7-day observation period with no ill effects.
- This test is not yet suitable for regulation or specification. It is intended for preliminary screening purposes, and the additional toxicity testing procedures listed in subsection B of this section need to be completed and evaluated before any new compound is marketed as a replacement for the current halons.
- The results of these tests must be combined with other toxic hazard information when making decisions on the suitable toxicity of a chemical for use as a fire suppressant. The additional factors include:
  - the toxicity of the combustion products from the materials on fire,
  - the toxicity of the combustion products of the suppressant,
  - the increased fire hazard if the fire is not suppressed rapidly,
  - the ventilation conditions,
  - the time needed for people to leave the vicinity of the fire.

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## APPENDIX A

### SELECTED TOXICITY SCREENING PROCEDURE

#### A. INTRODUCTION

The toxicity procedure designed to rapidly screen potential halon alternatives uses the heating system, the chemical analysis system, and the animal exposure chamber that were developed for the NBS Toxicity Test Method [22]. All three of these systems are not always needed. For example, the heating system is not necessary to screen gases and the analytical system is not necessary to screen liquids.

The apparatus is a closed design, in which the atmosphere containing the test chemical is kept within the animal exposure chamber and the chemical analysis system. The exposure chamber is equipped with a blower and a stirrer to assure that the chamber atmosphere is well mixed.

#### B. ANIMAL EXPOSURE SYSTEM

The nominally 200-liter animal exposure chamber is made of 12 mm (0.5 in.) clear polymethylmethacrylate (PMMA), with inside dimensions of 1220 x 360 x 460 mm (48 x 14 x 18 in.). Six animal ports are positioned as shown in Figure 1 and are constructed of PMMA tubing 63 mm (2.5 in.) I.D. having a 3 mm (1/8 in.) wall thickness. Animal restrainers, designed to permit exposure of only the heads of the rats, are inserted into the animal ports. A blow-out panel is provided in the top of the exposure chamber on the right side away from the furnace to provide pressure relief in case of an explosion (Figure 1).

#### C. ESTABLISHING THE EXPOSURE CONCENTRATION

The amount of the test chemical needed in each test is twice its measured fire extinguishing concentration, as determined using the screen in Section III. A reasonable initial loading for a chemical with an unknown fire extinguishing capacity is about 10 percent. Before the start of the experiment, the literature on the compound should be reviewed to determine the boiling point of the compound and if its explosive limits have been delineated.

**CAUTION:** Compounds should not be tested at concentrations within their explosive limits.

##### 1. Gases

A gaseous test chemical is metered into the chamber using a calibrated rotameter. For simplicity, the concentration of the test gas in the exposure chamber is approximated using the reduction of oxygen ( $O_2$ ) in the chamber. Therefore, continuous measurement of the oxygen level must be made and recorded. An instrument operating on the paramagnetic principle is recommended. The expected concentrations of the test gas will be up to 24 percent of the atmosphere in the chamber. Therefore, the instrument has to measure oxygen concentrations from 21 percent to 16 percent. To know the test gas concentration sufficiently well, the instrument must measure to an accuracy of 0.1 percent  $O_2$ . A non-continuous gas chromatographic sampling technique may be used, as long as the same accuracy is maintained. In this case, measurements of  $O_2$  are to be made and recorded every 2 to 3 minutes.

The continuous monitoring of  $O_2$  is accomplished by flowing, at approximately 2 liters per minute, some of the chamber atmosphere to the oxygen sensor, where it is analyzed and pumped back into the chamber. The gas sampling port should be at the animal nose level in the geometric center of the

exposure chamber (Figure 2). Instrumentation for the measurement of O<sub>2</sub> must be calibrated before each test using air or standard gas mixtures of O<sub>2</sub> in nitrogen.

## 2. Liquids

A test liquid with a high boiling point is added to the chamber gravimetrically. The liquid sample is weighed in a porcelain dish such that when completely volatilized the desired concentration is achieved. The dish with the liquid is placed over the quartz beaker (9 cm I.D. by 15 cm high) which is in the cup furnace<sup>1</sup> (Figure 1) located directly below the animal exposure chamber. The furnace is gently heated to a suitable temperature to insure that the liquid compound is completely volatilized. The system is designed so that the vapor from the test compound is volatilized directly into the chamber. To avoid condensation, the chamber may also be heated by an electric bulb to assure the chamber temperature is kept above ambient.

A test liquid with a too low boiling point may evaporate as it is being weighed in the porcelain dish. Injection of a known volume may be necessary. In this case, knowing the density of the liquid allows calculation of the concentration in the chamber.

In both the gas and liquid cases, the exposure chamber is equipped with a blower and a stirrer to assure that the chamber atmosphere is well mixed.

## C. TEST ANIMALS

Adult male rats weighing 225 to 300 grams that are 3 to 4 months of age are used. Fischer 344 rats or equivalent are suggested. Normal steps must be taken to assure that healthy animals are used in testing. Animals received from a supplier should be housed at the testing laboratory for a minimum of 7 days to allow acclimation to the laboratory conditions before being used in testing. All rats should be weighed daily

- to ensure normal weight gain during this initial acclimation period and
- to monitor the effects of the chemical during the post-exposure period.

Animal care and maintenance is performed in accordance with the procedures outlined in the National Institutes of Health's "Guide for the Care and Use of Laboratory Animals." The rats should be housed individually in suspended stainless steel cages and provided with food and water *ad libitum*. Twelve hours of fluorescent lighting per day shall be provided using an automatic timer. All animals (including the controls) are weighed daily from the day of arrival until the end of the post-exposure observation period. This is one basis for assessing the health of the animals.

## D. PRE-TEST AND TEST CONDITIONS

The tests are to be conducted in a room or enclosed space having an ambient temperature of  $22 \pm 3^{\circ}\text{C}$  and relative humidity of  $50 \pm 10$  percent at the time of test.

The interior exposure chamber wall surfaces must be cleaned when changing the test chemical, or following test runs where toxicologically significant products are suspected of accumulating as particulates, or as visual inspection may indicate. Following cleaning, rubber stoppers are inserted into the animal ports from inside the chamber.

---

<sup>1</sup> A furnace and controller meeting this requirement are commercially available from Thermcraft, Inc., Winston Salem, NC as model no. 375-A-1183.

Before beginning a test, the operator must verify that the heating system is operating correctly and that the oxygen analyzer is calibrated. As mentioned above, the oxygen concentration is recorded prior to initiation of the exposure.

For liquids, the furnace is raised to the desired temperature, the liquid is weighed, and its container is placed in the quartz cup. After visual inspection indicates that the liquid has completely volatilized, the system is allowed 10 minutes to reach equilibrium before the start of the experiment.

**CAUTION:** Provisions must be made for removing test compounds from the exposure chamber without contaminating the work area and exposing the test operators. The exposure chamber should, therefore, be housed in a chemical hood or other ventilated enclosure.

#### E. TEST PERFORMANCE

For each test compound, two experiments are performed as follows:

- The six animals are placed in the restrainers.
- The test chemical is added to the chamber atmosphere, as described above.
- After equilibration, the restrainers are then inserted into the six portholes, located along the front of the exposure chamber, pushing the stoppers into the chamber, and exposing the heads of the animals to the chamber atmosphere.
- The animals remain in place for 30 minutes. Animals dying within the 30 minutes are counted.
- O<sub>2</sub> is measured throughout the exposure to monitor the concentration of the test gas and to assure little or no leakage of the system.
- The surviving animals are observed, as described in the following section, and returned to their cages, where they are further observed and weighed daily for at least 7 days.

#### F. POST-TEST PROCEDURES

Immediately following the test, the porcelain dish is removed from the furnace, allowed to cool, and then weighed to determine the mass of compound consumed.

Observation of the animals' conditions up to 7 days following the exposure is necessary to determine whether delayed toxicological effects occur. Therefore, immediately following the 30-minute exposure, while still in the restrainer, the surviving animals are examined for the following responses:

- The animal's eyes are examined for reflexes, redness, tearing, corneal opacity.
- The animal's nose and mouth are examined for any discharge, and respiratory difficulties (gasping, wheezing, rapid or slow breathing).

After removal of the animal from the restrainer, the investigator should examine each animal's:

- exploratory behavior (does the animal explore his surroundings and try to escape),
- righting reflex (animal is placed on his back and the ability to right himself is scored as rapid, slow, or non-existent), and
- posture (animal is lifted from table by his tail and placed back on table noting irregularities such as limp hind legs).

After checking these responses, the animals are returned to their cages and weighed daily for 7 days. If still losing weight on day 7, they are kept until they show signs of recovery (three successive days of weight gain) or die. Death at any time during the post-exposure observation period is recorded and becomes a basis for placing the chemical into Class 2. Animals are not used in more than one experiment.

#### G. REPORTING REQUIREMENTS

The principal datum is the number of deceased rats. This result places a chemical into one of two classes:

- |          |  |
|----------|--|
| Class 1: | All test animals survived both the 30-minute exposure period and a 7-day observation period with no lasting ill effects. |
| Class 2: | Any of the test animals died during either the 30-minute exposure or the 7-day observation period.                       |

A single rat dying during only one of the two tests may well be due to an initially unhealthy animal or other factors not related to smoke toxicity. If this has happened, a third exposure of six animals will have been performed. If no animals died in this third test, then the chemical should be placed into Class 1; if any died, then the chemical should be placed into Class 2.

The following additional data are included in a report for each test performed on each compound:

- description of the compound;
- literature data on its boiling point and explosive limits;
- exposure condition (i.e., gas or heated liquid; temperature of heated furnace);
- weight of porcelain dish and liquid to be volatilized;
- amount of compound consumed (difference between amount placed in dish and amount of residual material after the 30 minute exposure);
- time-weighted average (over the 30 minute exposure) for O<sub>2</sub>;
- when the animal died: during the 30 minute exposure, or which day following; and
- other notable toxicological effects.

**SECTION VII**  
**STABILITY UNDER LONG-TERM STORAGE**

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Center for Fire Research

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## SECTION VII

### STABILITY UNDER LONG-TERM STORAGE

#### SECTION SUMMARY

Chemical fire extinguishing agents are typically stored in metal cylinders for long periods of time. Sources of instability which are present in the cylinder can promote degradation leading to the evolution of undesirable products and a concomitant loss of fire suppression effectiveness. A test method was developed to screen halon replacement candidates for storage stability in metal cylinders.

The test is performed by storing the candidate in a carbon-steel cylinder for two days at a temperature of 170°C. The infrared spectrum of the original and aged samples are compared. Degradation is indicated by the presence of new peaks, which are not attributable to the presence of a contaminant, in the spectrum of the aged sample. Relative stabilities are determined on the basis of qualitative and quantitative measurements of the extent of degradation. This information is summarized by a three-tier classification system:

- Class 1: Those compounds which do not exhibit any signs of degradation. Since the storage temperature was set at the maximum value which did not produce measurable degradation in either halon 1211 and 1301, Class 1 candidates may be considered to possess storage stabilities which are comparable (or better) than these halons.
- Class 2: Compounds which undergo measurable degradation, as indicated by the appearance of new peaks in the IR spectrum of the aged sample.
- Class 3: Compounds which either exhibit significant degradation ( $\approx$  10 percent or more) or which tend to generate highly toxic (or otherwise deleterious) degradation products. The rationale for adopting 10 percent as the criterion is that this degree of degradation would be expected to have a measurable effect on the fire suppression effectiveness.

This test method was used to screen methyl chloride, dibromomethane, halon 1301 and halon 1211. Dibromomethane was determined to be the least stable in a carbon-steel cylinder and is considered to be a Class 3 candidate. Methyl chloride is an example of a Class 2 candidate, whereas both halons are Class 1 candidates by definition.

The procedure requires about two days and requires only about 0.1 mole of sample. A typical assessment will cost about \$150, not including the cost of procuring the chemical. Any number of commercial laboratories having infrared spectrometers could perform this test.

#### A. BACKGROUND

##### 1. Problem Definition

The outbreak of a fire is always critical, and there is no margin for failure on the part of the fire suppression system. However, significant losses in fire suppression effectiveness and increases in toxicity are possible if the extinguishing agent degrades during storage. Thus, stability in the storage environment is

an important concern. Halons 1211 and 1301 are known to be stable in metal containers for many years. This is clearly a property which their replacements will be expected to share.

The storage environment harbors conditions which may have an adverse effect on the stability of halon replacements. Stored chemicals may engage in oxidation-reduction reactions, hydrolysis, and other corrosive interactions with the metal cylinders. They are also subject to unimolecular decomposition and attack by reactive impurities. Water and oxygen, for example, will sorb to the surfaces of cylinders and transfer lines and can never be completely excluded. These sources of instability, along with the possibility of catalytic interactions with the cylinder walls, can promote the evolution of undesirable products and a concomitant loss of fire suppression effectiveness. Toxicity and corrosiveness are particularly important concerns with respect to halogenated compounds, which represent an important class of replacement candidates, because of their tendency to liberate hydrogen halide (HX) in the process of degradation. Halon 1211, for example, hydrolyzes to form HCl.<sup>1</sup>

The development of a screen test for storage stability will facilitate the identification of viable halon replacement candidates. A simple procedure is needed for performing repetitive assessments on a large number of candidates which possess a wide range of chemical and physical properties. The test method should be safe, inexpensive, and capable of providing results in a timely fashion. In addition, sample size requirements should be modest because there may be limited quantities of some candidates.

## 2. General Characterization of the Field

Stability depends on the thermodynamic [1] and kinetic [2] properties of the compound of interest and its interactions with the storage environment. The potential for a substance ( $R_1$ ) to undergo chemical change as depicted in the following reaction scheme:  $r_1R_1 + r_2R_2 + \dots \rightarrow p_1P_1 + p_2P_2 + \dots$ , is given by the Gibbs free energy function

$$\Delta G = \Delta H - T\Delta S. \quad (1)$$

In this equation,  $\Delta H$  is the difference in enthalpy between the products ( $P_i$ ) and reactants ( $R_j$ ),  $\Delta S$  is the corresponding difference in entropy, and  $T$  is the absolute temperature measured in Kelvins. The enthalpy of the reaction is equivalent to the amount of heat absorbed in an endothermic reaction ( $\Delta H \geq 0$ ) or released in an exothermic reaction ( $\Delta H \leq 0$ ) at constant pressure. The dependence of the free energy of a chemical reaction on the concentrations of reactants and products is summarized in the following equations:

$$\Delta G = \Delta G^0 + RT \ln Q, \quad (2)$$

where  $R$  is the gas constant,  $\Delta G^0$  is the free energy difference when the reactants and products are at unit activity and

$$Q = \frac{\prod_i^{n_p} [P_i]^{p_i}}{\prod_i^{n_r} [R_i]^{r_i}}. \quad (3)$$

---

<sup>1</sup> Private communication from Douglas Parylski, Naval Sea Systems Command, Code 56Y51, to Marc Nyden regarding in-use experience with the current halogenated fire suppressants.

In these equations the superscripts are the stoichiometric coefficients for the  $n_r$  reactants and  $n_p$  products in the balanced chemical equation and the brackets refer to dimensionless concentrations (or partial pressures).

The sign of the free energy indicates the direction of spontaneous change. In an exothermic reaction, heat is released to the environment as a result of the decrease in the enthalpy of the system. Heat is a form of energy and, by definition, energy is the ability to do work. However, not all of the heat released is available to do work on the environment. A minimum amount, which is equivalent to  $T\Delta S$ , is required for the change in the entropy of the system. The difference ( $\Delta G$ ) represents the maximum amount of work that can result from the process. As long as  $\Delta G \leq 0$ , there is a potential for doing work and the process will continue. At equilibrium  $\Delta G = 0$  and there is no further accumulation of products. Substituting this condition into Equation (2) gives

$$\Delta G^0 = -RT \ln K, \quad (4)$$

where the equilibrium constant ( $K$ ) is the value of the reaction quotient ( $Q$ ) when the products and reactants are at their equilibrium concentrations. In an endothermic process, the increase in the entropy of the system provides the driving force. On the other hand, a positive free energy indicates that the reverse process,  $p_1P_1 + p_2P_2 + \dots \rightarrow r_1R_1 + r_2R_2 + \dots$ , is spontaneous.

In principle, the magnitude of the free energy change determines the relative amount of products that will form via Equation (4). However, the time it takes for the process to reach equilibrium does not depend on  $\Delta G$ . Many reactions which are thermodynamically favorable ( $\Delta G \leq 0$ ) fail to proceed at a detectable rate. In these cases, reactant stability is kinetically, not thermodynamically, controlled.

Chemical reaction rates usually depend on the concentrations of one or more reactants or intermediates. In a first order reaction, the rate is proportional to the concentration of a single reactant. The rate of a second order reaction is proportional to the square of the concentration of a single reactant or to the product of two reactant concentrations, and so on. The dependence of rate on concentration is summarized in the rate law. The constant of proportionality in this expression is called the specific rate constant and is denoted by a lower case  $k$ . The rates of most chemical reactions increase with temperature in a way which is consistent with the Arrhenius equation

$$k = A \exp\left(-\frac{E_a}{RT}\right). \quad (5)$$

The pre-exponential factor ( $A$ ) is related to collision frequencies in bimolecular rate constants and to vibrational frequencies in unimolecular rate constants. The activation energy,  $E_a$ , is the minimum amount of energy required to initiate the reaction.

Catalysts increase the rate of reaction by reducing the activation energy. In the process, the rates of the forward and reverse reactions are increased to the same extent. Therefore, the presence of a catalyst will affect the rate that equilibrium is attained, but not the value of the equilibrium constant. A catalyst acts like both a reactant and a product in the sense that it participates, but is not consumed, in the chemical reaction.

## B. EXISTING TEST METHODS

The most reliable way to assess storage stability is to determine the shelf life of each chemical by monitoring its degradation in the actual storage environment. This strategy is the basis of the ASTM standard

test methods [3] for assessing the storage stability of aircraft cleaning compounds (F 1104-87 and F 1105-87). The test is performed as follows: samples of the cleaning compounds are stored in their containers for a total of 12 months. The storage temperature is maintained between 10 and 33°C except during two 15 day intervals when the samples are subjected to heat (49°C) and cold (-8°C). At the end of the 12 months, the samples are inspected for signs of corrosion and sediment formation and their performance is tested against contract specifications.

Unfortunately, the time frame for identifying halon replacements is short. Furthermore, there is a formidable number of candidates, each of which must be screened for a total of nine different properties. Consequently, a direct measurement of long-term storage stability was not considered to be a viable option. This does not preclude the possibility that direct measurements might be made on a select few of the more promising candidates.

An alternative approach is to use temperature to increase the rate of reaction and thereby to accelerate the aging process. The temperature dependence summarized by Equation (5) can be dramatic. For example, the rate of a chemical reaction with an activation energy of 126 kJ/mole, which is reasonable for catalytic degradation, increases by almost a factor of  $10^9$  over the temperature range from 25 to 225°C. This is the basis of ASTM standard test methods for floor polishes (D 1791-87) and distillate fuels (D 4625-86). The liquid floor polishes are tested by storing 100 ml samples in sealed glass bottles for 30 days at 52°C. At the end of the test period the samples are inspected. Significant changes in viscosity, as evinced by the formation of a phase separation or gel, are indicative of instability. The ASTM test method for distillate fuels is performed by storing 400 ml samples in borosilicate glass containers at 43°C. The samples are inspected after 4 to 24 weeks for filterable or adherent insolubles.

The elevated temperatures used in these tests accelerate aging and make it possible to complete long-term stability assessments in the time frame of weeks, rather than years. Much higher temperatures can be used to test halon replacement candidates permitting further reductions in the amount of time required to complete the screening tests.

The strategy of using temperature to study stability is also the basis of differential thermal analysis (DTA). This technique is frequently used to study phase transitions and assess thermal stability in liquids and solids [4]. In DTA, thermocouples are used to monitor the temperature difference between the sample and an inert reference material as a function of increasing temperature. A thermal event is signaled by a peak in the trace of voltage versus temperature. The voltage results from the instantaneous difference in the temperatures of the sample and reference. The sign of the voltage indicates whether the reaction is exothermic or endothermic. In the former case, the temperature of the reference lags behind that of the sample, whereas the opposite occurs if the reaction is endothermic. DTA is useful for measuring transition temperatures and for determining the signs of the observed enthalpy changes. It does not ordinarily provide information about the magnitude of the enthalpy change or the amount of sample. A related technique, differential scanning calorimetry (DSC), however, incorporates a control loop which counteracts the voltage difference by supplying heat to the sample, in the case of an endothermic reaction, or to the reference in the case of an exothermic reaction. The amount of heat required to maintain a constant temperature is an exact measure of the reaction enthalpy and is proportional to the area under the corresponding peak in the thermogram.

An ASTM standard test method for assessing thermal stability using DTA (E 537-86) is performed by observing the temperature changes which result from heating the sample from room temperature to about 500°C at a rate of between 10 and 30°C/min. A sample size of no more than 5 mg is recommended to minimize the risk of explosion. In performing this test, the investigator makes note of all enthalpy changes, the temperatures at which these transitions occur, whether they are exothermic or endothermic, and the effects of changing the atmosphere in the test cell. The criteria for thermal stability is the absence of a reaction.

Unfortunately, neither DTA or DSC directly applies to the problem of interest. These techniques are conventionally used to detect chemical reactions and phase transitions in solids. They would be difficult, if not impossible, to apply to potential halon replacement candidates which are, almost exclusively, gases and volatile liquids. More importantly, DTA and DSC measure thermal, as opposed to storage, stability. The distinction is that it is the presence of reactive impurities and the possibility of heterogeneous catalysis which makes the storage environment potentially unstable. A realistic test method should account for these sources of instability.

One way to ensure that the test conditions are representative of the actual storage environment is to monitor degradation of the replacement candidates after they have been stored in a metal cylinder at elevated temperatures. Conventional analytical techniques, such as gas chromatography (GC) [5] or infrared (IR) spectroscopy [6] can be used to determine the extent of degradation.

A GC consists of a heated injection port connected to a column which is coated with an adsorbent material called the stationary phase. Mixtures are transported through the column by an inert gas. The components are separated on the basis of the amount of time they require to traverse the length of the column. Retention time in the column increases with the affinity of the component to the stationary phase. A detector is positioned so that it can respond to the individual components as they are sequentially eluted from the column. Ideally, the chromatogram, which is a plot of the detector response versus retention time, consists of a series of well-resolved peaks, each of which corresponds to a pure compound. In practice, however, co-elution of components is an important concern which must be addressed by temperature programming and careful selection of the stationary phase. Accurate measurements of the concentrations of identified mixture components are frequently made using a GC equipped with an ionization detector (FID) or electron capture detector (ECD). A stand-alone GC, however, cannot make definitive compound identifications. To do this, a hybrid instrument consisting of a GC interfaced to a mass spectrometer (MS) is frequently employed.

Chemical analysis by IR spectroscopy is based on the assumption that the IR spectrum of a compound is sufficiently unique to identify it. An IR spectrum is obtained by measuring the ratio of the intensity of IR radiation which passes through the sample ( $I$ ) to the intensity of the incident radiation ( $I_0$ ) as a function of frequency. Quantitative determinations are made from the application of Beer's law

$$C_i = \left( \frac{A_i(\nu)}{A_r(\nu)} \right) C_r, \quad (6)$$

where the subscript (r) designates known values obtained from a reference and

$$A(\nu) = -\log \frac{I(\nu)}{I_0(\nu)}. \quad (7)$$

## C. SCREENING METHOD DEVELOPED

### 1. Rationale

A detailed description of the procedure for performing the recommended test method is included in the following sections. The objective is to assess storage stability by comparing the IR spectra of the candidate before and after it has been stored in a metal cylinder at an elevated temperature. Degradation

is indicated by a systematic decrease in the absorbance of peaks attributable to the candidate and/or the appearance of new peaks in the IR spectrum of the "aged" candidate.

The selection of IR spectroscopy to monitor the degradation was done on the basis of the following considerations:

- The test method must be capable of detecting products of a large number of replacement candidates which possess a vast assortment of chemical and physical properties. IR spectroscopy is extremely versatile in the sense that almost all compounds, with the notable exception of homonuclear diatomics, are IR active. The actual selection rule is that the dipole moment of the molecule must change in the process of vibrating. In principle, the versatility of spectroscopic IR analysis makes it possible to monitor the degradation of each candidate and identify the corresponding products from a simple before and after comparison of the spectra.
- The analytical technique should be inexpensive and relatively easy to perform so that it facilitates repetitive long-term stability assessments. The replacement candidates, which should be exclusively gases or volatile liquids, are expected to require minimal sample preparation. Typically, it takes less than 5 minutes to measure a high quality spectrum on a Fourier transform infrared (FTIR) spectrometer [7]. Furthermore, IR spectrometers and personnel trained in their use are available in most chemical laboratories.
- The analytical technique should have sufficient sensitivity to detect low levels of degradation products. Indeed, one of the concerns which has motivated this study of storage stability is the possibility that degradation may result in the formation of potent toxins. The sensitivity of IR detection depends on the nature of the compound under study and on the presence of interferants. However, molecules which have polar functionalities such as halogens, which are expected to represent a majority of the replacement candidates, can be detected at extremely low concentrations. For example, parts per million (ppm) levels of halon 1211 can be detected in a gas cell with a path length of about two meters.

GC is much more sensitive than IR. The major disadvantage is the considerable effort and expense involved in column preparation and selection. The situation is exacerbated by the need to use different columns to resolve the wide variety of replacement candidates from their degradation products. In the final analysis, it was decided that IR was sufficiently sensitive for this application and that the improvement in sensitivity afforded by GC analysis would not justify the additional effort which would be required to do the screenings.

The IR spectra of halons 1301 and 1211 are displayed in Figures 1 and 2, respectively. These spectra, and all others cited in this chapter, were measured at 30°C and 760 torr over a path length of 2.25 meters with a resolution of 1 cm<sup>-1</sup>. The variable path length gas cell used in these measurements, which is commonly referred to as a White cell, is equipped with a temperature controller and pressure gauge. The partial pressures of the samples actually varied from about 3 to 30 torr. A total pressure of 760 torr was reached by adding N<sub>2</sub>.

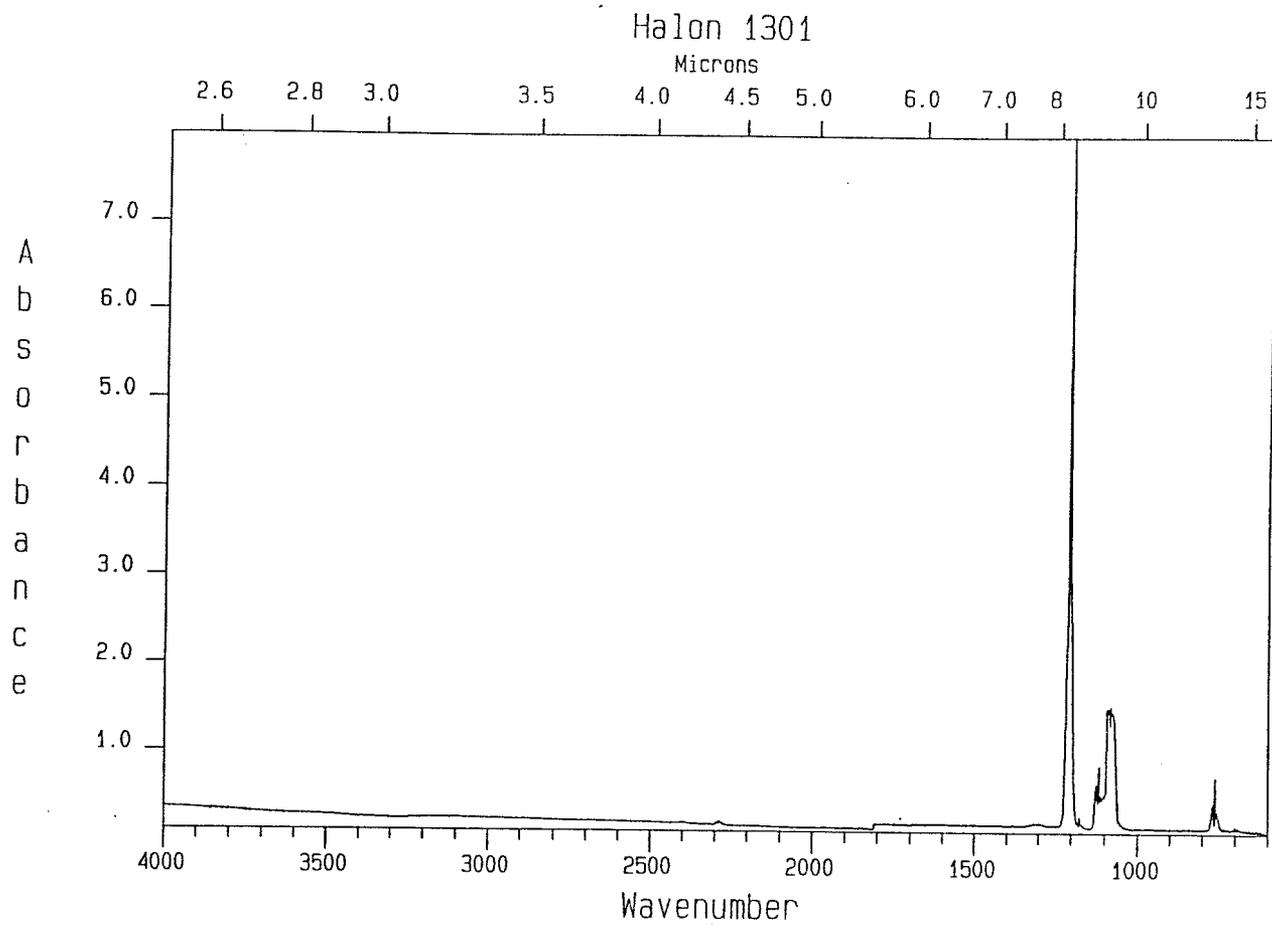


Figure 1. IR Spectrum of Halon 1301.

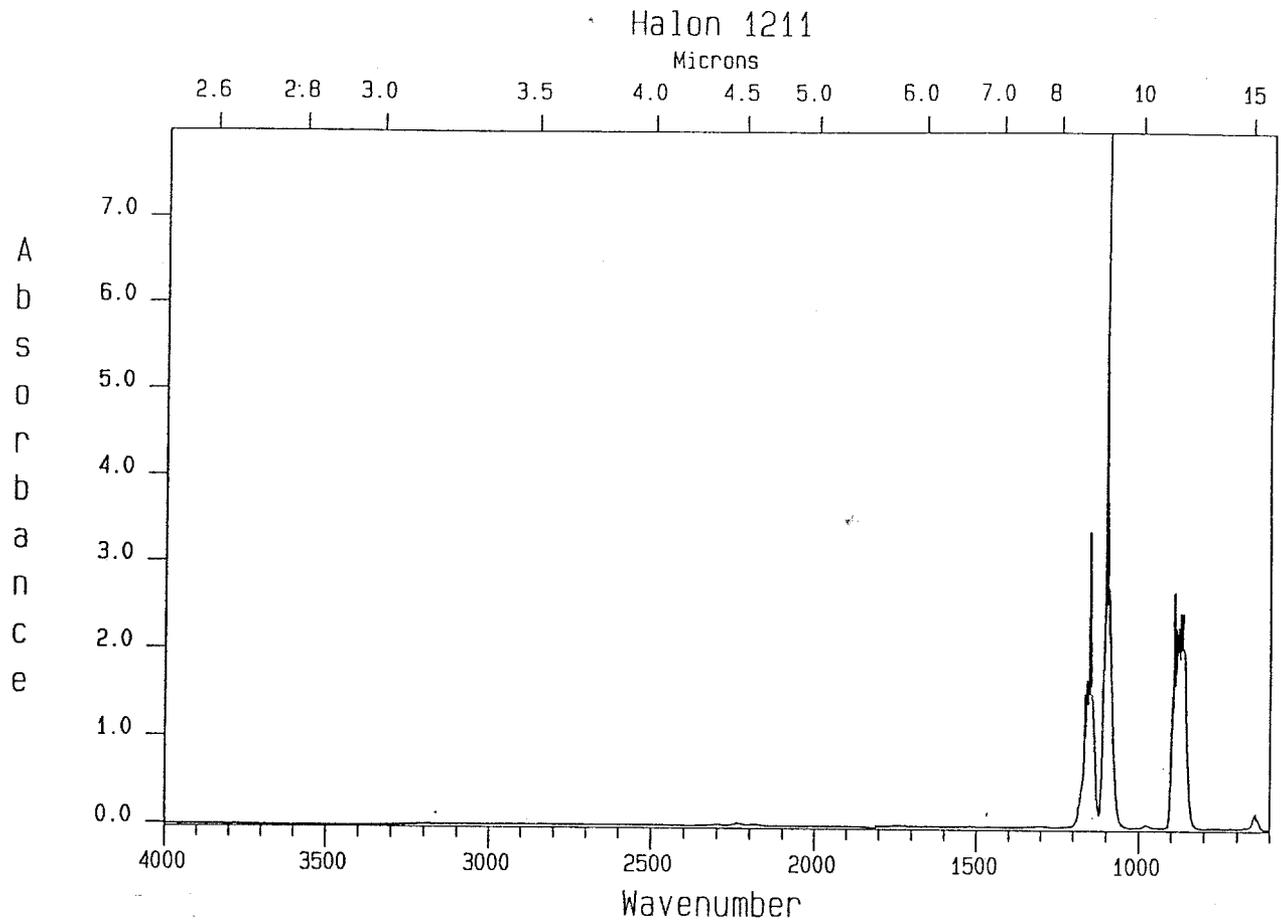


Figure 2. IR Spectrum of Halon 1211.

## 2. Experimental Determination of Test Conditions

A series of experiments was performed to adapt the test procedure to the specific application of screening halon replacement candidates. It was decided in advance that the accelerated aging should be conducted in a carbon steel cylinder and that the storage time should not exceed 7 days. A carbon steel cylinder was selected because it is a typical storage environment for fire extinguishing agents. In fact, the aging experiments were actually carried out in an old CO<sub>2</sub> fire extinguisher ( $\approx 10$  l in volume). The storage temperature and the specific criteria on which to base stability predictions were open to question and were determined on the basis of experiments.

Clearly, there is a trade-off between storage time and temperature. Thus, a fast turn-around necessitates using a high temperature. Model calculations indicated that a storage temperature of at least 150°C would be required as a consequence of the time constraint imposed on this screen. In fact, the first set of aging experiments were conducted at a much higher temperature (250°C) to ensure that there would be measurable degradation. Eventually, it was realized that because there was no need to discriminate among more stable compounds, the storage temperature could be reduced to the highest temperature which was compatible with the stability of halons 1211 and 1301 (170°C). It was further determined that some halogenated hydrocarbons exhibited significant degradation after only 2 days of storage at this temperature. Since there was no valid reason to prolong the tests, the decision was made to monitor the degradation after 2 days. In this regard, it should be noted that the extent of degradation is much more sensitive to temperature than it is to the duration of storage. Should the need to promote additional degradation arise in the future, this can be more effectively accomplished by increasing temperature rather than time of storage.

The cylinder was prepared for the accelerated aging experiments as follows. The original valve was replaced by one which was capable of withstanding high temperatures. Next, the cylinder was placed in an oven at 250°C for 48 hours, with the valve open to allow gases which were adsorbed on the interior surface to vent. The intention was to exercise reasonable care, but not to purge the cylinder of all impurities. [A sterile cylinder is hardly a realistic environment for a fire extinguishing agent.]

The residual off-gassing was measured in the following experiment. The cylinder was evacuated to about 0.2 torr and then filled with N<sub>2</sub> to a pressure of about 100 torr. A small amount was allowed to leak into the evacuated White cell where its infrared spectrum was measured. No evidence of any

TABLE 1. CONCENTRATIONS OF DEGRADATION PRODUCTS AT 250°C

Chemical	Cylinder Type	CO(%)	CO <sub>2</sub> (%)
N <sub>2</sub>	carbon-steel	0.02	0.10
CF <sub>3</sub> Br	carbon-steel	0.40	0.67
CF <sub>2</sub> ClBr	carbon-steel	1.27	1.57
CF <sub>2</sub> ClBr	stainless-steel	0.09	0.20

IR-absorbing species was observed in this spectrum. The cylinder and its contents were then transferred to an oven where they were stored at a temperature of 250°C for 48 hours. The cylinder was allowed to cool to ambient temperature and IR spectra of three samples were measured. The only absorbance present in these

spectra were characteristic peaks for CO and CO<sub>2</sub>. The corresponding concentrations were obtained from Equation (6) using the IR absorbencies of CO at 2116 cm<sup>-1</sup> and CO<sub>2</sub> at 2359 cm<sup>-1</sup> measured in standardized mixtures obtained from Matheson Gas Products. The average concentrations of CO and CO<sub>2</sub> computed from the three spectra are reported in Table 1.

Once the background levels for off-gassing of CO and CO<sub>2</sub> were established, accelerated aging experiments were conducted on halon 1301. The cylinder was pumped down to about 0.2 torr in an effort to remove the residual from the previous experiment and filled to a pressure of about 100 torr ( $\approx$  0.05 moles) with halon 1301. The IR spectrum of a sample of the original halon (Figure 3) and the spectrum of a sample which was aged at 250°C for 42 hours (Figure 4) are displayed in a window extending from 2500 to 2000 cm<sup>-1</sup>. The peaks corresponding to CO and CO<sub>2</sub>, which are labelled in the spectrum of the aged sample, are obviously not present in the spectrum of the original sample. The average CO concentration in the aged samples of halon 1301 (Table 1), was more than an order of magnitude larger than the background level. The magnitude of the disparity suggests that CO is produced during the degradation this halon.

The identical procedure was followed for halon 1211. A comparison of the spectra displayed in Figures 5 and 6 clearly indicate that CO and CO<sub>2</sub> were produced in the process of aging the halon. The average concentration of CO in the aged samples of halon 1211 (Table 1) is a factor of three larger than the value observed for halon 1301. On the basis of this comparison, halon 1211 would be predicted to be less stable in the storage environment than halon 1301. Comparable results were obtained for each halon when the experiments were repeated. It is also interesting to note that the presence of CO and CO<sub>2</sub> was also observed when halon 1211 was aged in a stainless-steel container. As expected, these concentrations (Table 1) were considerably less than the values observed when the sample was aged in carbon-steel.

Carbon monoxide and carbon dioxide were not the only halon degradation products observed in these experiments. The spectra of original (Figure 7) and aged (Figure 8) samples of halon 1301 are displayed in a window extending from 1400 to 1250 cm<sup>-1</sup>. The distinct peak, centered at 1283 cm<sup>-1</sup> in the spectrum of the aged sample, is not present in the spectrum of the original sample. Similarly, the spectra of aged samples of halon 1211 exhibit a peak at about 922 cm<sup>-1</sup> (see Figures 9 and 10) which is not observed in any of the other spectra. The anomalous peaks have not been assigned. Their proximity to bands in the original halon, however, suggests that they derive from molecules which are structurally related to the parent halon.

The results of these experiments clearly demonstrate that halons 1301 and 1211 undergo measurable degradation in carbon-steel cylinders at 250°C and that this process is accompanied by the evolution of both CO and CO<sub>2</sub>. Unfortunately, CO<sub>2</sub> is a ubiquitous contaminant and its presence in the spectrum of the aged sample does not necessarily indicate that degradation has occurred. The detection of CO in the IR spectrum of the aged sample, however, appears to be a reliable marker for halon degradation.

In principle, it is possible to determine the extent of degradation from a systematic decrease in the IR absorbance of the compound of interest. The appearance of a new peak, however, is a more sensitive and informative measure of degradation. The peak intensities in the absorbance spectrum of halon 1301 and 1211, for example, are not reproducible with an accuracy that approaches the detection limit of CO. In addition, it is often possible to identify degradation products on the basis of band shapes and frequency. Clearly, the identification of CO and CO<sub>2</sub> as degradation products reveals something about the mechanism of halon degradation in steel cylinders. This type of knowledge might be very helpful if it ever becomes necessary to find compatible cylinder materials for a promising, but unstable, replacement candidate.

The stability of halons 1301 and 1211 under actual storage conditions has never been identified as a major problem. The fact that degradation was observed in tests on both of these compounds suggests that the conditions might have been too stringent for the intended purpose. In response to this, a second set of experiments was conducted using the procedure described above, except that the storage

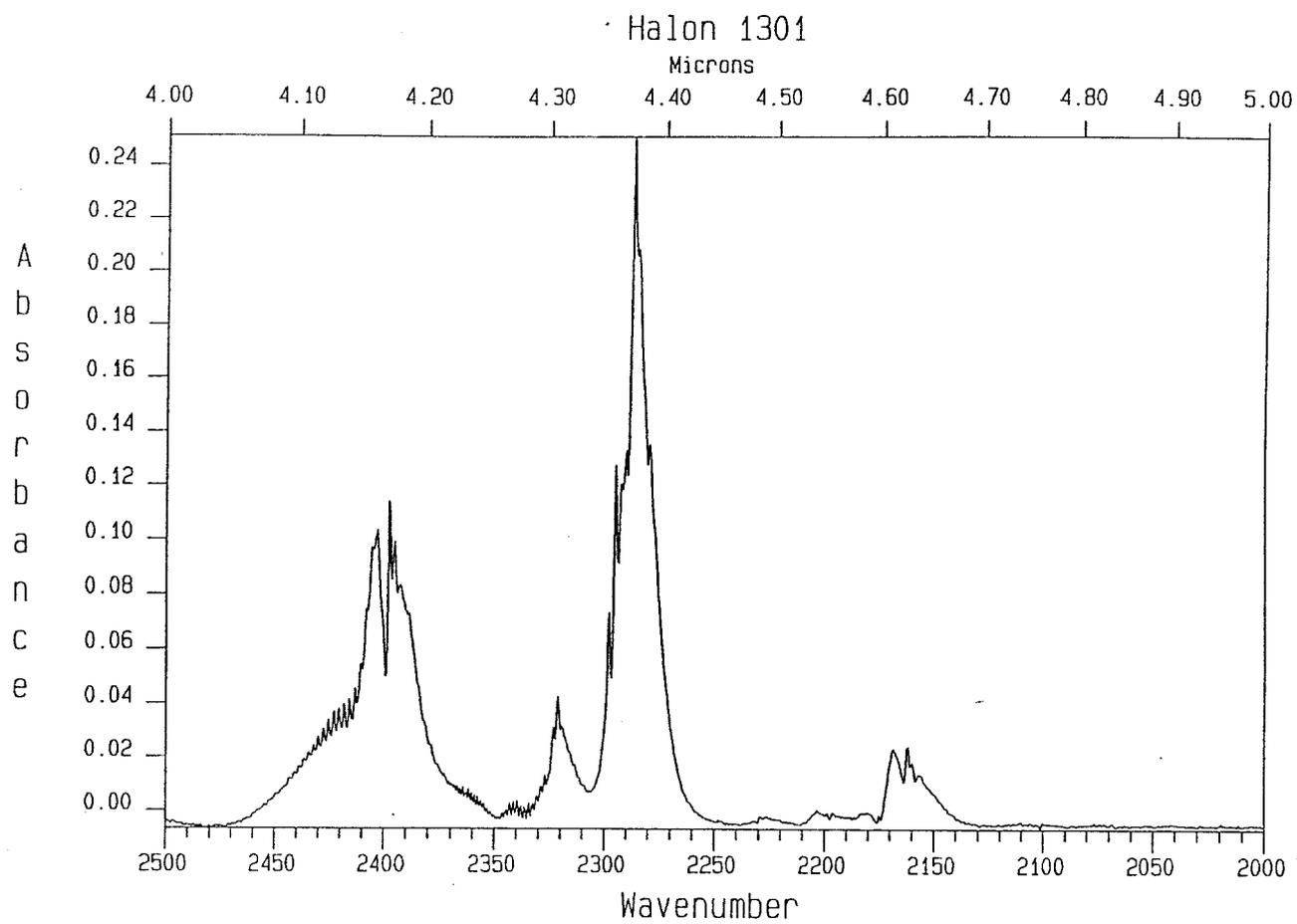


Figure 3. An Expanded View of the IR Spectrum of Halon 1301 Focusing on the Region Extending from 2500 to 2000  $\text{cm}^{-1}$ .

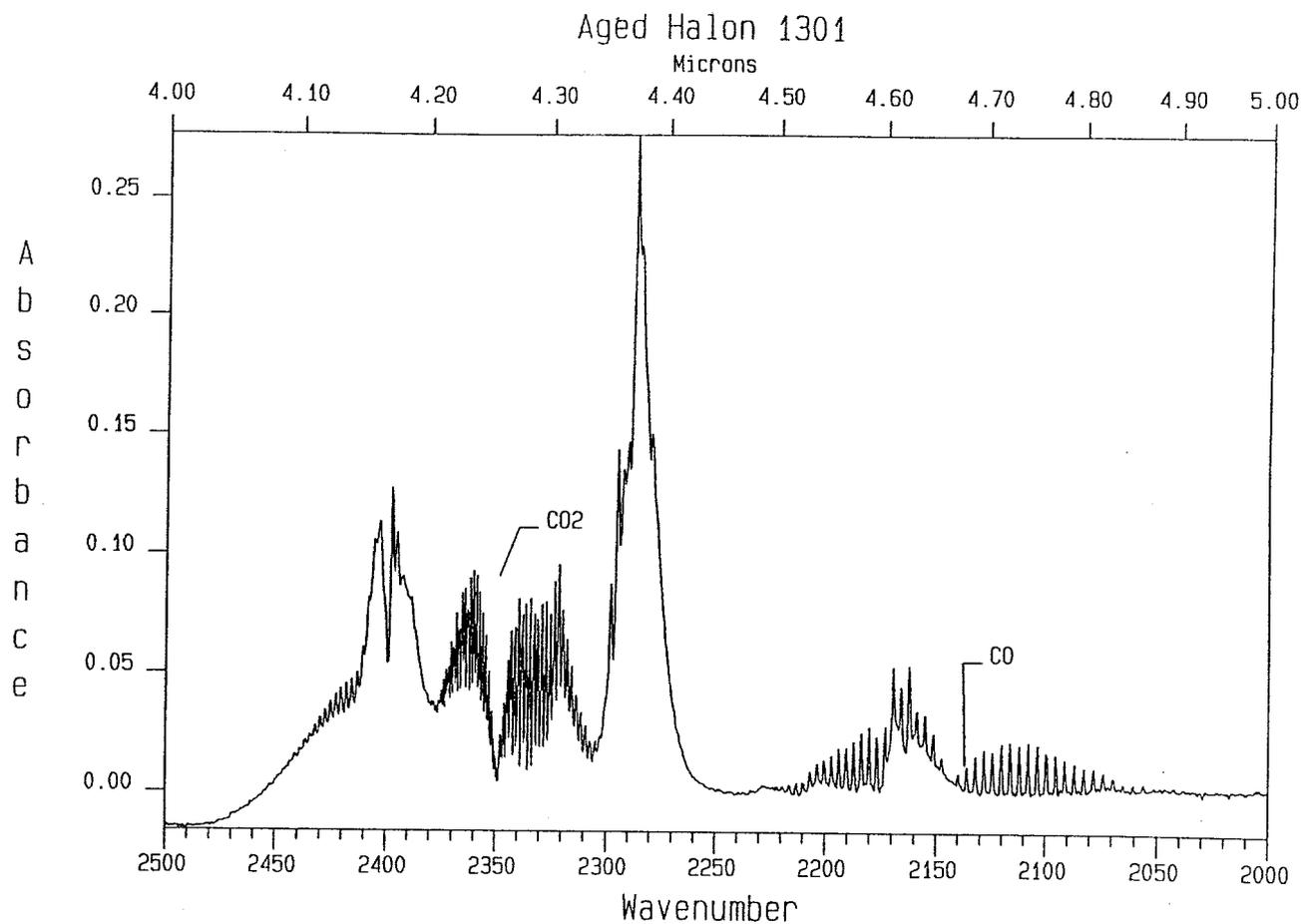


Figure 4. The Presence of CO and CO<sub>2</sub> are Revealed in the Expanded View of the IR Spectrum of a Sample of Halon 1301 Which was Aged at 250°C for Approximately 2 Days.

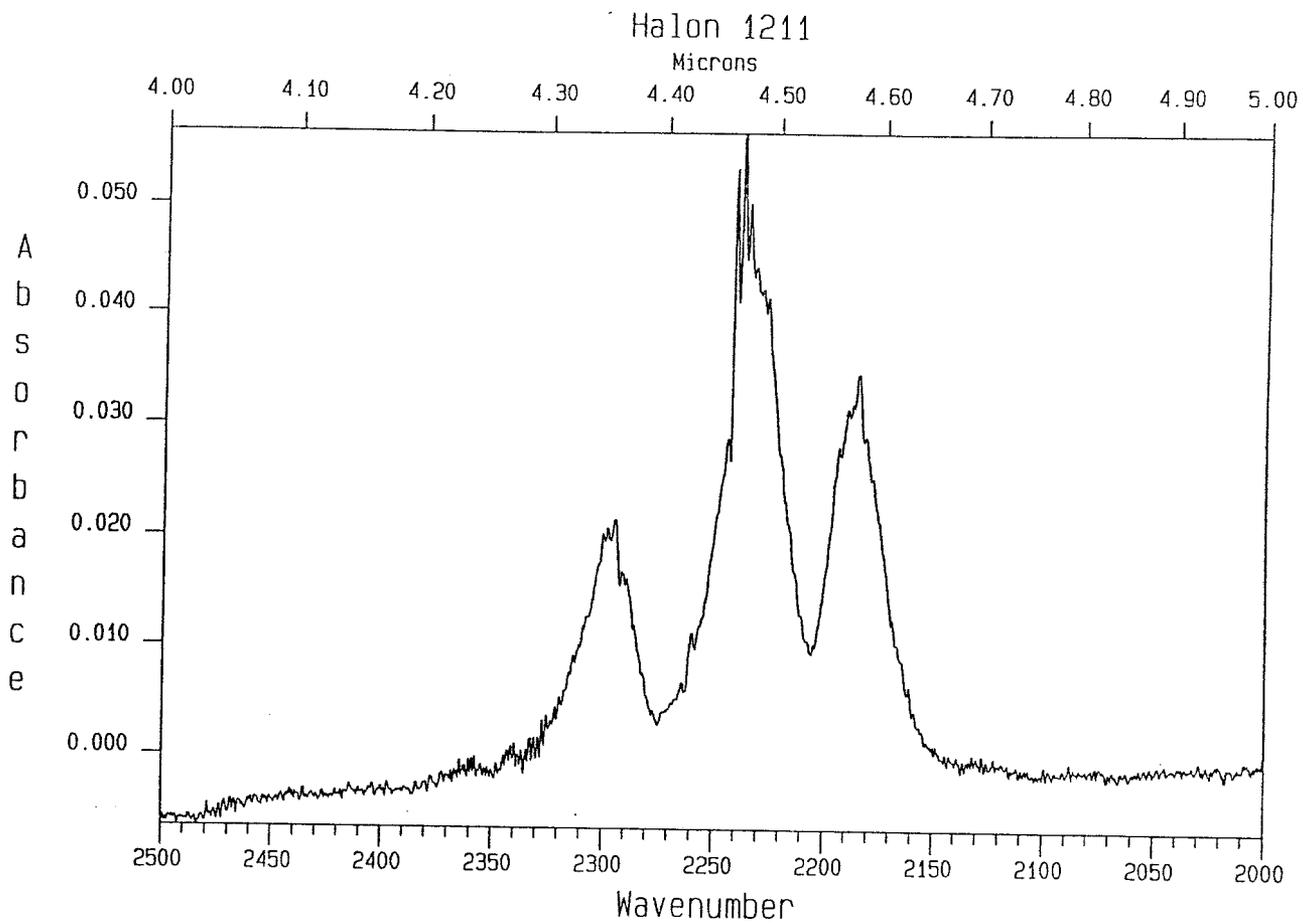


Figure 5. An Expanded View of the IR Spectrum of Halon 1211 Focusing on the Region Extending from 2500 to 2000  $\text{cm}^{-1}$ .

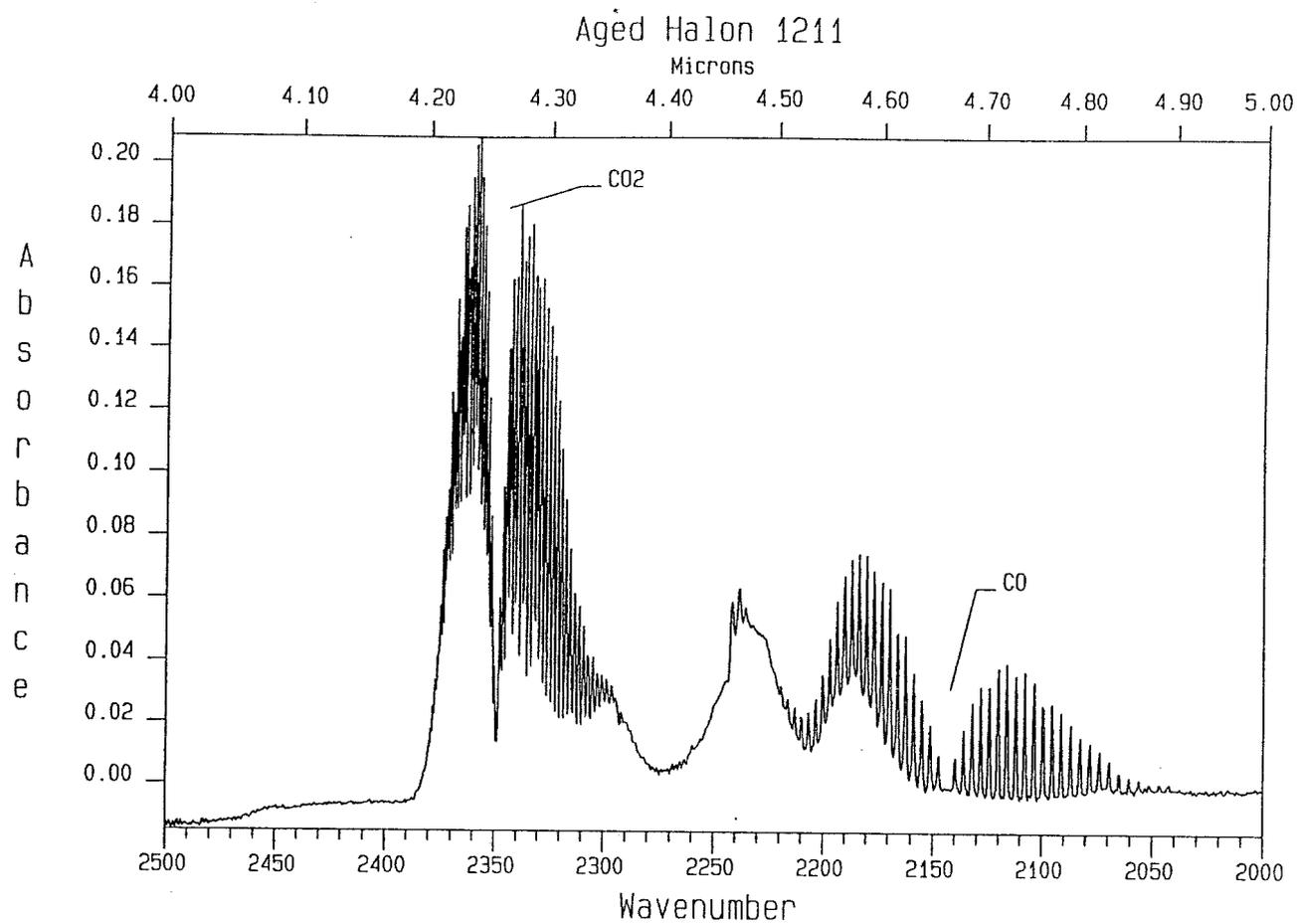


Figure 6. The Presence of CO and CO<sub>2</sub> are Revealed in the Expanded View of the IR Spectrum of a Sample of Halon 1211 Which was Aged at 250°C for Approximately 2 Days.

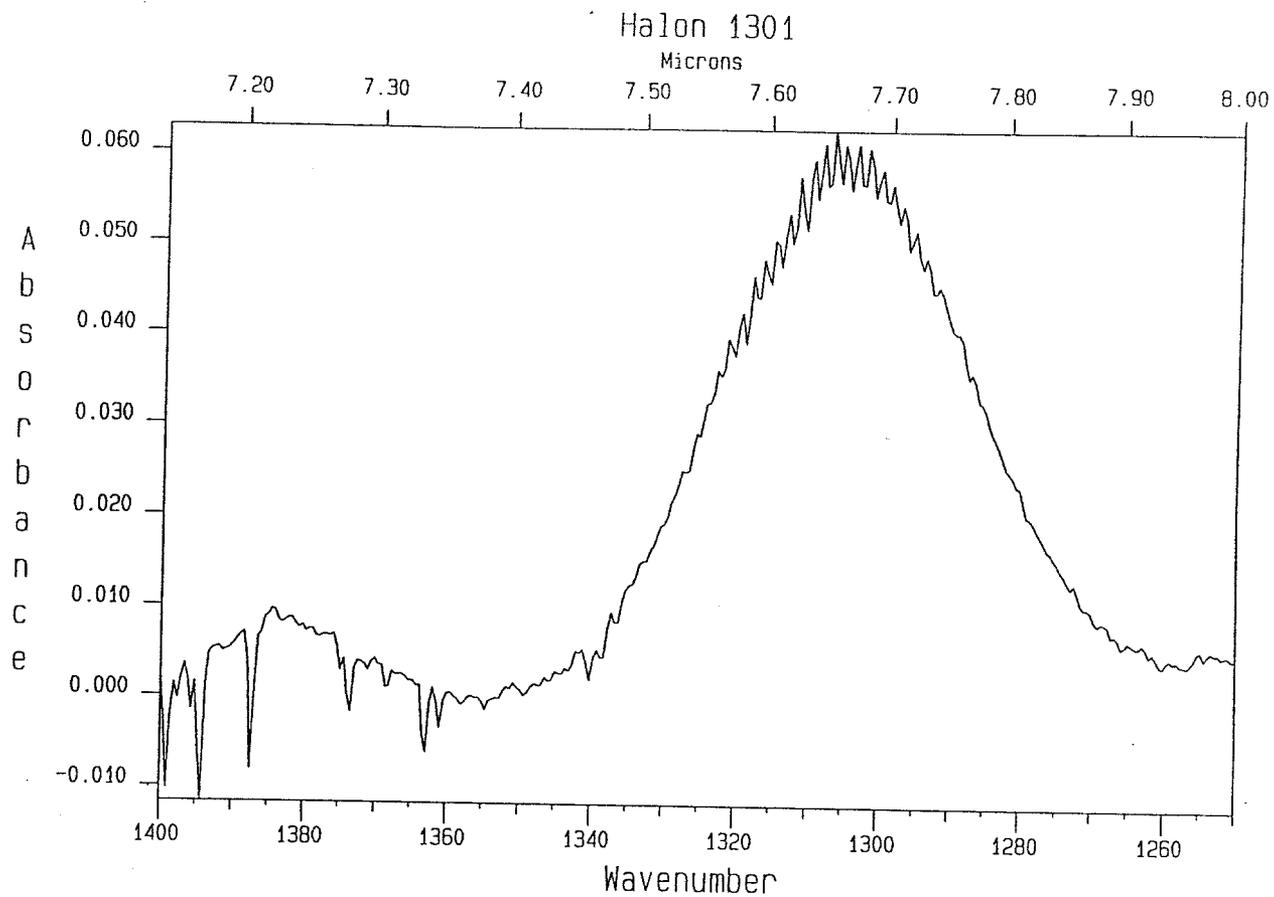


Figure 7. An Expanded View of the IR Spectrum of Halon 1301 Focusing on the Region Extending from 1400 to 1250  $\text{cm}^{-1}$ .

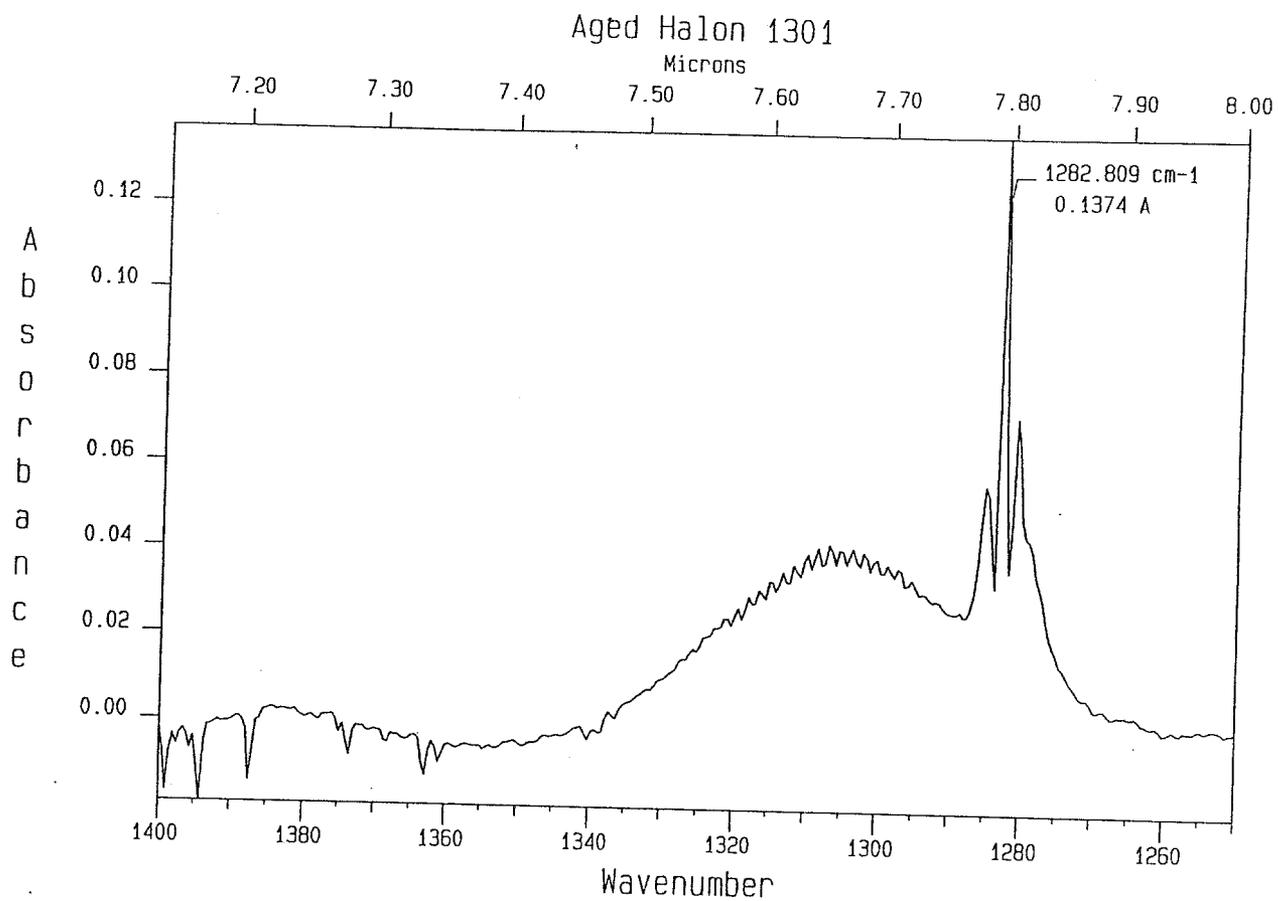


Figure 8.    The Unidentified Peak in the Spectrum of Aged Halon 1301.

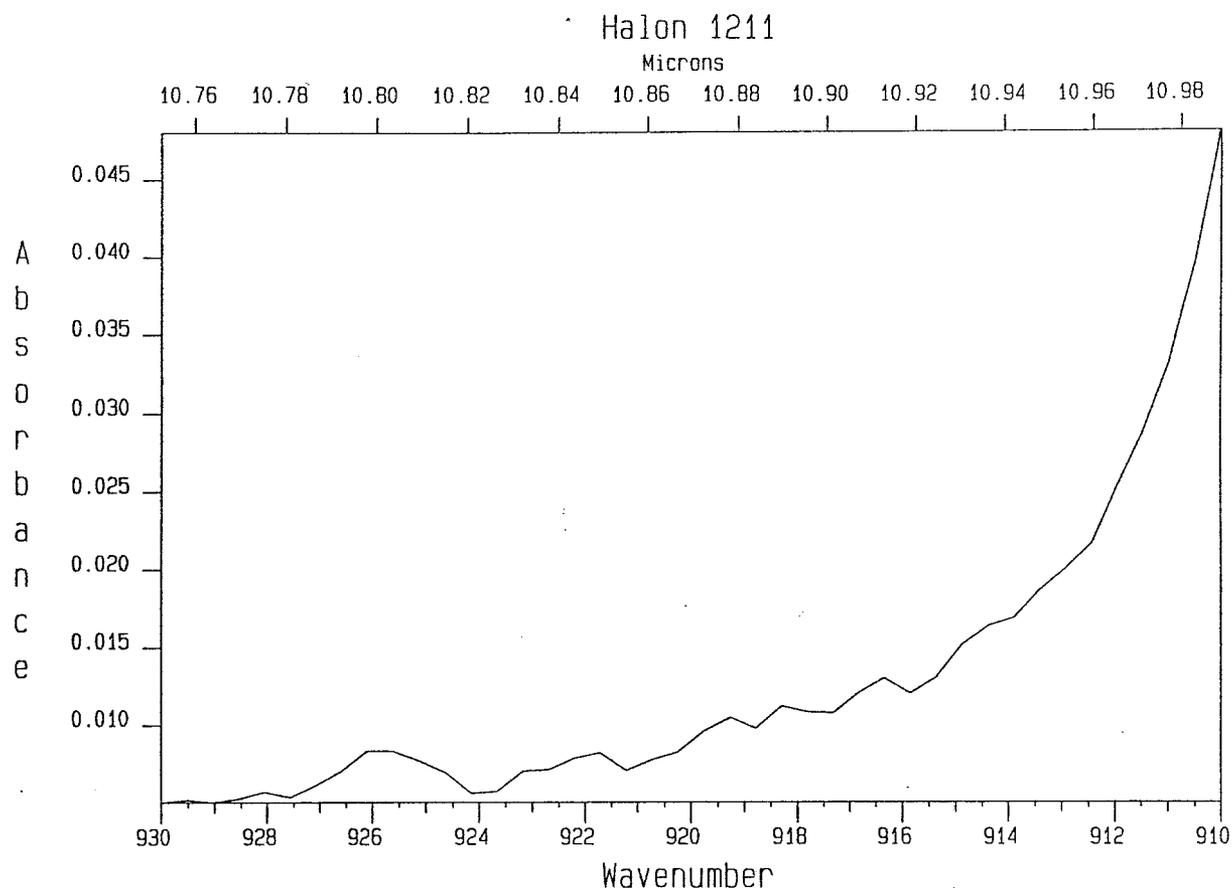


Figure 9. An Expanded View of the IR Spectrum of Halon 1211 Focusing on the Region Extending from 930 to 910  $\text{cm}^{-1}$ .

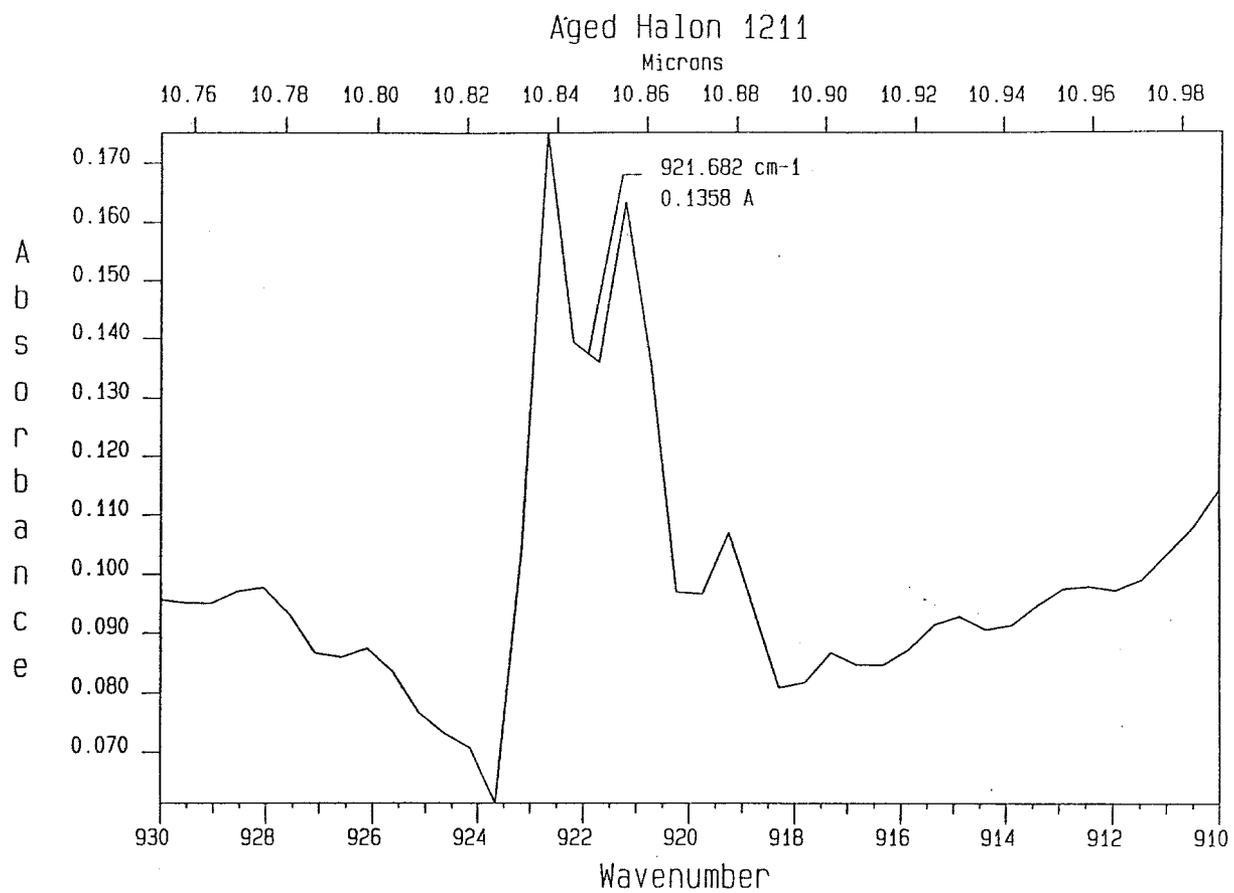


Figure 10. The Unidentified Peak in the Spectrum of Aged Halon 1211.

TABLE 2. CONCENTRATIONS OF DEGRADATION PRODUCTS AT 170° C

Chemical	Cylinder Type	CO(%)	CO <sub>2</sub> (%)
CF <sub>3</sub> Br	carbon-steel	0.00	0.43
CF <sub>2</sub> ClBr	carbon-steel	0.00	0.00
CH <sub>3</sub> Cl	carbon-steel	0.03	0.20
CH <sub>2</sub> Br <sub>2</sub>	carbon-steel	0.73	0.37

temperature was reduced to 170° C. The corresponding spectra of the aged samples of halons 1301 and 1211 are displayed in Figures 11 and 12, respectively. The characteristic CO peak, which had been prominent in the spectra of the halons which were aged at 250° C, is absent from both spectra. The average concentrations of CO and CO<sub>2</sub> obtained from 3 spectra are reported in Table 2.

The aged sample of halon 1301 contained a significant amounts of CO<sub>2</sub>. The source of this CO<sub>2</sub> was not immediately obvious. In the previous experiments, CO<sub>2</sub> concentrations which were significantly above the level of background off-gassing had always been accompanied by comparable concentrations of CO. If the CO<sub>2</sub> was coming from the degradation of the halon 1301, why wasn't there any CO? It also seemed unlikely that halon 1301 would degrade at a lower temperature than halon 1211. The paradox was resolved when a close inspection revealed that the CO<sub>2</sub> was present in the spectra of the original samples of halon 1301. The details of the mechanism have not been determined; however, the contamination must have occurred when the halon was transferred from the supply cylinder. Since there was no mechanism for purging the transfer line, atmospheric contamination must have also occurred in each of the preceding experiments. In this particular case, however, very little halon 1301 remained in the supply cylinder. Evidently, a significant fraction of the gas that was transferred was actually atmospheric CO<sub>2</sub> rather than halon 1301. Clearly, basing the extent of degradation of halons on the formation of CO<sub>2</sub> would be misleading. The evolution of CO is a much more reliable marker for halon degradation.

#### D. CRITERIA

A three-tier classification system was formulated on the basis of the results obtained from the experiments described above.

- Class 1: Those compounds which do not exhibit any signs of degradation. Since the storage temperature was set at the maximum value which did not produce measurable degradation in either halon 1211 and 1301, Class 1 candidates may be considered to possess storage stabilities which are comparable (or better) than these halons.
- Class 2: Compounds which undergo measurable degradation, as indicated by the appearance of new peaks in the IR spectrum of the aged sample.
- Class 3: Compounds which either exhibit significant degradation ( $\approx$  10 percent or more) or which tend to generate highly toxic (or otherwise deleterious) degradation products. The rationale for adopting 10 percent as the criterion is that this degree of degrada-

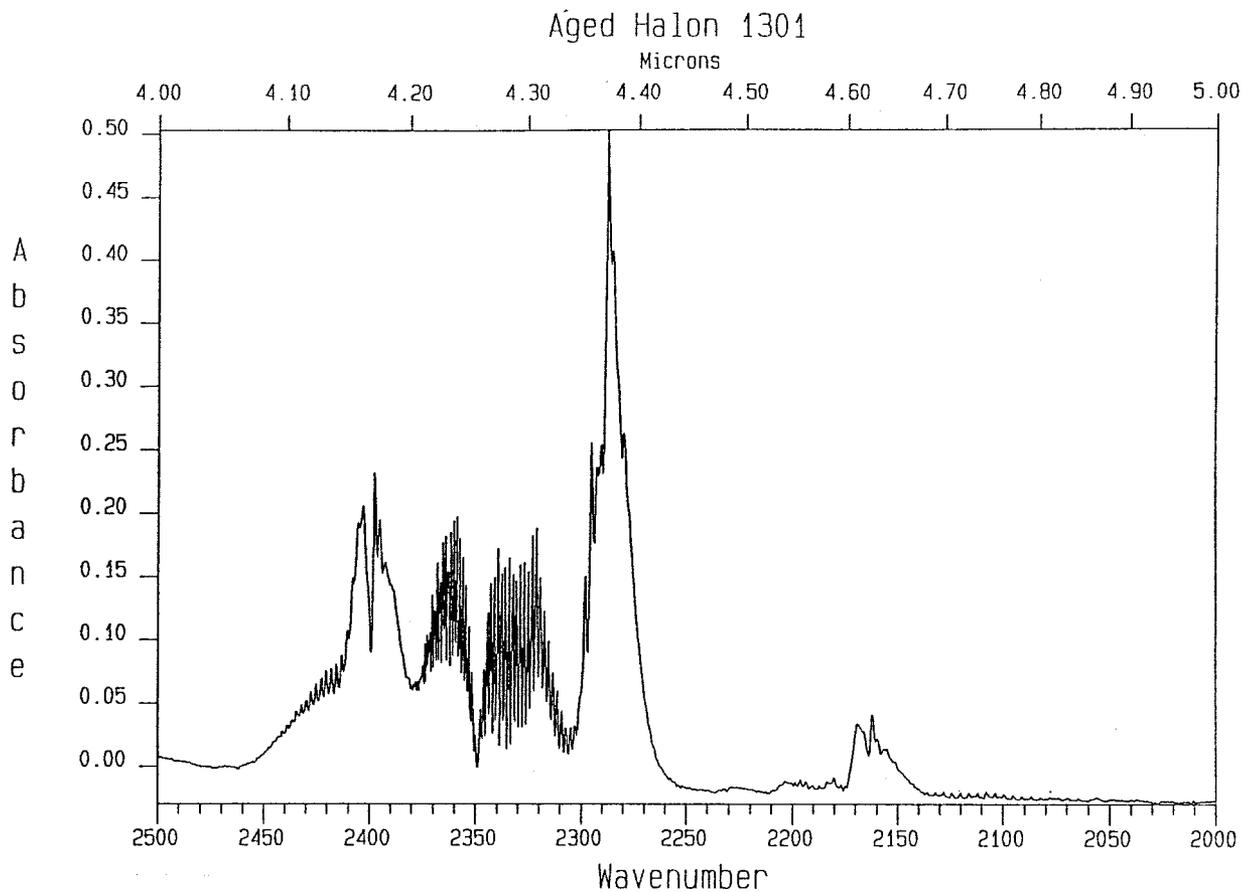


Figure 11. The Presence of CO and CO<sub>2</sub> are Revealed in the Expanded View of the IR Spectrum of a Sample of Halon 1301 Which was Aged at 170°C for Approximately 2 Days.

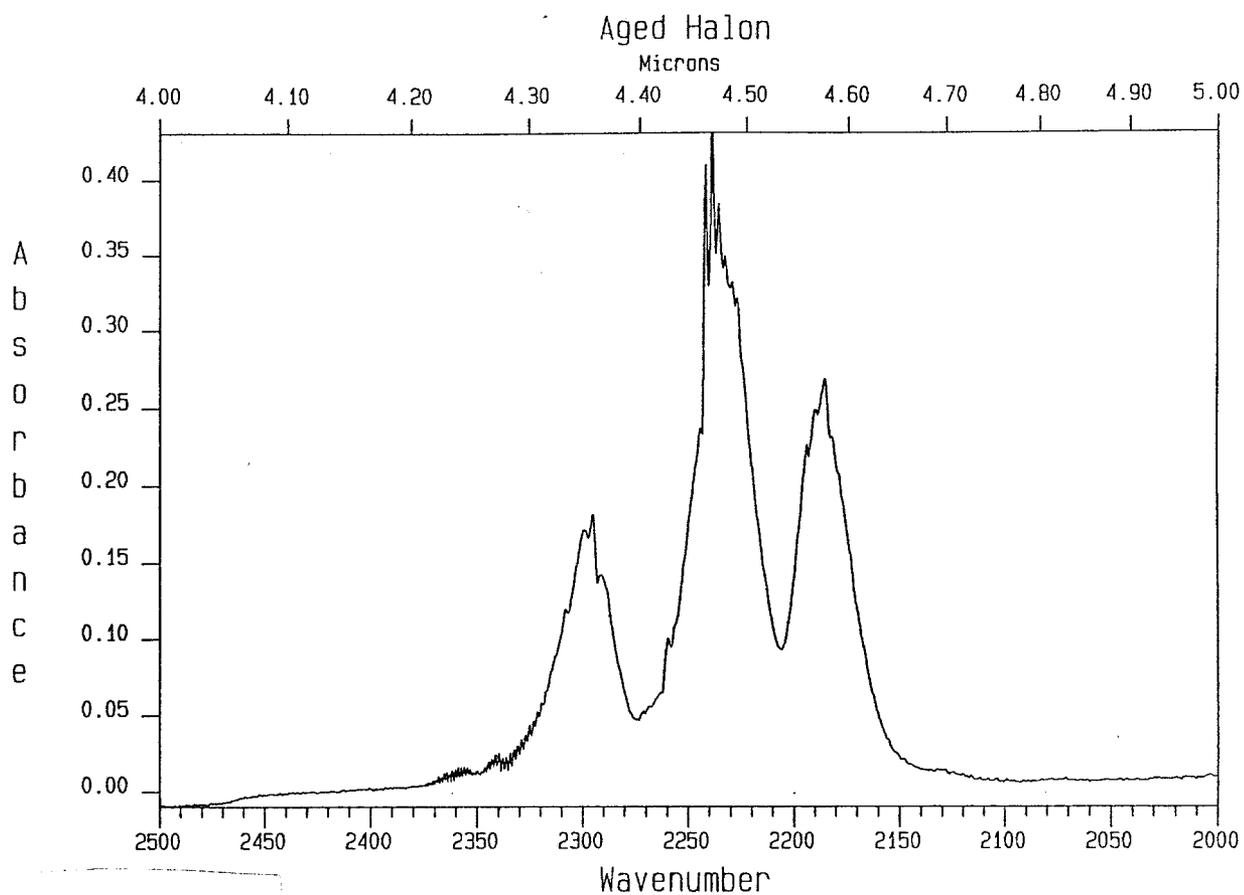


Figure 12. The Presence of CO and CO<sub>2</sub> are Revealed in the Expanded View of the IR Spectrum of a Sample of Halon 1211 Which was Aged at 170°C for Approximately 2 Days.

tion would be expected to have a measurable effect on the fire suppression effectiveness.

## E. PERFORMANCE DATA

### 1. Additional Test Chemicals

Two halogenated hydrocarbons,  $\text{CH}_3\text{Cl}$  (methyl chloride) and  $\text{CH}_2\text{Br}_2$  (dibromomethane), were selected to assess the predictive capability of the test method. These particular compounds were selected for a variety of reasons:

- Both compounds are flame inhibitors. The effectiveness of  $\text{CH}_2\text{Br}_2$  in suppressing n-heptane/air flames has been measured and is comparable to halons 1301 and 1211 [8].
- These compounds are expected to have significantly lower ODP values than halons 1301 and 1211. Both compounds contain hydrogen atoms which, in principle, are capable of reacting with atmospheric OH. This property tends to reduce the probability that significant quantities will penetrate to the stratosphere where they can contribute to the destruction of the ozone layer.
- These compounds are expected to be less stable than halons 1301 and 1211, thus providing an effective comparison. The relative instability is due to the absence of any carbon-fluorine bonds, which are exceptionally strong ( $\approx 480$  kJ/mole), in these molecules. The close proximity of the two carbon-bromine bonds, which are considerably weaker ( $\approx 270$  kJ/mole) than either carbon-fluorine or carbon-hydrogen ( $\approx 420$  kJ/mole) bonds, should make  $\text{CH}_2\text{Br}_2$  susceptible to degradation.
- Finally,  $\text{CH}_2\text{Br}_2$  exemplifies the application of the test method to compounds which are liquids under standard conditions.

### 2. Test Procedure

$\text{CH}_3\text{Cl}$  and  $\text{CH}_2\text{Br}_2$  were screened for long-term stability using the test method described above. The IR spectra were measured with  $1\text{ cm}^{-1}$  resolution over a path length of 2.25 meters in a White cell maintained at a temperature of  $30^\circ\text{C}$  and approximately one atmosphere pressure. Spectra were measured from samples which were extracted from a carbon-steel cylinder before and after aging the chemicals at a temperature of  $170^\circ\text{C}$  for 48 hours. Liquid  $\text{CH}_2\text{Br}_2$  was introduced into the evacuated cylinder with a syringe. Some atmospheric contamination was introduced during the brief time that the valve was opened. The cylinder was then connected to the White cell and the system was pumped down to about 0.2 torr with the cylinder valve closed. When this process was completed, the valve was opened to allow some  $\text{CH}_2\text{Br}_2$  vapor to leak into the evacuated White cell where the spectrum was measured. Degradation was indicated by the presence of new peaks, which are not attributable to the presence of a contaminant, in spectrum of the aged sample.

### 3. Results

The spectra of the samples of aged  $\text{CH}_3\text{Cl}$  suggest that modest degradation has occurred. It is therefore a Class 2 chemical. The characteristic peak due to  $\text{CO}_2$  is prominent in the expansion of this spectrum in the window extending from  $2800$  to  $2000\text{ cm}^{-1}$  (Figure 13). However, the average CO concentration in the aged samples (Table 2), was not significantly higher than the background level established with  $\text{N}_2$ . The presence of a small amount of HCl, perhaps on the order of 10 ppm, is indicated by six evenly

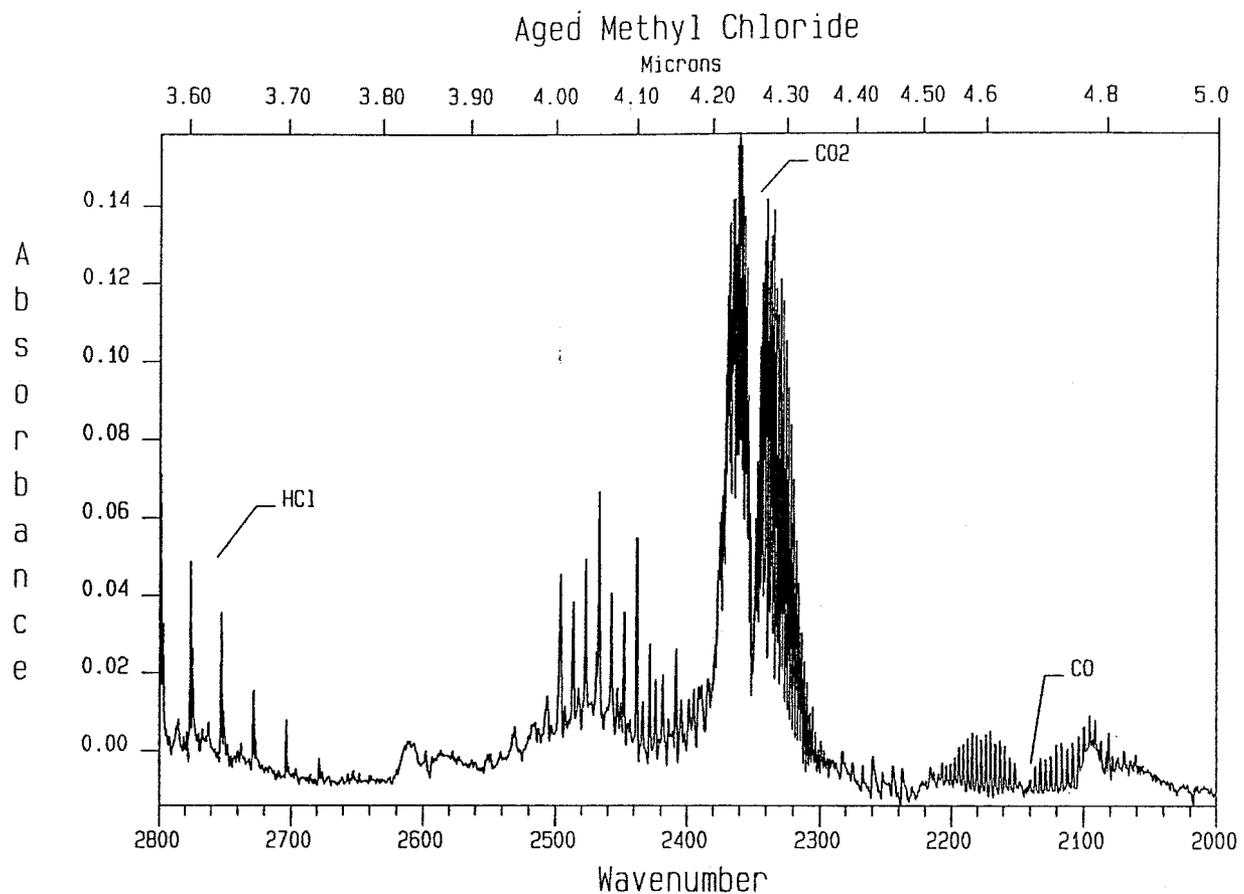


Figure 13. The Presence of HCl, CO and CO<sub>2</sub> are Revealed in the Expanded View of the IR Spectrum of a Sample of Methyl Chloride Which was Aged at 170° C for Approximately 2 Days.

spaced peaks between 2800 and 2675  $\text{cm}^{-1}$ . Close inspection reveals that each peak is actually a doublet corresponding to  $\text{HCl}^{35}$  and  $\text{HCl}^{37}$  (weaker).

More dramatic changes are evident in the spectra of the samples of aged  $\text{CH}_2\text{Br}_2$ . Consequently it is a Class 3 chemical. The expansion of the spectrum displayed in Figure 14 reveals that significant amounts of  $\text{CO}$  and  $\text{CO}_2$  (Table 2) were evolved in the accelerated aging process. The features which remained after subtracting the spectrum of the original (which was scaled to account for partial pressure differences) from the spectrum of an aged sample is displayed in Figure 15. The prominent peaks were assigned to  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_2\text{ClBr}$ . The most likely source of the  $\text{Cl}$  was the  $\text{HCl}$  formed in the degradation of  $\text{CH}_3\text{Cl}$  in the previous experiment.

## F. EVALUATION OF SCREENING METHOD

The test method provides data for making relative assessments of the storage stability of halon replacement candidates. It also can be used to determine if there is a potential for the compound to form toxic, or otherwise undesirable, products in the process of degradation.

The test method can be applied without difficulty to gaseous or liquid samples. However, liquid samples will be vaporized during the accelerated aging process. No provision has been made to account for the differences in the reactivities of the liquid and its vapor. The interaction between the sample and the cylinder wall is the critical factor influencing storage stability. In general, the duration of the encounters between the molecules and the wall are longer in liquids than in gases, whereas the number of encounters is less. It does not seem unreasonable to assume that a large number of short collisions is as effective as a small number of long collisions in promoting reactions with the cylinder walls. To the extent that this is true, the tests which are actually carried out on the vapor provide a meaningful appraisal of the storage stability of the corresponding liquid.

The test method satisfies all criteria delineated in the first section of this chapter. It is safe, quick, inexpensive, and has very modest sample size requirements.

Contamination is a major problem affecting the performance of this test. The results are extremely sensitive to the nature of the impurities and the state of the cylinder. This is not surprising. Stability is not a property of an isolated system of molecules. It is determined by the interaction of these molecules with their environment. The motivation for using a carbon-steel cylinder in the first place was to imitate the actual storage environment of fire extinguishing agents. Unfortunately, it is difficult to maintain the distinction between a dirty cylinder and a realistic storage environment. It is clear, however, that meaningful comparisons between compounds are not possible if they were tested under a completely different set of conditions. A procedure for purging the cylinder of residuals from the previous test is necessary to ensure consistent test conditions.

## G. LABORATORIES/COST

Most of the test procedure is readily performed by an experienced technician. A qualified spectroscopist is needed to interpret the IR spectra, leading to the Class assignment. A large number of chemical test laboratories have this capability. The procedure requires only about 0.1 mole of a test chemical. It takes about two hours to set up and measure two sets (i.e., before and after aging) of three spectra on an FTIR. The results from each screen are available after two days, the accelerated aging process being the rate determining step. The estimated cost of performing this screen is \$150 per chemical (plus the cost of the chemical).

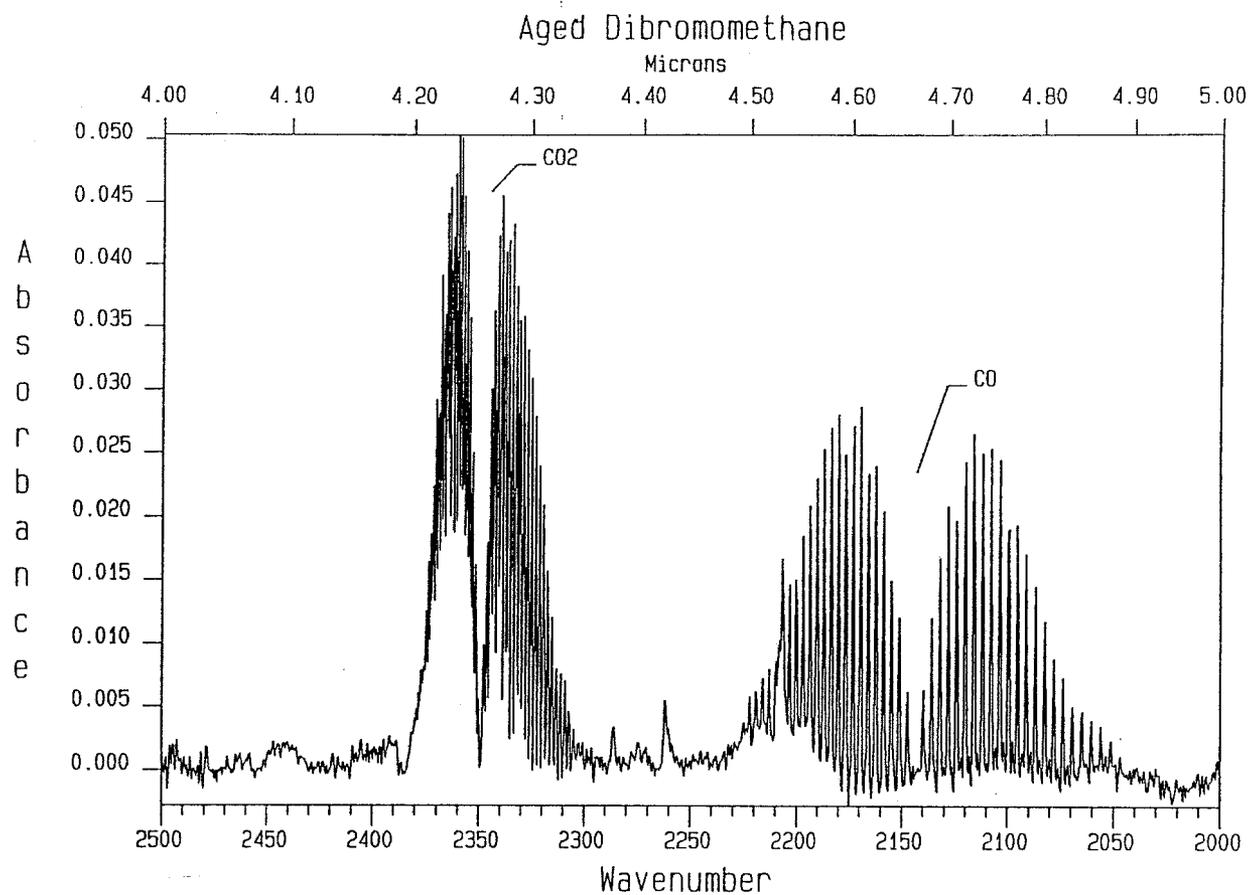


Figure 14. The Presence of CO and CO<sub>2</sub> are Revealed in the Expanded View of the IR Spectrum of a Sample of Dibromomethane Which was Aged at 170°C for Approximately 2 Days.

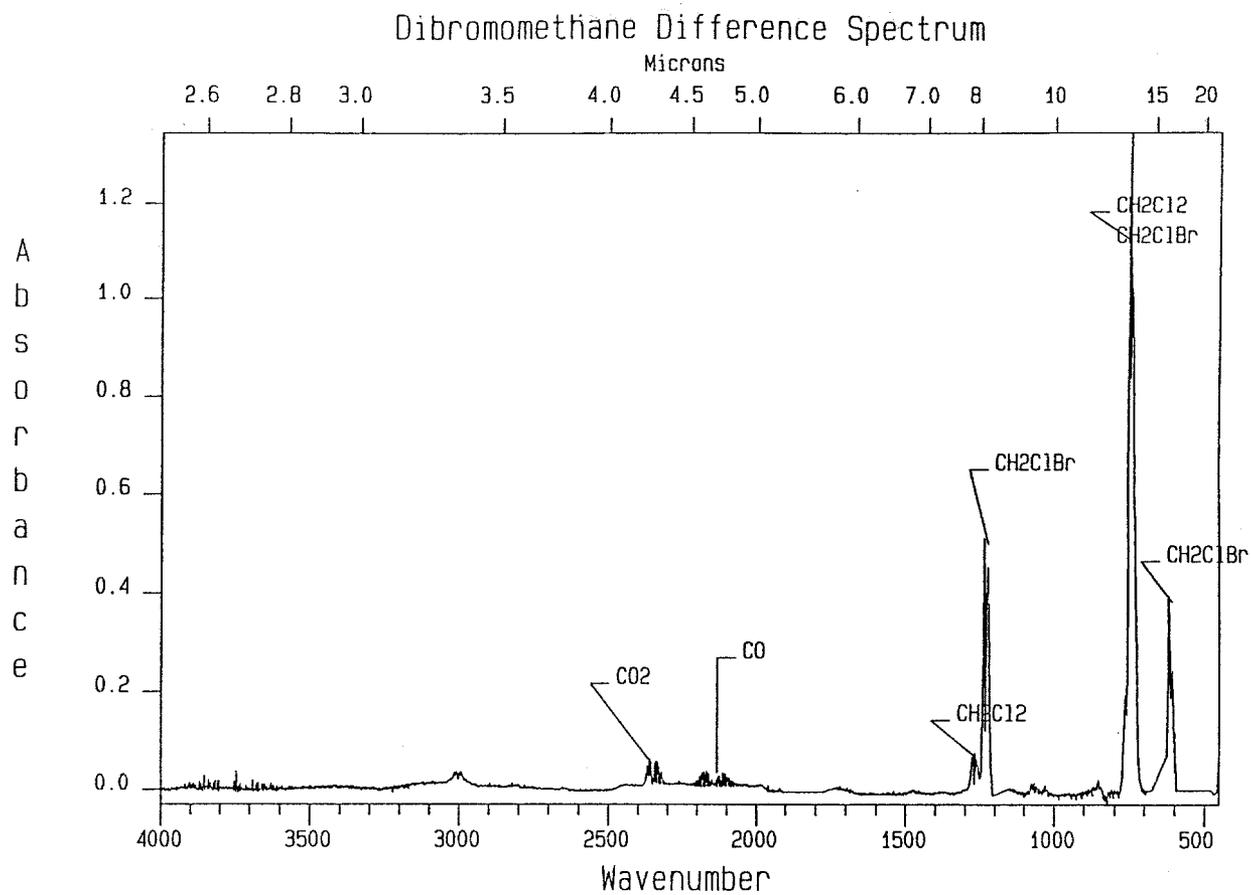


Figure 15. Difference Spectrum Obtained by Subtracting the Spectrum of the Original Sample of Dibromomethane from the Spectrum of the Aged Sample.

## H. CONCLUSIONS

- For some chemicals, it may be possible to identify obvious sources of instability in the molecular structure. If this is sufficient to make a meaningful assessment of storage stability, then no laboratory test is needed.
- For those chemicals whose molecular structure is not clearly unstable, we have developed a screen test method to estimate the long-term storage stability. Performance is determined by measuring decreases in the IR absorbance of the compound of interest or the appearance of new chemicals in the IR spectrum after the sample has been heated. It should be determined whether any new peaks in the IR spectrum represent highly toxic products that might be produced in storage.
- The conditions of the screen have been adjusted so that no degradation will be observed unless the instability of the candidate exceeds that of halons 1301 and 1211.
- Contamination of the test container is a major source of error. The cylinder must be purged at elevated temperatures, and the level of background off-gassing should be measured prior to each application.
- An absolute scale, obtained by calibrating the test results with actual storage data, would facilitate more advanced appraisals of storage stability.
- For candidates that appear superior in the tests for other properties, efforts should be made to identify more suitable modes of storage.

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# SECTION VIII

## METALS CORROSION

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## SECTION VIII

### METALS CORROSION

#### SECTION SUMMARY

This section describes test methods that can be used to evaluate the relative corrosion resistance of selected metals and alloys used in fire extinguishing storage and distribution systems when exposed to halon replacement candidates. These tests are intended to provide corrosion data suitable for the preliminary evaluation of uniform corrosion, crevice corrosion, pitting corrosion, intergranular corrosion, dealloying corrosion, and stress corrosion cracking .

The corrosion behavior of aluminum, copper, galvanized steel, mild steel, and stainless steel exposed to pure halons 1211 and 1301, halons 1211 and 1301 contaminated with water, and distilled water itself were quantified using a test method selected for screening. The results from these tests allow the suppressants to be placed in one of three classes based on their corrosion effects:

- Class 1: Corrosion not observed on any of the test metals after 7 days of immersion in the test chemical [corrosion rates generally less than  $1 \times 10^{-6}$  mm/year].
- Class 2: Corrosion observed on some, but not all, metals after 7 days of immersion in the test chemical, and the corrosion rates are generally in the range from  $1 \times 10^{-6}$  to  $1 \times 10^{-4}$  mm/year.
- Class 3: Corrosion observed on all metals after 7 days of immersion in the test candidate, and/or the corrosion rates are greater than  $1 \times 10^{-4}$  mm/year.

Test candidates that exhibit corrosion behavior similar to or better than halons 1211 and 1301 should later be evaluated more extensively for long-term exposure effects.

The screening required 0.3 liter of liquid or 1.0 liter of gas and 3 staff days of effort. The cost of performing the test is about \$200 per agent plus the cost of the agent. A large number of commercial testing laboratories are capable of performing this screen.

#### A. BACKGROUND

##### 1. Introduction

A variety of metals and alloys are used in fire extinguishant storage systems. Poor pairing of these metals with a new fire suppressant could result in corrosion, which could cause the system to fail if a fire occurs.

The type of internal corrosion that can occur when metals are exposed for long periods to a fire extinguishing agent can range from uniform general attack and tarnishing to more complex processes such as pitting, crevice corrosion, intergranular corrosion, and/or stress corrosion cracking. As a result, it was decided potential halon alternatives should be screened for their relative corrosion of the metals commonly used in fire extinguishing systems.

The first step in the process of identifying an appropriate corrosion screening test was to search the literature for experimental data on the corrosion of metals and alloys exposed to halons 1301 and 1211 in simulated storage environments. Very little information was found outside of the data provided in the technical bulletins from the manufacturers of halons [1-3]. Their data suggest that the currently used halons and the products of their decomposition have little adverse effects on the metals. However, if moisture is present, localized corrosion may occur during long term exposures.

## **2. A Review of Potential Corrosion Failure Modes**

There are eight categories of corrosion failure modes, based on the appearance of the corroded metal [4].

- General corrosion is due to chemical or electrochemical reactions which proceed over the entire exposed surface of the material. An example of general corrosion is illustrated by the immersion of zinc in dilute sulfuric acid. The zinc will dissolve at all points on its surface. This type of attack causes the metal to become thinner and eventually fail.
- Crevice corrosion denotes accentuated damage because of differences between the environment of an occluded region and openly exposed surfaces. The accelerated attack is due to differences in electrical potential. Crevice corrosion is most intense in media containing halogen ions (especially  $\text{Cl}^-$ ). It frequently requires a long incubation period before it initiates; but, once started, may propagate rapidly. Metals or alloys which are normally protected by passive films are particularly susceptible to crevice corrosion.
- In pitting corrosion, holes grow in the surface of the metal. In some cases, the holes may be relatively small, with the surface diameter about the same as or less than the depth of the pit. Pitting is an autocatalytic process; the corrosion conditions produced within the pit tend to accelerate the corrosion process in the pit, and rapid perforation may occur. Usually, pitting is observed in passive metals (aluminum alloys, stainless steels, etc.) exposed to environments containing halogen ions (especially  $\text{Cl}^-$ ).
- Intergranular corrosion is accelerated attack at or adjacent to the intercrystalline or grain boundaries of the metal. There may be little or no corrosion away from these boundaries. This type of attack may cause grains to fall out, resulting in complete loss of mechanical strength. Intergranular attack can be rapid or slow.
- Stress corrosion cracking results from the simultaneous presence of tensile stress and a corrosive environment. These stresses may be from the design load or from residual stresses remaining in the material from fabrication. There may be little outside evidence of corrosive attack while these cracks nucleate and grow possibly causing catastrophic failure.
- Dealloying, or selective leaching, is the removal of one of the elements from the surface of an alloy by corrosion processes. This attack leaves a porous residue having little or no mechanical strength. The selective removal of zinc from brass alloys is an example of dealloying called dezincification. Dealloying can be either uniform or localized.

- Galvanic, or two-metal, corrosion results when two dissimilar, connected metals are immersed in a corrosive or conductive medium. The potential difference that exists between the metal couple accelerates the rate of corrosion of the less noble metal while slowing the rate of attack of the more noble metal. This effect can be used to protect the more noble metal from attack. However, if the active metal is a critical component, catastrophic failure may result.
- Erosion corrosion is an increase in the rate of attack caused by the movement of a fluid over a metal surface. Thus, both mechanical and corrosive processes are involved. Although most metals and alloys are susceptible to erosion corrosion damage, passive metals such as aluminum and stainless steels are especially susceptible. This is of marginal applicability to this project.

### 3. Common Metals and Alloys Used In Fire Extinguishing Systems

A variety of metals and alloys are used in portable and stationary fire extinguishing systems. Some of the most common metals and alloys used in storage vessels, piping, and fittings are described below.

- **Stainless Steel** - These are iron-based alloys containing at least 10.5 percent chromium. They are called "stainless" because of their excellent corrosion resistance, which is primarily due to this high chromium content. The addition of chromium to iron causes the formation of a protective surface oxide film. Stainless steels are grouped into four major classes based on their composition and crystallographic structure. The four classes are: ferritic, austenitic, precipitation-hardening, and duplex stainless steels.

The stainless steels most commonly used in fire extinguishing storage vessels are type 302 and type 321. These austenitic stainless steels are ternary iron-chromium-nickel alloys containing 16 to 25 percent Cr and 7 to 20 percent Ni. Type 302 is classified as a general purpose alloy and can be used in wide applications ranging from jewelry to aircraft structures. Type 321, a stabilized grade, contains the carbide-stabilizing element titanium. Type 321 can be used in applications requiring high temperature service and weldments subjected to corrosion conditions. The addition of carbide-stabilizers to this type of stainless steel helps prevent intergranular corrosion.

- **Carbon Steel** - In 1985, carbon steels accounted for over 64 million tons, or approximately 88 percent, of the steel produced in the United States [5]. Carbon steels have a wide range of properties and are relatively low in cost. As a result, carbon steels are used in a wide variety of applications such as marine applications, transportation, construction, pipelines, and chemical processing. Carbon steels have relatively limited corrosion resistance. They, therefore, frequently have organic or inorganic coatings to prevent corrosion. In aqueous solutions, the corrosion rate of carbon steels is frequently determined by the rate of the cathodic reaction:



which is determined by the amount of dissolved oxygen present. As a result, the rate of attack of sealed carbon steel fire retardant distribution systems may be very low because of the limited availability of cathodic reactants.

Carbon steels have a low alloy content, with all the alloying elements accounting for less than 2 percent by weight. These low levels generally do not produce dramatic changes in corrosion resistance. However, small alloying additions of copper, chromium, nickel, and/or phosphorus have been found to reduce the corrosion rate in certain environments. For example, the corrosion rate has been shown to decrease by a factor of two or three by the addition of 0.05 percent copper [6,7].

Carbon steels, such as ASTM A 106 Grades A and B, are the most commonly used materials of construction for pipelines. These steels are frequently coated with zinc using the hot dip galvanizing process. The zinc coating provides a both barrier and cathodic protection to steels.

- Copper - Copper has many properties which make it desirable for many engineering applications and is frequently used in many applications where corrosion is a concern. Dry fluorine, chlorine, bromine, and their hydrogen compounds are not corrosive to copper and copper alloys, but corrosion occurs when moisture is present in these environments.

Copper-zinc brasses are the most widely used group of copper alloys. Brasses, such as yellow brass, have excellent workability and are significantly stronger than pure copper. The corrosion resistance of brasses in aqueous solutions is strongly influenced by the zinc content. When the zinc content exceeds 15 percent, dezincification may occur and susceptibility to stress corrosion cracking increases.

- Aluminum - The excellent corrosion resistance of aluminum is due to its surface oxide film. In environments where this film is unstable, aluminum and aluminum alloys will corrode very rapidly. However, in environments where this film is stable, the film will rapidly reform whenever it is damaged. This film is stable in many environments and frequently is grown deliberately. In addition to its excellent corrosion resistance, aluminum is light in weight, and has good electrical and thermal conductivity. Some alloys have greater strengths than those of structural steels. These properties make aluminum one of the most versatile engineering materials for construction.

## **B. EXISTING TEST METHODS**

A large variety of standard tests can be used to evaluate corrosion behavior in the absence of service history or when time or budgetary considerations prohibit simulated service testing. These tests may also be used for screening before simulated-service testing, particularly for materials and environmental comparisons. These tests, most of them accelerated tests by design, range from simple weight-loss tests to sophisticated electrochemical tests. Factors involved in the selection of the most pertinent testing method(s) include defining the objectives, duplication of test conditions representative of those encountered in service, and the measurement and reporting of results in such a way that they can be used as part of the basis for making a decision.

The Annual Book of ASTM Standards (Vol 03.02, Metal Corrosion, Erosion, and Wear) describes standardized tests methods for both routine and specialized corrosion testing. Test methods are also described in product specifications. However, special conditions may require modification of these tests.

## 1. Electrochemical Test Methods

Corrosion is an electrochemical process. Electrochemical reactions occur at anodic and cathodic sites that are in electrically and ionically conducting contact with each other [8]. Electrons and ions flow between these anodic and cathodic sites. If the potential of the corroding metal does not change, then the rates of the anodic and cathodic reactions are equal. In the absence of an applied potential, both the anodic and cathodic reactions occur on the surface of the corroding metal and cannot be measured directly [9-12]. As a result, the corrosion rate cannot be directly measured; but electrochemists have developed methods for using electrochemical measurements to provide qualitative and semi-quantitative information about the corrosion rate.

A schematic diagram of a typical polarization experiment is shown in Figure 1. The electrochemical polarization of the sample or working electrode is produced by a potentiostat. The working electrode is polarized by a current produced by an auxiliary electrode. The potential between the working electrode and the reference electrode is monitored. The potential can be applied as a function of time, held constant, or applied in a ramp fashion [13]. The current can also be applied to the working electrode in either a ramped or step fashion.

Several electrochemical techniques are used to determine the corrosion performance of metals in aqueous solutions. The basic requirement for the test system includes equipment in accordance with "ASTM Recommended Practice for Standard Reference Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements" (ASTM G 5).

Most of the typical forms of corrosion, including uniform, localized, galvanic, dealloying, and stress corrosion cracking, can be evaluated by electrochemical techniques. Examples of some of the most common electrochemical methods used to evaluate these forms of corrosion will be discussed.

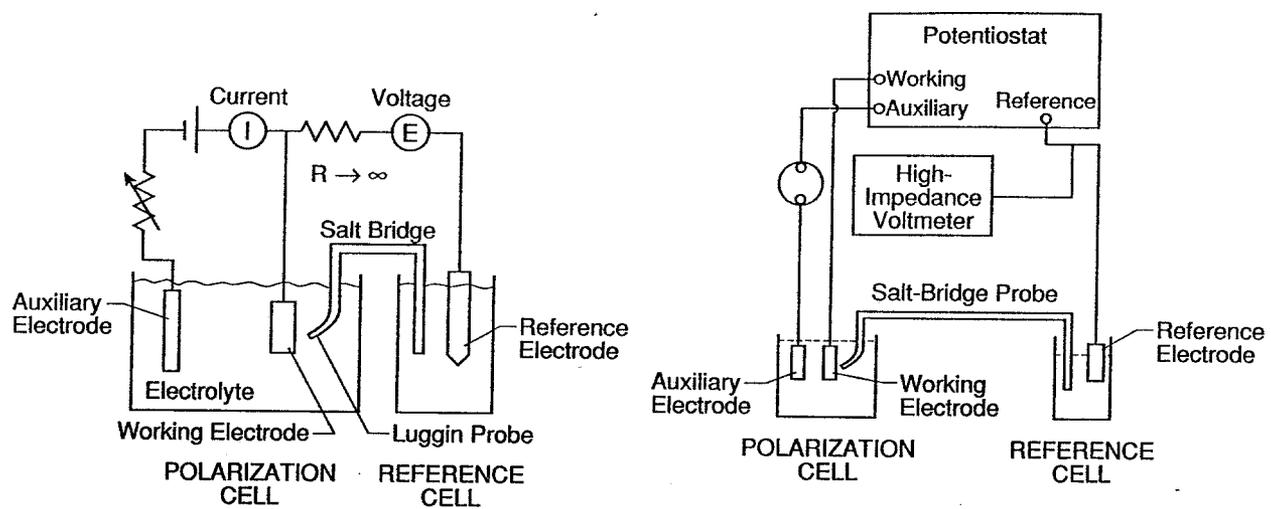
### a. Electrochemical Methods for the Evaluation of Uniform Corrosion

(1) **Polarization Methods.** A plot of the potential vs. the log of applied current, obtained from polarization measurements, will give a linear relationship between the current density and the applied potential, according to the Tafel equation [9,10,14]:

$$i_{app} - i_{corr} \left[ \exp \left( 2.3 \frac{E - E_{corr}}{B_a} \right) - \exp \left( -2.3 \frac{E - E_{corr}}{B_c} \right) \right] + C \left( \frac{dE}{dt} \right) \quad (1)$$

where  $i_{app}$  is the applied current density based on the electrochemical surface area;  $i_{corr}$  is the corrosion current density;  $E$  is the applied voltage;  $E_{corr}$  is the open-circuit potential;  $C$  is the interfacial capacitance associated with the electrochemical double layer;  $B_a$  and  $B_c$  are the anodic and cathodic Tafel coefficients related to the slopes of the polarization curve in the anodic and cathodic regimes, respectively; and  $dE/dt$  is the time rate of change in applied potential, or the voltage, scan rate. The corrosion current can be measured from the intersection of the corrosion potential and either the anodic or cathodic Tafel regions [4,9,12,14]. The Tafel slopes of these measured regions are constant. This method is illustrated in Figure 2.

The main advantage of this technique is that it is quick. Curves can be generated in about one hour. The main disadvantage of this method is that, for real measurements, it is frequently difficult to identify a linear region and solution conductivity and the diffusivity of ions in the solution cause deviations from the ideal Tafel behavior.



**Figure 1.** Schematic Diagram of a Typical Polarization Experiment.

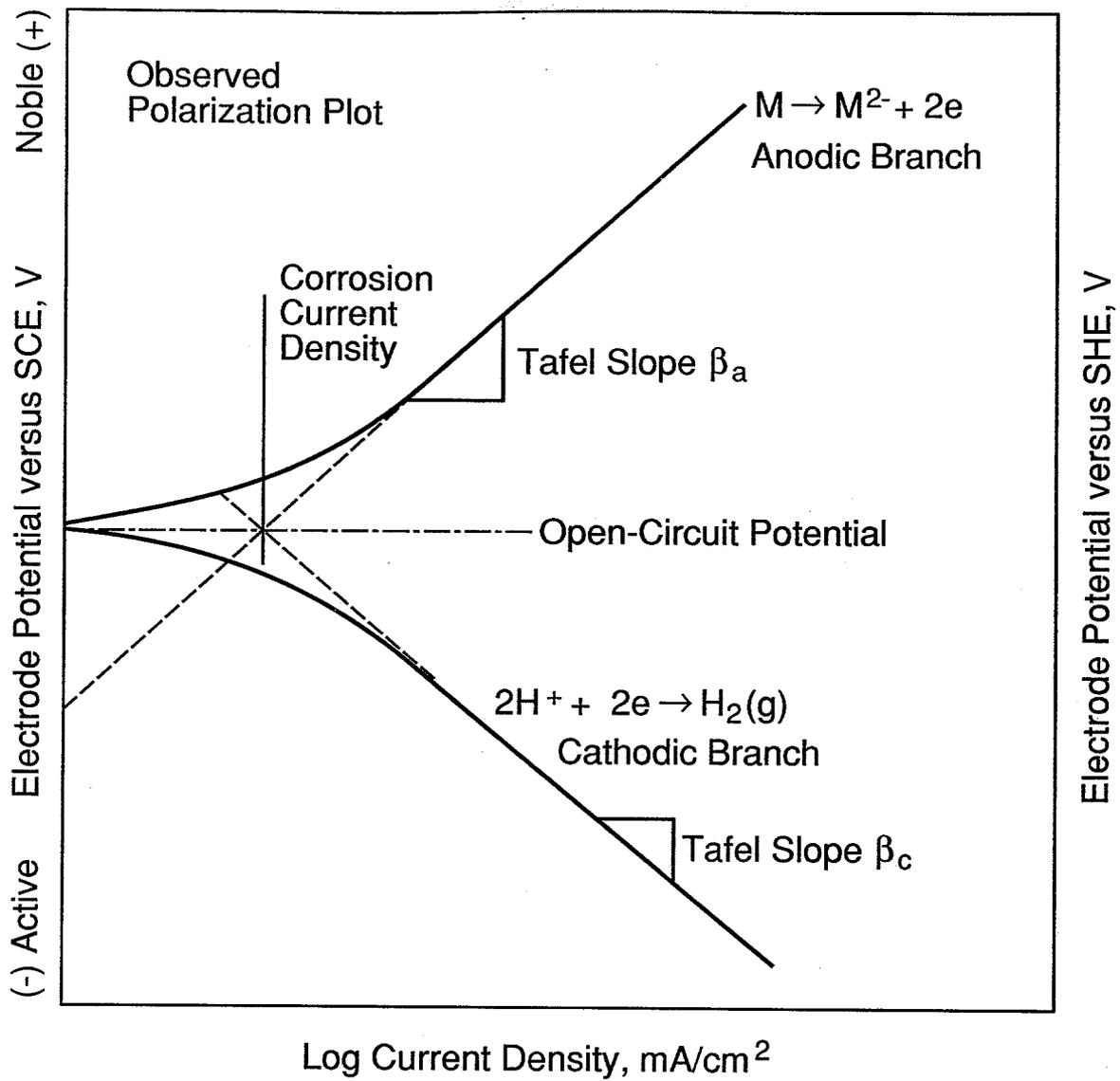


Figure 2. Typical Output from a Polarization Experiment.

(2) **Polarization Resistance Methods.** Theoretically, the corrosion rate can be determined from the slope of the potential vs. current curve at the rest potential of the freely corroding metal. Experimentally, applied current density is frequently linear with potential for anodic and cathodic polarization within 10 mV of the corrosion potential [9]. The slope of this plot is determined at the corrosion potential and is known as the polarization resistance. The polarization resistance and Tafel slope values permit direct determination of the corrosion rate at any instant in time [15-17].

Although this is a quick technique, there are several sources of error:

- the oxidation of some other electroactive species besides the metal is not considered,
- a change in the open-circuit potential during the test is not considered, and
- departure from linear current density versus potential behavior may occur [18,19].

**b. Electrochemical Methods for Evaluating Galvanic Corrosion**

Direct measurement of galvanic corrosion rates is a technique which involves immersing a metal couple of two dissimilar metals in an electrolyte. The materials are electrically connected together by using a zero-resistance ammeter, which measures the current [20]. The measured current is the galvanic current and can be determined as a function of time. If it is assumed that anodic reactions occur only on the less noble metal and the cathodic reaction occur only on the more noble metal, then the corrosion rate can be calculated from the measured galvanic current.

**c. Electrochemical Methods for Evaluating Localized Corrosion**

(1) **Cyclic Potentiodynamic Polarization Method.** Pitting and crevice corrosion are usually associated with the breakdown of passivity [21]. Potentiodynamic anodic polarization scans can give qualitative information of the passivation tendencies of an alloy under different environmental conditions.

A procedure for conducting cyclic potentiodynamic polarization measurements to determine relative susceptibility to localized corrosion is found in the "ASTM Standard Practice for Conducting Cyclic Potentiodynamic Measurements for Local Corrosion" (ASTM G 61). The cyclic anodic polarization scan is performed at a fixed potential scan rate. From the cyclic anodic polarization curve, the potential at which the anodic current increases rapidly is called the breakdown potential and indicates the initiation of localized attack. When the direction of the potential scan is reversed, the potential where the current drops rapidly is called the repassivation potential.

This method may be used for screening variations in alloy compositions and environments but there are several problems involved with potentiodynamic and cyclic potentiodynamic anodic polarization curves. Both the breakdown potential and the protection potentials are a function of the scan rates; thus these rates must be chosen carefully so that time is allowed for pitting and repassivation to occur. Also, the presence of a crevice in the sample may promote pit initiation and prevent repassivation.

(2) **Potentiostatic Method.** The potentiostatic method involves monitoring the current or current density versus time at a constant applied potential. This method can be used to study either initiation or propagation and repassivation mechanisms.

Two variations of potentiostatic measurements are commonly used. The first method, primarily associated with initiation studies, measures the change in current density over time at potentials greater than and less than the breakdown potential,  $E_b$ , determined from the potentiodynamic method. The initiation of localized corrosion is indicated by a current increase. The second method is associated with propagation and repassivation. Pits are intentionally initiated by applying a potential above the breakdown potential and then quickly shifting to a potential below that value. Propagation of existing pits will continue and the current will increase. However, at  $E$  less than the repassivation potential, pits are repassivated and the current decreases with time.

(3) **Galvanostatic Method.** The galvanostatic technique measures potential versus time at a constant applied current. Measurements are generally made as the potential decreases in time until a constant potential is reached. This potential is called the protection potential. Although the measurement of potential versus time at constant current is very quick and easy using this technique, the periodic oscillations of the potential may cause difficulty in interpreting the data.

(4) **Scratch-Repassivation Method.** The scratch-repassivation method measures the current as a function of time while the surface of the alloy is scratched at a constant potential [22]. The potential dependencies of the induction time and the repassivation time are determined by monitoring the current change over a range of different potentials. The critical pitting potential can be determined from this information.

(5) **Electrochemical Impedance Spectroscopy (EIS).** EIS has made it possible to perform electrochemical laboratory tests for applications where traditional DC techniques could not be used, such as organic coatings and low conductivity media, especially for test systems having high resistance, such as non-polar media or specimens having non-conductive coatings [23-25].

The technique is sensitive to changes in the resistive-capacitive nature of passive films or coatings. The applied signal used in EIS consists of a broad bandwidth in frequencies, usually from the mHz range to the kHz range. This enables EIS to discriminate between the resistive properties of the passive film or coating because of its weak ionic and/or electronic conductance and the capacitive nature of the passive film or coating due to its dielectric constant, area, and thickness.

Overall, the advantages of electrochemical techniques are that the tests are nondestructive and that corrosion rates can be measured rapidly, within hours, compared to days or weeks with the weight-loss technique. They can be used to accurately measure very low corrosion rates which would be difficult and tedious to perform with conventional weight loss techniques. These techniques allow corrosion rate measurements to be obtained for structures which cannot be visually inspected or subjected to weight-loss tests.

## 2. Environmental Simulation and Exposure Test

Immersion testing remains the best method to eliminate those materials that obviously cannot be used [26]. This technique is frequently the quickest and most satisfactory method of making a preliminary selection of the best candidate materials. It involves the immersion of small pieces of the candidate metal in a liquid, gas, or solid medium. The loss of mass of the metal is then measured for a given time. The general guides for immersion testings have been developed by ASTM [27] and the National Association of Corrosion Engineers (NACE) [28].

Immersion tests may be classified into three groups: (1) total immersion, which involves the complete immersion of test specimens in a medium; (2) partial immersion, which involves the partial immersion of the test specimen in a medium, thus simulating conditions commonly found in service environments and allows for the determination of localized corrosion at the liquid line; and (3) intermittent immersion which involves the immersion and emersion of test specimens in a medium, simulating situations in which the specimen is totally removed from the medium for some period of time and then re-immersed, such as rise and fall of tidal waters.

The solution composition, temperature, aeration, volume, velocity, and water line effects; specimen surface preparation; method of immersion or specimens; duration of test; and method of cleaning specimens at the conclusion of the exposure will all affect the interpretation of test results.

Possibly the most serious disadvantage of this method of corrosion study is the assumption that the corrosion rate does not vary with time. The corrosion rate could be high initially and then decrease with time, or fall to zero. In other cases, the corrosion rate may increase with time. Another problem with this technique is that corrosion product films or scales can cause weight loss measurement errors. To weigh the remaining metal accurately, it is necessary to remove the corrosion products without removing any of the solid metal. This is difficult to achieve at times. These shortcomings are less critical for screening purposes.

**a. General, or Uniform, Corrosion**

The rate of uniform attack can be accurately estimated from either weight loss or specimen thickness change measurements. The rate of attack may vary with time. Thus, measurements should be made at more than one time interval. The rate of uniform attack can be expressed as millimeters per year (mm/y) or mils per year (mpy).

**b. Crevice Corrosion**

The immersion technique for crevice corrosion involves the use of a crevice created by two metal test specimens clamped together or a metal specimen in contact with an inert plastic or ceramic. Crevice corrosion is evaluated based on weight loss measurements, microscopic examination and by measurements in accordance to ASTM G 48.

**c. Pitting Corrosion**

The evaluation of pitting damage is difficult to predict by laboratory tests. Pitting usually requires an extended initiation period, that can vary from a few seconds to several months or a year, before visible pits appear. After initiation, pits penetrate the metal at a rapid rate. Weight-loss measurements usually give no indication of the true extent of damage. The weight loss is low, and the measurements do not indicate the depth of penetration. Evaluation is based on pit density or loss in mechanical properties. It is also difficult to obtain a quantitative measurement and make comparisons between samples because of the varying depths and number of pits that may occur under identical conditions.

**d. Intergranular Corrosion**

Intergranular corrosion is difficult to evaluate from simple immersion tests except under severe conditions when grain fall-out may be readily observed. Metallographic examination is made on test coupons after bend tests.

**e. Stress Corrosion Cracking**

The susceptibility of a material to stress corrosion cracking is generally measured by the time required to produce fracture after a stressed specimen is exposed to a corrosive environment. No quantitative design information is derived from this test method; only cracking or no-cracking results are obtained from this simple and inexpensive test method. More quantitative information can be obtained by applying the principles of fracture mechanics and measuring the crack growth rate as a function of the applied stress intensity factor, but this requires large specially designed samples and takes considerable preparation and calibration.

**f. Dealloying**

Dealloying requires more sophisticated evaluation than simple weight-loss measurements. However, the measurement of a significant weight loss without observing any surface corrosion damage would be an indication that dealloying may be occurring.

**g. Galvanic Corrosion**

Evaluation from galvanic couples give only qualitative results. The galvanic couple is compared to an insulated specimen which was exposed on the same holder as the couple.

**h. Erosion Corrosion**

Erosion corrosion is characterized by the appearance of grooves, gullies, waves, rounded holes, and valleys, and usually exhibits a directional pattern.

## **C. SCREEN METHODS SELECTED**

There is clearly a wealth of appropriate standard methods. We selected the following tests and operating conditions:

- Environmental simulation and exposure tests. These are reliable, quick, easy, and inexpensive to perform. They also require small quantities of test materials. A general procedure is in Appendix A.
- Two screening procedures, based on ASTM G 31 and G 30 test methods.
  - Specimen size, preparation, and cleaning procedures, and data interpretation are all based on these two test methods.
  - Modifications to the test procedures include the use of sealed glass tubes [29], which allows the test metals to be exposed to the agents at a given pressure, and the use of a modified U-bend test specimen that also allowed for the evaluation for crevice corrosion.
  - As an option, the tests could be conducted in an autoclave instead of the sealed glass tubes. This would allow exposure to pressures typical of service conditions, facilitate the periodic removal of specimens for evaluation, and provide a safer test environment.

- The metal samples should be only partially immersed, so that their relative susceptibility to localized corrosion at the liquid line can be evaluated. (Note: the samples tested here were totally immersed.)
- ASTM G 46 was also used in interpreting the results for pitting corrosion
- The following common materials used in fire extinguishing storage and distribution systems as subjects for determining the level of corrosion from candidate fire suppressants:
  - 2024 aluminum,
  - copper,
  - 1020 steel,
  - 302 stainless steel, and
  - galvanized steel.
- Evaluations at 1 day and 7 days of exposure. Chemicals that are highly reactive with the selected metals may be eliminated after one day. Test results from the seven days exposure can be used to determine whether or not further evaluation is warranted for the test candidate.
- The following chemicals as test agents:
  - pure halons 1211 and 1301,
  - double-distilled water,
  - halon 1211 + 3 volume per cent distilled water, and
  - halon 1301 + 3 volume per cent distilled water.

The pure halon corrosion data serves as baseline data for candidate agents; water contamination is a known major corrosion factor in current fire suppressant storage systems. [Because of poor conductivity, halons 1211 and 1301 are not suitable media for uses in electrochemical test systems.]

- Testing can also be conducted in an autoclave instead of the sealed glass tubes. An autoclave would allow testing to be conducted at pressures typical of service conditions, facilitate the periodic removal of specimens for evaluation, and provide a safer test environment.

## D. CRITERIA

Decision trees (Figures 3 and 4) have been developed to assist in the screening of the test candidates. The results from these tests allow a chemical to be placed in one of three classes based on its corrosion behavior:

- Class 1: Corrosion not observed on any of the test metals after 7 days of immersion in the test chemical [corrosion rates generally less than  $1 \times 10^{-6}$  mm/year].
- Class 2: Corrosion observed on some, but not all, metals after 7 days of immersion in the test chemical, and the corrosion rates are generally in the range from  $1 \times 10^{-6}$  to  $1 \times 10^{-4}$  mm/year.

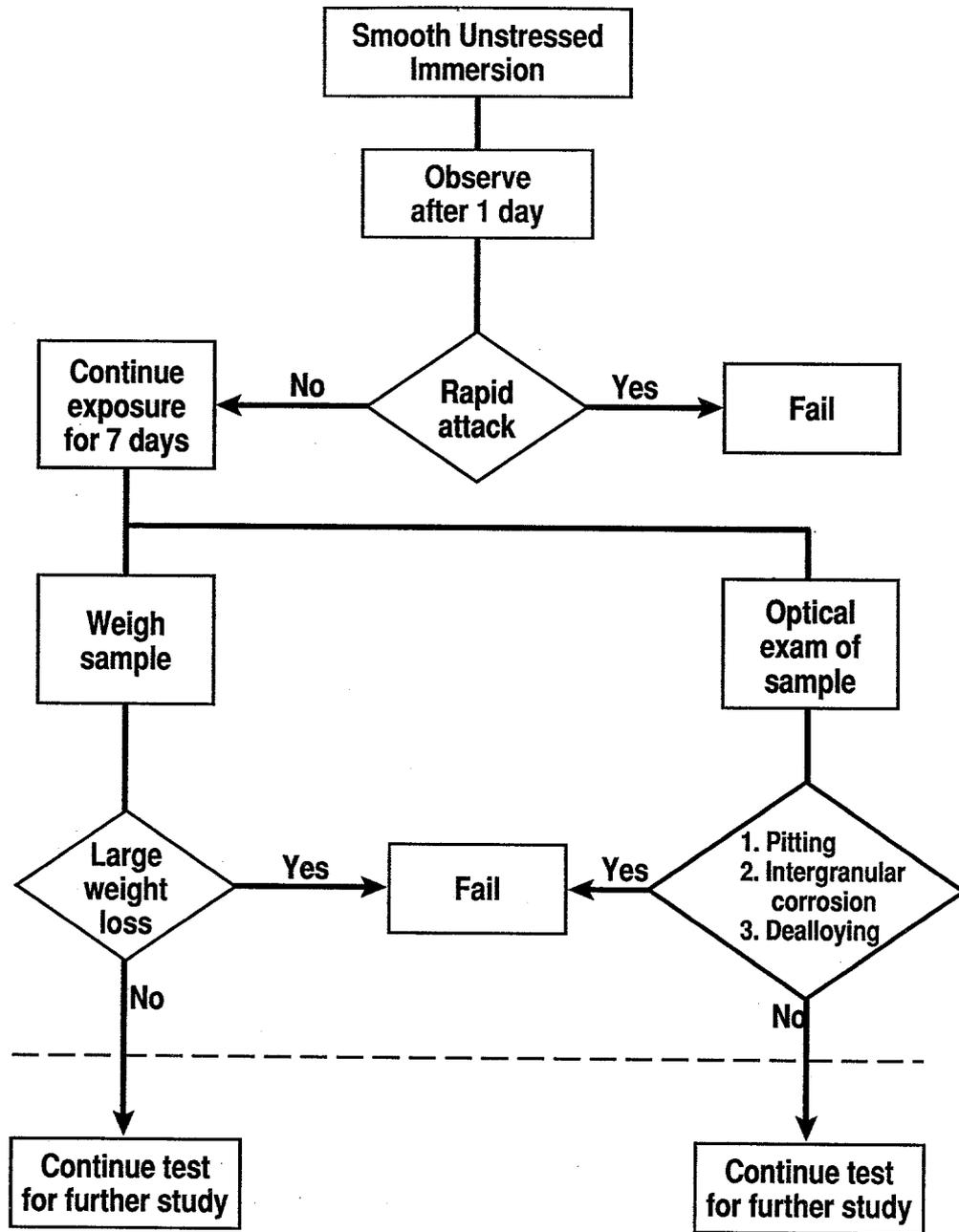


Figure 3. Decision Tree for Corrosion of Unstressed Metals

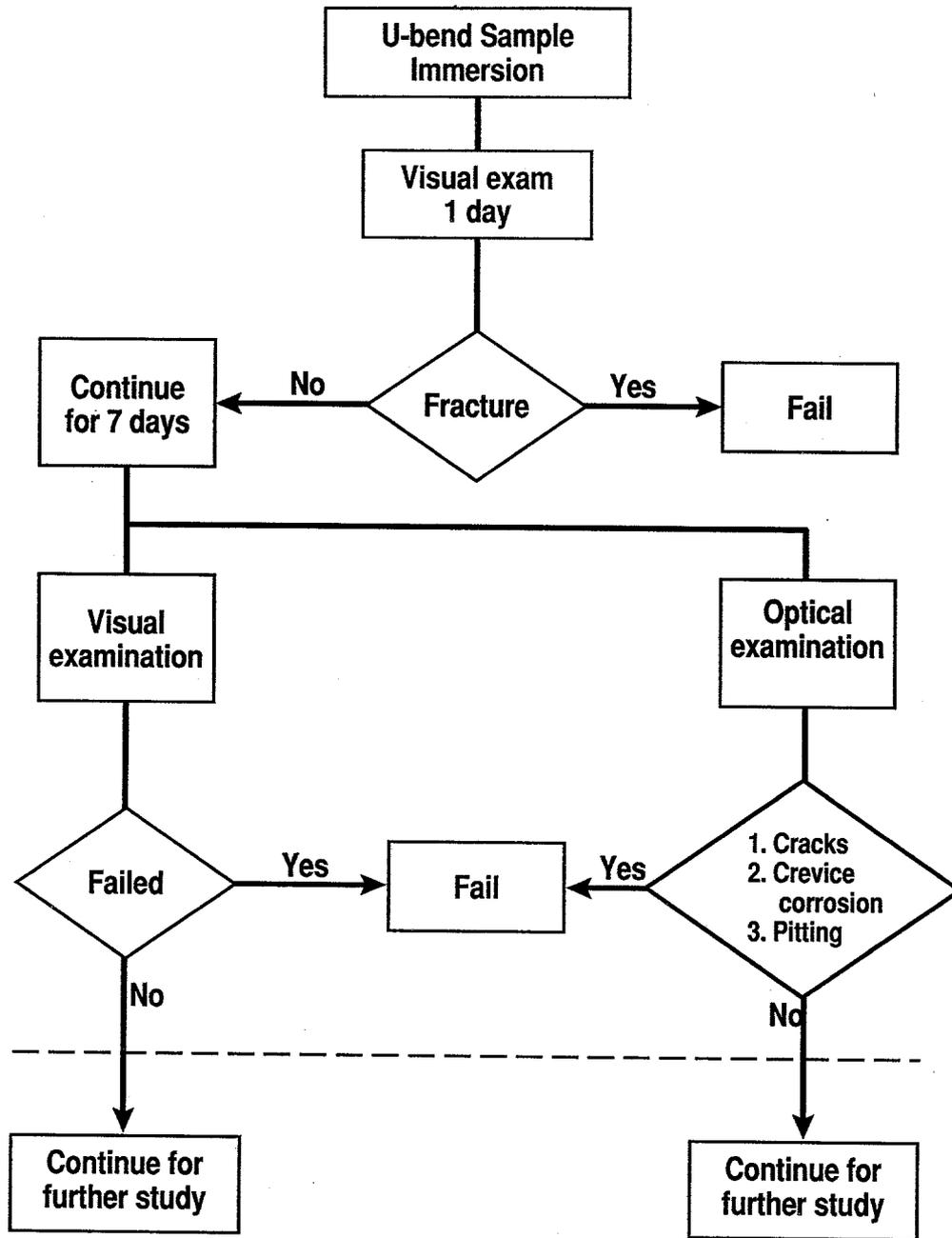


Figure 4. Decision Tree for Corrosion of Stressed Metals.

Class 3: Corrosion observed on all metals after 7 days of immersion in the test candidate, and/or the corrosion rates are greater than  $1 \times 10^{-4}$  mm/year.

Test candidates that exhibit corrosion behavior similar to or better than halons 1211 and 1301 should later be evaluated more extensively for long-term exposure effects.

## E. PERFORMANCE DATA

Copper, aluminum alloy 2024, stainless steel alloy 302, galvanized steel, and 1020 carbon steel coupons were separately exposed to the test agents for seven days at ambient temperature (24 to 26°C) and pressure (one atm) using the two test methods described in the appendices to this section, with the modifications described above.

The test coupons were examined visually after one day without removal from the glass tubes. No signs of corrosion were detected for any of the samples in any of the tubes.

After seven days of immersion, the test coupons were removed for closer examination. Both visual and optical observations of the coupon surfaces indicated that the mode of attack was due to general corrosion. Evidence of pitting corrosion, or intergranular corrosion was not observed. The mean weight loss data from duplicate specimens in the immersion tests are shown in Table 1. The data indicate that the corrosion rates for the halons and "wet" halons were very low, less than  $1 \times 10^{-5}$  mm per year, except for the carbon steel. These values were somewhat higher, but still allowed a Class 2 rating. The corrosion rates due to the distilled water were quite high, resulting in a Class 3 designation.

The U-bend crevice corrosion coupons were examined after being exposed to the test agent for seven days at ambient temperature (24-26°C) and pressure (one atm). Optical examination of the stressed area showed no signs of cracks or fractures. Signs of crevice corrosion were observed in the 2024 aluminum and 1020 steel coupons, but the amount was too small to be measurable.

The resulting classification for each agent is given below:

<u>Agent</u>	<u>Classification</u>
1211	Class 2
1211 + 3 vol. % water	Class 2
1301	Class 2
1301 + 3 vol. % water	Class 2
Water	Class 3

## F. EVALUATION OF SCREENING METHOD

This screening method is capable of evaluation and ranking test agents for the corrosion behavior of selected metals. The two test methods are reliable, quick, and easy to perform and interpret.

An agent should be tested both in its pure state and after being contaminated with a small amount of water. This will capture the effect of contamination introduced while filling the storage cylinder. It should

TABLE 1. EFFECT OF TEST AGENTS ON METALS FOR SEVEN DAYS AT ROOM TEMPERATURE

Metal	Agent	Corrosion rate (mm/y)	Metal	Liquid
Copper	1211	$6.7 \times 10^{-6}$	No change	No change
	1211 + water	$7.3 \times 10^{-6}$	Tarnish	No change
	1301	$6.3 \times 10^{-6}$	No change	No change
	1301 + water	$6.9 \times 10^{-6}$	Tarnish	No change
	water	$4.7 \times 10^{-4}$	No change	No change
302 Stainless steel	1211	$5.8 \times 10^{-6}$	No change	No change
	1211 + water	$6.2 \times 10^{-6}$	No change	No change
	1301	$5.2 \times 10^{-6}$	No change	No change
	1301 + water	$6.4 \times 10^{-6}$	Tarnish	No change
	water	$5.3 \times 10^{-4}$	Tarnish	No change
2024 Aluminum	1211	$4.8 \times 10^{-6}$	No change	No change
	1211 + water	$5.2 \times 10^{-6}$	No change	No change
	1301	$4.6 \times 10^{-6}$	No change	No change
	1301 + water	$4.9 \times 10^{-6}$	No change	No change
	water	$5.6 \times 10^{-4}$	No change	No change
Galvanized steel	1211	$6.8 \times 10^{-6}$	No change	No change
	1211 + water	$6.3 \times 10^{-6}$	Tarnish	No change
	1301	$6.6 \times 10^{-6}$	No change	No change
	1301 + water	$6.1 \times 10^{-6}$	Tarnish	No change
	water	$3.6 \times 10^{-4}$	Dark tarnish	No change
1020 steel	1211	$7.2 \times 10^{-5}$	Tarnish	No change
	1211 + water	$8.5 \times 10^{-5}$	Dark tarnish	No change
	1301	$6.9 \times 10^{-5}$	Tarnish	No change
	1301 + water	$7.9 \times 10^{-5}$	Dark tarnish	No change
	water	$3.2 \times 10^{-3}$	Dark tarnish	No change

particularly be noted whether the addition of the water changes the performance class of the chemical being investigated.

This procedure uses an extreme condensation of the real-world exposure time. Therefore, it is critical that longer-term testing be initiated as soon as it is known that the chemical does well under the other screens.

As with the screen for long-term storage stability, poor performance indicates an incompatibility between the chemical and the storage materials. Should a chemical perform well under the other screens, alternative storage might be worth considering.

## G. LABORATORIES/COST

Because this screening method consists of slightly modified ASTM standard procedures, it is within the capability of an experienced technician, with some participation of a staff scientist in interpreting the results. Therefore, any number of independent laboratories could perform the test as described in this section [31].

Numerous samples can be run concurrently, since little laboratory space is needed. Thus, several chemicals can be tested during a single seven-day exposure period. The full battery of tests, including the tests with water contamination, requires less than 0.1 mole of agent. It is estimated that the cost for performing this screen is about \$200 plus the cost of the chemical.

## H. CONCLUSIONS

- We have selected a set of modified standard test methods that can serve as a screening tool for metals corrosion.
- Exposing selected metals and alloys to a chemical for seven days allows for the classification of the chemical based on their corrosion.
- Since some types of corrosion have longer initiation times than others, those candidates that pass the screen after seven days should be subjected to further study.
- This test should be low in a screening hierarchy. Poor performance indicates an incompatibility between the chemical and the storage materials. Should a chemical perform well under all the other screens, other materials might be worth considering.

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## APPENDIX A

### LABORATORY TESTING OF METALS CORROSION BY HALON REPLACEMENT CANDIDATES

#### A. Apparatus

The test is performed using a sealed glass tube as described in reference [29].

Glass tubes, made from 19 mm o.d. x 16 mm i.d. x 150 mm lengths of borosilicate glass.

Teflon washers.

Tube-charging apparatus, used to evacuate the glass tube containing the metal sample, add test solution, and seal it. The amount of the test solution added to the tube is determined by the change in pressure on the manometer.

Individual pipe chambers, used to store the sealed tubes and in a vertical position. The chambers will contain the tubes and its contents in the event of breakage. They will also maintain temperature uniformity.

#### B. Test Specimens

Weight loss coupons: 55 x 15 x 1.6 or 3 mm.

U-bend coupons: 80 x 20 x 2.5 mm, ground to 600 grit finish.

Wash the specimens ultrasonically in water and dry with acetone.

#### C. Test Solutions

Candidate agent.

Candidate agent plus 3 volume percent distilled water.

Distilled water.

#### D. Procedure

Clean the glass tubes by flushing with deionized water, followed by a rinse with acetone. To insure that all contaminants are removed, the tubes may also be cleaned by annealing in a furnace for one hour at 580° C.

For Weight Loss Coupons:

Duplicate tests are to be performed. Insert the test specimen in the tube, attach it to the filling port of the tube-charging apparatus, and add the fire suppression agent in accordance to Section 4.4 of the ASHRAE Standard, "Sealed Glass Tube Method to Test the Chemical Stability of Material for Use Within Refrigerant Systems" (ANSI/ASHRAE Standard 97). Seal the tubes with a torch. Place the tubes in the individual chambers immediately after sealing. The tubes are to be stored vertically in the chambers at room temperature for seven days. Inspect the specimen visually after one day for signs of corrosion. At the conclusion of the test, the specimens are removed from the sealed glass tubes in accordance to Section 6.3 of ANSI/ASHRAE Standard 97, and immediately rinsed in cold water. Rinse the specimen in distilled water, then in acetone, and dry in air. Examine the specimen

visually and note the color, thickness and physical nature of any deposits, and corrosion products on the metal surface. Remove the corrosion products and deposits from the specimen by brushing the surface lightly with a soft brush. If an additional cleaning procedure is required, the electrolytic cleaning procedures described in ASTM G 1 is used.

For U-Bend Coupons:

Stress the test specimens by a two-stage operation, in accordance with ASTM G 30. A Teflon washer will also serve as the crevice block. The block is fastened to the test specimen by passing the bolt through the hole in the specimen and positioning a block on either side of the specimen as in Figure 5. The torque on the bolt should be 0.280 N-m (40 oz-in.). The tubes should be placed in the individual chambers immediately after sealing. The chambers are stored at room temperature. Two separate tests are made: one for one day duration, and one for seven days duration.

#### E. Evaluation of Specimens After Test

The specimen is examined at the end of each test for signs of cracking. Remove the specimen from the sealed glass tube, wash it in water, dry it, and examine the areas stressed in tension under a 20 X binocular microscope. Examine areas under the crevice blocks for crevice attack using low power (20 X) magnification. Crevices are considered corroded if the local attack is one mil or greater, as estimated by either a needle-point micrometer gage or microscope with a calibrated fine focus knob.

Weigh the cleaned specimens to an accuracy of at least  $\pm 0.2$  mg and determine the weight loss during test determined making the appropriate weight loss correction for the "blank" loss during cleaning. The corrosion rate is calculated from this corrected weight loss using the following formula:

$$\text{corrosion rate} \left( \frac{\text{mil}}{\text{yr}} \right) = \frac{345 \times 10^6 (w_i - w_f)}{A \times t \times D},$$

where

$w_i$  = initial weight (g),  
 $w_f$  = final weight (g),  
 $A$  = area of coupon ( $\text{in}^2$ ),  
 $t$  = time (h), and  
 $D$  = metal density ( $\text{g/cm}^3$ ).

$$\text{corrosion rate (mm/yr)} = 0.0254 \times \text{corrosion rate (mil/yr)}$$

Inspect the cleaned specimen using a low-power (20 X) binocular microscope. Make a record of the surface appearance, noting any irregularities of the corrosion attack including a qualitative description of the number and distribution of pits. The nature of the pits is characterized, i.e., shallow or deep, rounded or steep-sided, narrow or wide. Examine the cleaned metal surface under ordinary light to approximate the size and distribution of pits. Follow this procedure by a more detailed examination through a microscope using low magnification (20 X).

Measure the pit depths with a micrometer or depth gage in accordance to the procedure in section 6.2.3 of ASTM G 46. Make a record of the ten deepest pits; the maximum depth and the average of the 10 measurements represents the metal penetration.

Examine the specimens metallographically to determine the severity of any subsurface corrosion effects; such as intergranular corrosion. If intergranular corrosion is suggested by either weight loss or microscopic examination following a bend test then section the sample lengthwise. After polishing and etching, the using standard metallographic techniques for the alloy being tested, examine the entire cross section at a magnification of 100 X. The maximum depth of subsurface attack is reported together with a description of its nature.

# SECTION IX

## ELECTRICAL CONDUCTIVITY

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## SECTION IX

### ELECTRICAL CONDUCTIVITY

#### SECTION SUMMARY

Halon fire suppression agents have as one of their prime uses the protection of areas with electrical equipment. This section develops a suitable screen for possible replacements for the halons so that compatibility with the use in the presence of electrical equipment will be maintained.

While the main requirement for the use of replacement agents in the presence of high powered equipment is the absence of electrical breakdown upon application, a preliminary screen for this requirement is not considered necessary. Most agents that pass the conductance screen can be expected to have a higher breakdown strength than air.

Delicate equipment requires that electrical conductance not exceed a critical value. Gaseous agents will pass this test since they have no conductance in the absence of breakdown. Liquids, however, can vary widely and must be screened.

Current specifications for the halons do not specify a conductance level since they correctly assume that the halons will be suitable for use. A screening level conductivity of  $1 \times 10^{-11} \Omega^{-1} \text{ cm}$  is proposed. This is based on present electronic devices and their characteristics. Also, replacements must leave no conductive residue, but this is addressed in Section 2.

A screen based on ASTM D 924, Standard Test Method for A-C Loss Characteristics and Relative Permittivity (Dielectric Constant) of Electrical Insulating Liquids is proposed. In compliance with this standard, a transformer bridge at 1 kHz and a glass-platinum cell provide detection of conductivity to  $10^{-13} \Omega^{-1} \text{ cm}$ . This is at a level consistent with most circuit considerations.

Measurements performed on halon 1211 show a conductance of  $8 \times 10^{-13} \Omega^{-1} \text{ cm}$ . Methylene chloride, which would be a poor choice, was measured at  $6 \times 10^{-9} \Omega^{-1} \text{ cm}$ . Trichlorofluoromethane was unmeasurably low. These results are consistent with standard reference data.

These results suggest that there need be only two classification schemes for a preliminary screen:

- Class 1:            Those chemicals that are either gases below  $-20^{\circ} \text{C}$  (intended for total flooding as a dilute gas), or those liquids that test for conductivity of less than  $10^{-11} \Omega^{-1} \text{ cm}$  when measured at the lower of  $25^{\circ} \text{C}$  or below their boiling point.
  
- Class 2:            Those liquids that are not used as gases and have conductivities greater than  $10^{-11} \Omega^{-1} \text{ cm}$ .

This screen can be being carried out at a large number of commercial laboratories. The apparatus is commercially available, although a small volume three-terminal liquid cell is not very common; the ASTM published designs use volumes of about 100 ml. The listing of the American Council of Independent Laboratories, the ASTM Directory of Testing Laboratories, and the Directory of Standards Laboratories indicate more than 30 different laboratories offering conductivity measurements. The cost for performing this

test is about \$100 plus the cost of the chemical; about 0.1 mole is required. This cost assumes the cell has to be cleaned after each test and includes possible setup charges (depending on the exact requirements).

Class 1 liquids should be compatible with most electrical equipment but this must be considered a preliminary screen and not final certification. That would include not only conductivity, but also sensitivity to contamination and electrical breakdown.

## **A. BACKGROUND**

### **1. Damage Minimization**

Since the current halons have a major use in suppressing fires in the presence of electrical equipment, it is clear that any substitute should have the same compatibility with electrical equipment that the halons do. This equipment includes not only high power equipment, such as A-C power lines, but also sensitive and costly electronic equipment, such as computers and other solid state equipment. The requirement for suitability in such uses is consistent with the idea of damage minimization.

This compatibility with electrical equipment is clearly mentioned in the ISO standard on halons [1]. It is also mentioned in the NFPA standards for halons [2],[3]. However, in both these standards, as well as the MIL specifications [4], there is no specification for actual conductivity levels. Only in the ISO standard is any mention of conductivity made, and that is only to state that it is suitably low. All of these standards do mention breakdown strengths in the presence of high voltage; but, again, they assume that the halons will be suitable without testing. Only in the NFPA standards is any level of breakdown strength mentioned, and that is that the halons are expected to be at least 1.8 times better than air.

As a result of these weak specifications and the general assumption in them that the halons are known to be suitable without further test, it is necessary to examine carefully what requirements any fire suppressant agent would have to meet so that they could replace the current halons. Based on this examination, it can then become possible to not only choose a suitable screening test method, but also to select a meaningful screening criterion for possible replacements for the halons.

This screen must be based on the electrical requirements, what is possible to expect for possible candidate materials, and what can be measured. The halons will be seen to be so good that a screening value set to their conductivity value may be too restrictive. In what follows, the electrical requirements for liquid conductivity will be addressed. Then, the possible range of values for liquid conductivity will be considered. Based on these criteria, a test method will be proposed. Sample data using this method will then be displayed to show its applicability. Finally, the importance of the screen will be discussed along with requirements from other screens.

### **2. Power Equipment**

The use of fire suppression agents in the presence of high power equipment requires not only that the agent minimize damage to the equipment, but also that use of the agent does not lead to increased power consumption to the point of adding energy to the fire. In general, with the possible exception of the presence of solid state controllers, most power equipment is rugged by design; and, if the compatibility issues addressed in other screens are met, damage by the suppressant agent will be minimal if electrical breakdown does not occur. Certainly, any requirements of sensitive electrical equipment will meet the needs for power equipment in terms of equipment damage not directly related to increased power levels.

**a. Voltage requirements**

Voltage requirements are related to how much additional energy will be dissipated in the electrical circuitry in the presence of the fire suppression agent. The presence of the agent can increase energy dissipation by either the conductivity of the agent or by electrical breakdown in the power equipment upon application of the agent.

Of the two mechanisms, electrical breakdown is directly tied to the voltage levels present in the electrical circuits. The breakdown voltage, in turn, need only be considered for the gaseous phase, since the breakdown strength of a liquid is generally higher than that of its vapor, especially at lower densities and pressures. Most gases will support an electrical discharge at low enough pressure, but only atmospheric pressure need be considered here. As for the liquid suppression agents, since they do vaporize, they too must meet the same requirements as the gaseous agents.

Fortunately, for screening purposes, the breakdown strength need not be tested for possible halon substitutes. The variation with purity will not be great, as shown by the lack of explicit batch tests on the halons. Also, since the agents will occupy the space normally occupied by air, the breakdown strength of any fire suppression agent just has to be higher than air. Since polyatomic molecules tend to have higher breakdown strength than diatomic molecules, such as nitrogen and oxygen, any halon replacement should have enough electrical breakdown strength so that it need not be tested as a screen.

**b. Current levels**

Not only must a fire suppression agent not cause electrical breakdown, which could lead to catastrophic damage from energy dissipation, but the agent must not, by itself, draw sufficient energy from the power circuits so that significant energy will be added to the fire. The mechanism for such dissipation is related to the electrical conductivity of the halon substitute.

This requirement naturally divides the possible halon substitutes into two categories: gases and liquids. This classification is based on the observation that gases, in the absence of any discharge mechanism or any other ion generator, do not conduct electrical energy. Since breakdown mechanisms are not being considered in this proposed screen, gases are of no further consideration.

For liquids, in the absence of strong dissolved salt concentrations, the current drawn from an electrical circuit is equal to

$$I = V * G ,$$

where

I = current,  
V = applied voltage, and  
G = conductance.

This conductance is equal to

$$G = \sigma * A/d ,$$

where

$\sigma$  = conductance of the liquid,  
A = area of the metal electrode contacting the  
fluid, and  
d = electrode separation.

For a voltage of 1000 V and for a material as conductive as distilled water,  $\sigma = 10^{-6} \Omega^{-1} \text{ cm}$ , the possible current levels, milliamperes, are clearly too small to damage large power circuits which are capable of carrying currents the size of amperes.

What can lead to large currents, in the presence of high voltages, is the presence of electrochemically ionizable species in the liquid. This can include both the liquid, such as water, any dissolved material, or, as in the case of water, the combination of the two. As most electrochemical potentials are less than 10 V, the presence of potentials of the order of 100 V can lead to currents much higher than expected from Ohm's Law.

Fortunately, the requirements for sensitive circuits should limit the screened liquids to those in which electrolysis will not be significant. The low conductivity requirements should rule out any ionizable liquids, since their conductance tends to be high. Also, liquids of low conductance tend not to dissolve much in the way of ionizable species so that, again, this should not be a consideration in the screening process.

### **3. Electronic Equipment**

There are two major classifications of electronic equipment that must be considered. These are analog and digital circuits. They have somewhat different requirements and considerations and so will be discussed separately. In both classes, the main consideration must be that the application of the halon substitute not damage the equipment. In both cases, the presence of the halon substitute must not lead to potentials and currents that can cause catastrophic failure. As is true for the halons, the correct operation of the circuits while the fire suppression agent is present will not be considered [5].

#### **a. Analog Equipment**

While analog circuits may represent a much smaller part of the number of circuits in use, they often are the most susceptible to damage. Analog circuits are used to provide the interface to sensors and actuators, even in computer-controlled situations. Since they must work with low power devices, such as most sensor modules, they can be vulnerable to damage from the presence of fire suppression agents. This potential for being damaged comes about from several sources. They are the impedance levels at which the circuits must operate, the potential for catastrophic failure if improper overloads are applied to the circuit elements, and the functionality that they must provide.

(1) **Impedance Levels.** Analog circuit elements can have widely varying impedance levels, depending on their function, but they often must work at very high impedance levels. These levels are most often found where there are connections to sensing devices. Sensors typically have very low electrical output that must be amplified and conditioned prior their utilization in electronic equipment. Current sensors can have outputs in the nanoampere range and voltage sensors can have outputs in the millivolt to microvolt range. In order to utilize such sensors, the input amplifiers must have high sensitivity.

Typically, high sensitivity amplifiers can have input impedances that are at least  $10^{12} \Omega$  with input bias currents of less than  $10^{-12}$  ampere. These sensitivity levels are commonly achieved by commercial operational amplifiers[6]. Charge sensitive detectors can require even higher sensitivities. Halons 1211 and 1301 have conductances that are consistent with these levels.

(2) **Overload sensitivity.** The impedance levels that can be typical for analog circuitry directly affect their overload sensitivity. At the input power levels at which they must operate, a small excess current can cause catastrophic failure. Often, it is not feasible to incorporate robust protective devices as they would interfere with the operation of the circuits.

The overload sensitivity of a circuit is set not only by its input impedance, but by the applied potentials. Most devices require that the input voltage be lower than the supply voltage. Often, there can be high voltages present and the separation of these voltages is maintained by the insulating properties of the circuit boards. The volume conductivity of circuit board material is typically  $10^{-10} \Omega^{-1} \text{ cm}$ . If potentials that are present are redirected by a halon substitute in contact with the electrical circuit and this fluid can carry currents, even as low as milliamperes or less, then sensitive circuitry can be damaged.

This consideration suggests that any halon substitute should have a lower conductivity than the circuit boards the circuits are made from. This would guarantee that no excessive, potentially damaging currents could be applied to the amplifier inputs. This also suggests that a liquid conductivity of  $10^{-11} \Omega^{-1} \text{ cm}$  would be a suitable cutoff level for any screen. As will be seen, halon 1211 easily meets this requirement, and suitable replacements should also. Halon 1301 also meets this requirement, but so would any gaseous reagent, since there can be no conduction in the absence of electrical breakdown.

(3) **Functionality.** The operation of a circuit element while it is in contact with a liquid should not be expected. Any commercial liquid could have enough conductivity so that it would disrupt the signal paths even if no damage were induced. Furthermore, the lowest dielectric constant a fluid is likely to have is 2, while most gases have a value of 1. The capacitive loading on a circuit can prevent its functioning correctly even in the absence of any conductivity.

The main possible requirement for maintaining circuit functionality is after the application a halon replacement, and this would be in what residues it leaves behind. Since the residue problem is being addressed by another screen, it will not be explicitly considered. However, if a residue-forming substitute is considered, then the residue should be evaluated separately. The screen proposed in this section definitely assumes that any electrical contamination comes from the direct application of the halon substitute. While no technical grade liquid is likely to be very pure, a possible halon substitute should not leave behind any conductive contamination.

#### b. Digital Circuits

Many of the considerations that apply to analog circuits also apply to digital circuits. While the requirements are not as severe, since digital circuits tend to use fixed amounts of energy per event, as power levels have dropped with CMOS circuitry, the considerations can be quite similar.

(1) **Impedance Levels.** For TTL and other bipolar circuit technologies, power and current levels are much higher than those found in many analog circuits. Typical TTL level currents are  $10 \mu\text{A}$  for digital high signals and  $1 \text{ mA}$  for digital low signals. Chips can dissipate  $50 \text{ mW}$  and, except for interface chips, can usually withstand supply voltage to any input.

This picture is less true for CMOS circuits which are often found in custom design integrated circuits and other low power applications, such as signal acquisition circuits and portable equipment. Memory chips are CMOS and definitely use very small amounts of charge per bit. The current levels can be less than  $1 \mu\text{A}$  and impedance levels at the input can be the order of  $10^{12} \Omega$ .

(2) **Overload Sensitivity.** As is true for analog circuits, the main possibility for damage is when too high a potential is applied to the input. While most digital circuits can take the full

supply voltage on the input, they cannot tolerate anything higher. Most logic power supplies operate at 5 V, but disc drives and other peripherals require voltages up to 15 V. This level, if accidentally applied to an input without adequate current limiting, will definitely lead to device failure.

In most instrumentation, the circuit board provides the function of separating the voltages required for operation of the circuitry. As for analog circuitry, the presence of a fire extinguishing agent should not lead to the wrong voltages present at the circuits. Such a misapplication would lead to catastrophic failure. This includes such complex pieces as computers. This problem is made worse by the increasing density of paths in modern computer circuits. Since the conductance of a path is inversely proportional to its path length for a given conductivity, even for the more fault-tolerant digital circuitry, it is clearly desirable for any halon substitute to have a lower conductivity than the insulation from which the circuit boards are made. This suggests that the criterion of  $10^{-11} \Omega^{-1} \text{ cm}$  derived from analog circuit considerations is just as applicable to digital circuits .

(3) **Functionality.** The requirements that digital circuitry retain its functionality after application of a fire suppression agent are, again, similar to that for analog circuitry. While current leakage is not as critical, any potential residue can be harmful. Unlike analog circuits, where the capacitance changes from the presence of a fire suppression agent can prevent proper operation of a circuit, digital circuitry usually is not affected. If the fluid is a good enough insulator, all but the most speed critical circuits could probably still function in the presence of an insulating liquid.

Similarly, the requirements for residues are just as important. Conductive residues can create problems for the circuitry and can lead to circuit deterioration. Digital circuitry often uses fine board traces and wires, with 30 Ga. wire common for board jumpers. A conductive residue could lead to galvanic corrosion and failure of the connections and any exposed metal. As indicated before, low conductance liquids would not be likely to leave such deposits.

#### 4. Gas Conductivity

It has already been stated that gases will not be considered in the screen for electrical conductivity. The reason is that in order for there to be a finite, measurable conductivity, there must be charge carriers in the gas. For a gas at atmospheric pressure, these carriers can come only from corona or breakdown.

For gases, as the gas molecules increase in complexity from monatomic to diatomic to polyatomic species, there is a trend towards higher inception voltages for a given set of conditions. The halon substitutes are all expected to be polyatomic molecules and, therefore, have higher inception voltages than air. Since that part of the electrical equipment that will be exposed to halon substitutes will normally be exposed to the atmosphere, any gaseous halon substitute will probably be satisfactory.

The halons themselves [2],[3] are assumed to have breakdown strengths 1.8 times greater than that of air. This breakdown strength is not a strong function of purity and is not, therefore, part of a specification test. It is expected that any substitute for the halons will be at least as good as air and should not need an initial screen for this parameter.

It should be mentioned here that, prior to any certification, any halon substitute must pass tests for not only breakdown strength but, also, for corona-inception voltage. This includes not only substitutes for halon 1301, but also for halon 1211. Any liquid will vaporize in use and, in the presence of high power equipment, the vapor could lead to electrical breakdown problems. For an initial screen, however, such tests would cost more than is necessary.

## 5. Liquid Conductivity

The only class of halon substitutes that is expected to have problems with electrical conductivity are those that could contact electrical equipment in the liquid state. While the time such liquids are expected to be in contact with electrical equipment is probably short, due to evaporation, modern solid state electronics react very quickly to potential damage-inducing conditions. This can be seen by noting that fuses in such equipment are more for protecting the power lines than the equipment itself. Most failure modes in solid state circuits are faster than any fuse failure. Similarly, if the liquid starts a damage condition, the condition can increase in intensity and spread in the absence of the causing agent. The presence of electrical energy is enough to require that any liquid meet requirements the halons themselves meet in practice.

While the simplest specification would be to require no detectable electrical conductivity, this may not be desirable. The level of detection is a strong function of the measuring circuit. Almost any liquid could have some conductivity, if only as a result of impurities. Furthermore, as indicated above, as long as a suitable level can be found, it should be sufficient. In order for that level to serve as a screen, it should not be so restrictive that it rules out, unnecessarily, any investigational compound.

This section discusses the contributions to liquid conductivity and display expected values. These considerations show that the criterion based on electrical requirements from the circuits themselves reflect a reasonable partition for liquids and can serve as a screen. Later results for halon 1211 and other compounds will show that the chosen level is obtainable.

### a. General Considerations

The conductivity of a liquid is a function of both its chemical nature as well as its purity. The liquid itself can generate charge carriers as ions. It also can dissolve other substances that can act as sources of ions that contribute to the measured conductivity of the liquid. In fact, the conductance of a liquid is used as a criterion of purity [7].

The sensitivity of the conductivity to small amounts of charge carriers, whether from the liquid itself or impurities, can be seen by simple dimensional analysis. Current levels of  $10^{-12}$  A can be measured. The number of coulombs, ampere-seconds, in a mole is the Faraday or 96,484 C. Thus, this current level is equivalent to  $10^{-17}$  mol/s or  $10^7$  ions/s. Compared to ordinary criteria of purity, which are measured in percent, this is very small indeed. Since the charge carrier level is so small, it is important, when developing selection criteria, that they are not too difficult to meet. Therefore, a brief review of liquid properties will be developed with respect to conductivity.

(1) **Chemical Bonding.** The ultimate limit on the conductivity of a liquid is set by the tendency of the liquid to generate its own charge carriers. This limit is a function of the inherent chemical structure and bonding of the liquid itself.

Chemical bonds are generally divided into ionic or covalent groups. If there is a large difference in the tendency of the atoms forming the bond to attract electrons, then the shared electrons forming the bond will be preferentially near the atom having the larger attraction, or electronegativity. When such a substance is in the liquid state, the two parts can separate as both positive and negative ions. The classic example of this is common salt, sodium chloride. When sodium chloride enters aqueous solution, as in sea water, the atoms separate as ions and such a solution has a very high conductivity.

For most compounds, the electrons are more equally shared in covalent bonds. For many compounds, the electronegativity of the component atoms is nearly equal and there can be no tendency to form any ions at all. Pure hydrocarbons, such as ethane and hexane, are such examples. Also included are such materials as carbon dioxide, carbon tetrachloride, and trichlorofluoromethane, where the molecular symmetry produces the same results.

(2) **Dissociation.** Even if the molecular species making up the liquid are not ionic but rather covalent, they still can contribute ions in the liquid state, either as a pure liquid or in solution. If the free energy of one of the parts of the molecule, typically a hydrogen atom, as well as the remainder of the atoms, is lowered by solvation in the liquid, then ionization occurs. Many organic compounds, such as acetic acid, are in this category.

Acetic acid, by itself in the vapor phase, forms dimers with itself and does not form ions. As soon as it is dissolved in water, the hydrogen atom attached to the oxygen atom can be solvated by the water and ionization occurs. Even the hydrogen halides, such as hydrogen chloride, in the gaseous or the pure liquid phase are molecular, non-conducting materials. Even more indirect is the case of carbon dioxide, which by itself is an inert gas. When it is dissolved in water, it reacts with the water to form carbonic acid, which in turn can be solvated and form ions. Sulfur dioxide is another example of such behavior.

There are many cases when ions are known to form in organic compounds where all the bonds are clearly covalent. What is common to all these cases is the presence of strong molecular dipole moments and the resulting electronic asymmetry of the molecules. In all cases, it must be remembered that all these phenomena are equilibria that can be strongly affected by impurities, especially water. Also, because of the small number of ions needed for easily measurable conductivity, disassociating species will be poor candidates for halon substitutes.

#### **b. Polarity**

Commonly, the bonding electrons preferentially reside near one of the constituent atoms. This can result in a charge asymmetry in the molecule so, that while no ions are formed, the centers of positive and negative charge are separated. This separation leads to a net dipole moment for the molecule. These polar molecules then can interact more strongly with an electric field, which gives rise to an enhanced dielectric constant or permittivity for the liquid.

The calculation of the dielectric constant of a liquid from its molecular properties is well established and can be calculated with some accuracy. The Froehlich-Kirkwood-Onsager Equation [8] is a good approximation for most cases. While it is not necessary to give details, for most liquids at ordinary densities, if the dipole moment is small then the dielectric constant will be near a value of 2. For liquids with large dipole moments but not associated in any way, the dielectric constant can approach 10. If there is molecular association so that one molecule influences the orientation of its neighbors, such as in water, then the dielectric constant can get as high as 100.

#### **c. Solvation**

While the dielectric constant does not play a direct role in the conductivity of a liquid, when it gets large, indicative of high polarity, the conductivity of the liquid often gets large also. This is due to possible ionization of the liquid and the presence of ionizable impurities. Given the limits of normal purification techniques and the possible impurities, this is unavoidable.

(1) **Solubility Considerations.** One of the most common rules in chemistry is the rule for solubility: like dissolves like. This refers not only to the exact chemical species present, but also to the polarity of the solute and solvent. Polar alcohols dissolve readily in water, but non-polar hydrocarbons do not. Hydrocarbons are completely miscible with each other.

Solubility is always enhanced when there is a chance for interactions that lower the free energy. Of particular concern are those interactions that lead to ionization. Again, as was shown by the Debye-Huekel Theory, the higher the dielectric constant, the more the free energy of an ion is lowered. This means that in the more polar liquids one will find more ionized impurities. Also, any chance of self-ionization will be enhanced in the more polar liquids.

(2) **Impurities.** The emphasis on impurities with respect to liquids is quite important. No liquid can remain long in an ultrapure state without extremely careful handling. Certainly a halon substitute must be able to endure normal handling and exposure. It also must be able to be used in the presence of possible contaminants on the equipment that it is protecting. Again, the more polar the solvent, the more troublesome will be the presence of species contributing to the liquid conductivity. In particular, water vapor, which is always present under normal handling, can play a larger role. For liquids of low polarity, even if there are impurities present, they are most likely to be ones that do not ionize, or, even if they are present, will not ionize.

## 6. Representative Values

Values for the conductivity,  $\sigma$ , dielectric constant,  $\epsilon$ , and dipole moment,  $\mu$ , are given in Table 1 for reference liquids to illustrate the above principles [7]. Those liquids with "nr" (not reported) for  $\sigma$  should be assumed to be unmeasurable. These values are intended to be representative of the pure solvents.

Attention should be paid to the entry for carbon tetrachloride. The given dielectric constant value is approaching being unmeasurable and would require an electrometer, a high applied potential, and a long measuring time. The value for conductance marked "nr" is probably just as low.

The above data show that most liquids seem to readily divide above or below the criterion of  $10^{-11} \Omega^{-1} \text{ cm}$  that was established from the consideration of the needs of electrical circuitry. While the above data are intended for purified samples, it is this author's experience that added impurities rarely raise the conductance of a commercial-purity liquid whose value is very low, while they significantly increase the conductance of a liquid whose conductance is much larger.

## B. EXISTING TEST METHODS

### 1. General Method

The basic principle in determining the conductivity of a liquid is always the same. The liquid is placed between a pair of electrodes, a voltage applied, and the current measured. The ratio of current to the applied voltage represents a conductance and, when the conductance is normalized to what would be measured if the sample had unit area and thickness, the result is the sample conductivity.

While the basic measurement is always the same, the actual implementation will vary with the expected values for the conductivity. This is why it was considered important to establish first what a desirable level of electrical conductivity would be. An inspection of the table of representative values reveals a range of conductivity values spanning 12 decades, and that range could have been made larger.

TABLE 1. CONDUCTANCE OF PURE SOLVENTS

Compound	$\sigma$	$\epsilon$	$\mu$
methanol	$1.5 \times 10^{-9}$	32.7	2.87
ethanol	$1.4 \times 10^{-9}$	24.6	1.66
glycerol	$6 \times 10^{-8}$	42.5	nr
p-dioxane	$5 \times 10^{-15}$	2.21	0.45
acetone	$5 \times 10^{-9}$	20.7	2.69
methyl acetate	$3 \times 10^{-6}$	6.68	1.61
chlorobutane	$1 \times 10^{-10}$	7.39	1.90
chlorobenzene	$7 \times 10^{-11}$	5.62	1.54
methylene chloride	$4 \times 10^{-11}$	8.9	1.14
1,1,1-trichloroethane	$7 \times 10^{-9}$	7.53	1.57
o-dichlorobenzene	$3 \times 10^{-11}$	9.93	2.27
carbon tetrachloride	$4 \times 10^{-18}$	2.24	0
1,1,2,2-tetrachloroethane	nr	8.2	1.71
hexane	nr	1.88	0.085
1,1,2-trichloro-1,2,2-trifluoroethane	nr	2.41	nr
1,1,2,2-tetrachloro-difluoroethane	nr	2.52	nr

If liquid screening is to be valid, two possible sources of error must be eliminated. One is from electrode polarization as a result of the electrochemistry that will be induced, and the other is from the measurable capacitance of the electrodes.

#### a. Electrode Polarization

In a liquid, the charge carriers are always ions. For current to flow at the electrodes, these ions must interact with the free electrons of the metal electrode. This results in chemical changes in the ions, as they must change their net charge at the boundary for charge flow to occur. From electrochemistry, it is known that this change can occur only with a change in electrical potential. Furthermore, this potential is a strong function of the ion and the electrode material.

Often there can be a condition where the ions cannot readily change their charge state because of restrictions on the possible electrode reactions. This phenomenon is known as electrode polarization and leads to large voltage drops across the liquid-electrode interface. When this occurs, the

measured electrical conductivity can be strongly affected. Also, this phenomenon can permanently change the electrode surface so that later measurements on other systems are affected.

Since the screening test will probably cover a wide range of liquid properties, it is important to minimize this problem. One method is to use chemically inert electrodes. Platinum electrodes are a classic solution, since not only is platinum inert, but it also catalyzes many electrode reactions and reduces the electrode potentials.

The other method is to use an alternating electrical field. If the frequency is high enough, not many ions need to change their state before the voltage is reversed and the opposed reaction must take place. At high enough frequencies, typically at frequencies above 1 kHz for most systems, the effect of electrode polarization can be minimized.

#### b. Electrode Capacitance

The electrodes in the liquid can be regarded as the plates of a capacitor. The conductance of a liquid between two electrodes is given by

$$G = \sigma A/d ,$$

where

A = area of the electrodes and  
d = separation between the electrodes,

and the capacitance is given by

$$C = \epsilon\epsilon_0 A/d ,$$

where

$\epsilon_0$  = permittivity of free space.

Since the current flowing through a conductance for an alternating field of magnitude V and frequency f is VG, where V is the applied voltage, and the current through a capacitor is  $2\pi fVC$ , the ratio of the currents is proportional to  $\sigma/\epsilon f$ .

As the conductance becomes smaller, the contribution of the conductance to the total current becomes sufficiently small so that it can become unmeasurable. Thus, while it is desirable to use as high a frequency as possible to minimize the effects of electrode polarization, the higher the frequency the more difficult it becomes to measure small conductances. Proper experimental design must balance these two competing demands. Fortunately, as the conductance becomes smaller, the electrode polarization problems become smaller even faster, so that for the level chosen for the screen, polarization will not be a problem.

Another potential source of error, when conductance is low, is that the leads leading to the electrodes can have capacitive coupling between them. Also, the equations above assume that all the electric field is applied to the sample. At the frequencies used in this screen, it is possible to use an experimental design such that any contributions to the total current from the leads and other stray paths are not measured. This is the three-terminal method where any currents flowing to or from ground are not measured. With proper shielding and the use of guard rings, it becomes possible to make a measurement self-calibrating with the cell constant, A/d, determined from the measured capacitance of the empty cell.

## 2. ASTM Test Methods

Since electrical measurements are readily done, capable of high precision, and of broad importance, many ASTM specifications for the determination of the conductivity of liquids exist. Many of these test methods are a direct result of the electrical power and equipment industry, where liquids are routinely used for high quality insulation.

The relevant ASTM tests are D 1169, for D-C conductivity of liquids, and D 924, for A-C loss in liquids [9],[10]. To these, should be referenced ASTM D 150 for A-C loss in insulating solids [11]. These standard test methods will be used as the basis for the screen used for the halon substitutes.

All three ASTM methods use three-terminal measurements with both liquid test methods [9],[10] showing the same set of reference drawings for possible sample cells. A typical cell is shown in Figure 1. This cell is designed so that only the electrode area between the inner and outer electrodes is measured and all coupling through ground, including any leads to the cell, can be excluded from the measuring path. Test ASTM D 924 references ASTM D 150 for the measuring circuits for A-C measurements which includes an inductive-ratio-arm bridge shown in Figure 2. Test D 924 specifies a frequency between 60 and 1000 Hz. Test D 1169 specifies the use of a DC potential for 5 minutes and a reversal for 1 minute, with the average current for both polarities used. All tests leave discretion to the person carrying out the test as to the exact configuration of the measurement as long as it conforms to a set of criteria.

## C. SCREEN TEST SELECTED

The test to be used for screening is based on the three ASTM tests D 1169, D 924 and D 150. The allowable discretion within the standards will be taken to ensure that the desired screening criterion for liquid conductivity is easily measurable, is indicative of the liquid under investigation, and can be done quickly.

Two cells are available in this laboratory. One is a reproduction of one of the designs in the ASTM standard, similar to Figure 1 but with the inner electrode a solid piece of metal. It is constructed of gold plated brass and has an empty cell capacitance of 11.5 pF. The other is similar to that of Figure 1, except that a lower guard ring is added to the inner electrode, the outer electrode is open, and the entire cell is enclosed in glass. The electrodes are fabricated from platinum and the empty cell capacitance is 4.3 pF. Both cells require about 10 ml of liquid for filling.

The platinum-glass cell was chosen because it is easier to clean and rinse, is easier to fill, and has a somewhat better cell geometry, especially for the more conductive liquids that will be probably encountered. Also, this cell's platinum electrodes should give the least interference from any electrode polarization.

The method chosen is that of ASTM D 924 [10], which is the A-C method with a measuring frequency of 1000 Hz. The use of 1000 Hz A-C minimizes any electrode polarization problems and optimizes the bridge that will be described below. For the liquids that will be investigated, which are volatile, low viscosity fluids with only a small number of atoms per molecule, the conductivity measured either by A-C or D-C should be exactly the same in the absence of any electrode polarization. Any contribution to the measured conductivity from dispersion in the dielectric constant as a function of frequency should occur only at much higher frequencies, typically in the microwave region and is of no concern.

The measuring instrumentation is an inductive-ratio-arm transformer bridge with a circuit similar to that of Figure 2. It is direct reading in both capacitance and conductance. Its optimal frequency is at 1000 Hz and can be brought to balance using a high-quality phase-sensitive detector in less than 5 minutes. With

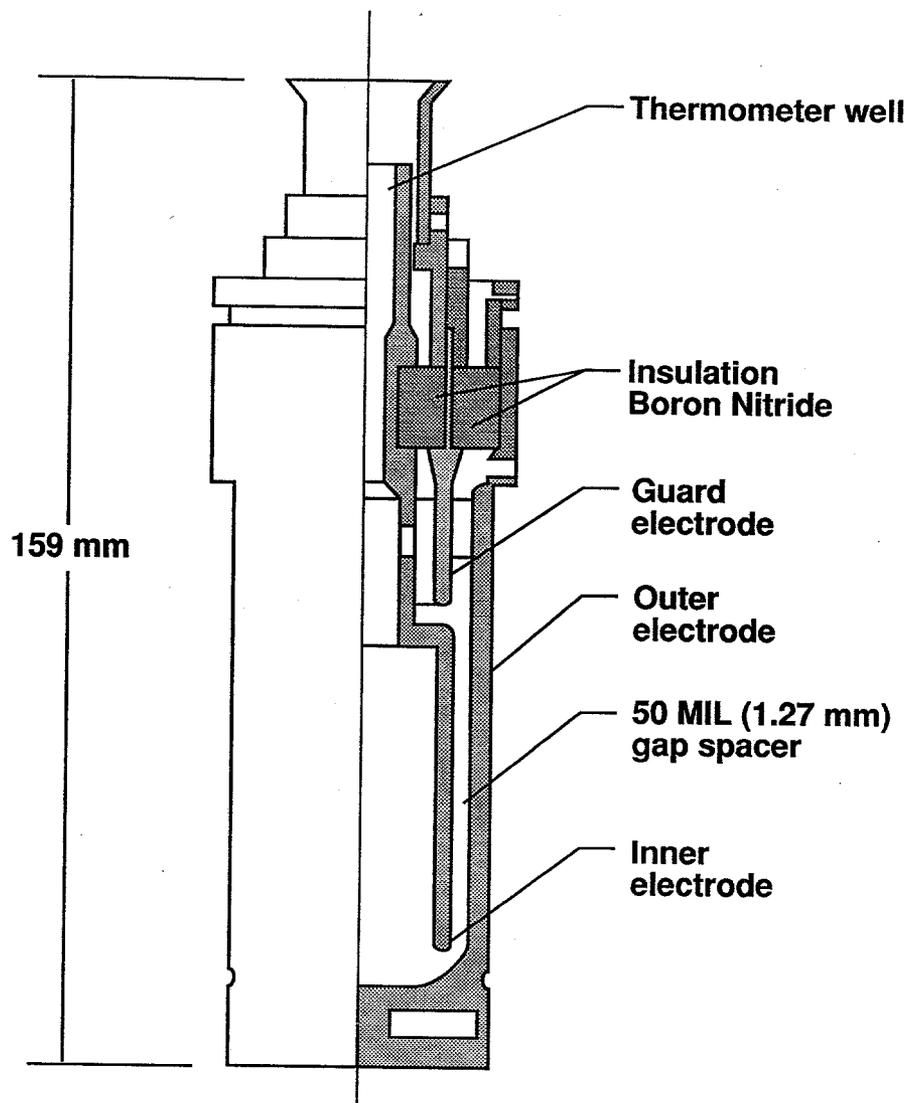
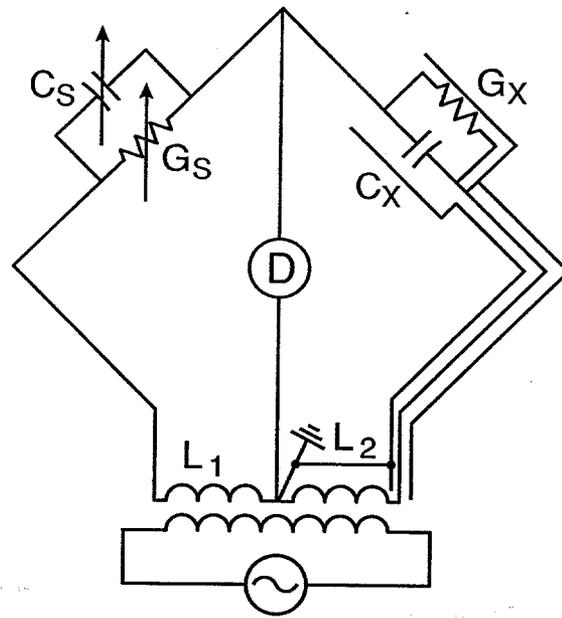


Figure 1. A Typical Liquid Cell Conforming to ASTM D 924 and ASTM D 1169. The Guard Ring at the Top of the Cell Isolates the Measurement to Only That Electrode Area Where the High and Low Electrodes Have Field Lines Directly Between Them.



Equations

$$C_X = (L_1/L_2)C_S$$

$$G_X = (L_1/L_2)G_S$$

$$D_X = (G_S/\omega C_S)$$

Figure 2. An Inductive-Ratio-Arm Admittance Bridge. Bridge Balance is When the Unknown and Reference Admittances are Equal. Any Shunts to Ground, such as Through the Use of Coaxial Leads is not Measured.

the platinum-glass cell, by direct calibration with low-loss standards, the minimum conductance measurable at 1000 Hz is less than  $10^{-13} \Omega^{-1} \text{ cm}$ .

Temperature control is by a refrigerated water bath using a 50 percent ethylene glycol solution. The temperature is settable to temperatures as low as  $-20^{\circ}\text{C}$  with settability to  $0.1^{\circ}\text{C}$  and control to  $\pm 0.01^{\circ}\text{C}$ . While ASTM D 924 specifies a forced air oven as a test chamber, the liquid bath has the advantage of higher heat transfer rates and better temperature control. The measurement temperature for these screens will be at  $25^{\circ}\text{C}$  for all liquids that boil above this temperature. For those that have boiling points below this point, a temperature at least  $5^{\circ}\text{C}$  lower than the boiling point will be chosen down to  $-20^{\circ}\text{C}$ . Any liquid boiling at temperatures below  $-20^{\circ}\text{C}$  will be considered a gas for this screen. For reference, the boiling point of halon 1211 is  $-4^{\circ}\text{C}$  [4].

The variability of the test temperature is not expected to be a major problem in the screening procedure. Just as the measuring frequency can be picked for convenience, so can the temperature. None of these liquids will be used near its glass transition temperature, and most will not be glass formers. The conductance is, therefore, expected to be a relatively weak function of temperature. For halon 1211, varying the temperature  $10^{\circ}\text{C}$  changed the conductance by only 20 percent. This behavior is expected to be typical. Furthermore, since conductance increases with temperature, and since the liquids will be in contact with electrical circuitry near their boiling point, measuring a liquid lower than the boiling point should not exclude any promising material.

#### D. CRITERIA

The screen gives an actual, physical value for the given sample, and that value should be reported. However, to maintain a perspective on the results, since they need not be intrinsic to the pure liquid, it is suggested that the liquids be divided into two classes. They are:

- Class 1: Those chemicals that are either gases below  $-20^{\circ}\text{C}$  (intended for total flooding as a dilute gas), or those liquids that test for conductivity of less than  $10^{-11} \Omega^{-1} \text{ cm}$  when measured at the lower of  $25^{\circ}\text{C}$  or below their boiling point.
- Class 2: Those liquids that are not used as gases and have conductivities greater than  $10^{-11} \Omega^{-1} \text{ cm}$ .

#### E. PERFORMANCE DATA

The following three liquids were tested using the proposed screening method: halon 1211 taken from a non-pressurized extinguisher (no nitrogen), HPLC grade methylene chloride, and reagent grade trichlorofluoromethane. As mentioned earlier, halon 1301 is used as a gas and needs no screen test. The halon 1211 will serve as a bench mark. The methylene chloride is an example of possible screen failure as indicated by the data given in Table 1. The trichlorofluoromethane is an example of a high-purity liquid with no expected measurable conductivity. The results are given in Table 2.

The results for halon 1211 were not very sensitive to contamination. In the setup for it, a contaminated copper line was accidentally used for delivery. The liquid actually became yellow, but the conductivity was not affected by more than a factor of 2, so that it still passed the proposed screen of  $10^{-11} \Omega^{-1} \text{ cm}$ . It was also stable with time, even though it was considerably below room temperature and no special precautions were taken to exclude moisture. The methylene chloride, on the other hand, has a much higher

TABLE 2. SCREENING TEST RESULTS

Liquid	T (°C)	$\sigma$ ( $\Omega^{-1}$ cm)	$\epsilon$
Halon 1301	not measured		
Halon 1211	-20	$7.8 \times 10^{-13}$	2.66
Methylene chloride	25	$5.93 \times 10^{-9}$	10.6
Trichlorofluoromethane	20	0	2.32

value than the one cited in Table 1 and, even at room temperature, drifted substantially upward, indicating moisture sensitivity.

#### F. EVALUATION OF SCREENING METHOD

This method is a practical approach for screening the potential for an alternative fire suppressant to cause electrical damage when deployed. It is an ASTM standard test, with the electrode kept small to minimize the amount of sample needed. The procedure can be carried out by a technician. Many testing labs should have the equipment. Preliminary results indicate the test can readily distinguish among chemicals with high and low conductivity.

A major concern is the presence of contaminants, which can raise the conductivity. Only pure chemicals should be screened. However, commodity chemicals often contain or gather impurities. Therefore, further examination is needed at later stages of the selection process.

#### G. LABORATORIES/COST

This screen can be carried out at a large number of commercial laboratories. The apparatus is commercial, although a small volume three-terminal liquid cell is not very common, as the ASTM published designs used volumes of about 100 ml. A check of the listing of the American Council of Independent Laboratories, the ASTM Directory of Testing Laboratories, and the Directory of Standards Laboratories indicated over 30 different laboratories offering conductivity measurements. An approximate cost is \$100 per test, assuming the cell had to be cleaned after each test and possible setup charges depending on the exact requirements.

#### H. CONCLUSIONS

- A practical screen has been selected that is easy to perform, gives quantitative results, requires a small amount of material, and can be performed by a large number of laboratories. The measurements are performed with an apparatus only slightly modified from ASTM D 924.
- Only liquids need be tested. The gases used for total flooding systems have electrical conductivity values that are too low to cause damage.

- The issue of breakdown strength, important for any high voltage equipment, will be left to more detailed acceptance testing after the screens have been made. The normal expectation is that the candidates would be acceptable so that this delay should not be a major drawback.
- This proposed screen is not intended for full-scale acceptance testing for a halon substitute. The conductance would have to be studied as a function of possible contamination. Also, any final test should be considered by appropriate producers of electrical equipment to ensure full compatibility. The screen proposed here should ensure this, but the final test will probably be more stringent.

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**SECTION X**  
**COMPATIBILITY WITH PLASTICS**

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## SECTION X

### COMPATIBILITY WITH PLASTICS

#### SECTION SUMMARY

Historical experience indicates that the halons currently in use are relatively benign toward plastics under conditions of incidental exposure. The result has been that assessments of interactions between fire suppression agents and plastics under these conditions have not played a significant role either in the design of fire fighting systems or of products made from plastics. Replacement agents may, however, prove to be more aggressive toward plastics.

This section describes a test method in which specimens of selected polymers are exposed to candidate fire suppression agents in the vapor phase or to neat liquids at ambient pressure and temperature for 24 hours. At the conclusion of the test the specimens are studied for changes in mass, appearance, dimensions, and other properties as the situation warrants. An incompatibility rating is determined by combining results for mass uptake and linear swell using a Classification Diagram. This results in one of the following assignments:

- Class 1: Effects less severe than or equally severe to those from exposure to halons 1301 or 1211. It is expected that such changes would not result in permanent damage to plastic parts.
- Class 2: Effects more severe than those from exposure to halons 1301 or 1211. Alterations of polymers to the extent implied by this rating may be a cause for concern. Further investigation of the polymer-reagent pair is needed.
- Class 3: Effects significantly more severe than those from exposure to halons 1301 or 1211. Alterations of polymers to the extent implied by this rating may be sufficient cause to preclude the exposure of the plastic to the reagent.

The screening procedure was examined by running tests using halon 1301, halon 1211, and trichlorotrifluoroethane as the fire suppression agents and specimens of neoprene, Viton A, and a polyurethane as representative plastics.

The Classification Diagram is quite approximate and is application-dependent. Before this method is applied, additional work should be done to identify a proper set of polymers to be used in the testing and a more rigorously-determined Classification Diagram.

There is an ample number of organizations who would be capable of performing testing of the sort described herein. The tests themselves are inexpensive; run in triplicate, the cost is estimated to be about \$200 per polymer-reagent pair plus the cost of the chemical. Each of the triplicate samples requires about 10 ml of liquid or about 25 ml of vapor at 1 atm.

The consequences of failure of plastic components of storage and distribution systems due to prolonged exposure at high agent concentrations are critical enough to deserve case-by-case evaluation, to which the screening procedures described here are inapplicable.

## A. BACKGROUND

### 1. Current Practices in Using Plastics

Polymeric materials are ubiquitous in modern engineering practice. Table 1 lists some of the characteristics that make these materials attractive for high-performance applications together with some of the factors that limit their usefulness. The terms "plastics" and "polymeric materials" will be used

TABLE 1. CHARACTERISTICS OF PLASTICS FOR ENGINEERING APPLICATIONS

Desirable	Undesirable
Ease of Processing	Limited Service Temperature Range
Resistance to Corrosion	Susceptibility to Organic Solvents
Transparency	Susceptibility to Chemical Attack
Impact Resistance	
High Electrical Resistance	
Good Barrier Qualities	

interchangeably throughout this section to denote materials that are formed by chemically stringing small molecules together into long chains.

With proper materials selection, polymeric materials find many applications. Table 2 lists some of these, and it is clear that one can expect to encounter plastics everywhere. On this basis, it is reasonable to conclude that any plastic used in modern society could potentially be exposed to a fire

TABLE 2. TYPICAL ENGINEERING APPLICATIONS OF POLYMERS

Structural Members	Enclosures
Coatings	Potting Materials
Windows	Packaging Materials
Adhesives	Substrates for Electronics
Coverings	Seals and Gaskets
Fabrics	Lubricants
Electrical Insulation	Power Transmission Components

suppression agent. Given that the currently-used halons and their likely replacements are low molecular weight chemicals, it is certain that they will interact with at least some polymers. In some of these cases, the

interaction will irreversibly alter the physical or chemical state of the polymer, and parts made from the polymer will have to be replaced even if they are not damaged by the fire itself. It is desirable to minimize the risks associated with such occurrences by proper selection of plastics and/or fire suppression agents.

## 2. Chemical and Physical Characteristics of Polymers

Polymers are formed by covalently bonding low molecular weight chemical species (called "monomers") into long chains. As can be seen under "Molecular Structure" in Table 3, there are a variety of kinds of monomers and a variety of ways of linking them together. Naturally occurring polymers, such as cellulose, keratin, and collagen, must also be considered. The result is an enormous chemical variety of available polymeric materials. Even if one restricts consideration to the most "important" materials as defined by tonnage produced, dollar value, end use, or some similar factor, the range is still quite large.

If one considers only polymers of fixed chemical composition, it is possible to modify the properties of plastic products by altering process variables that control such characteristics as molecular weight, chain branching, and crosslinking, to mention only a few. Some polymers exhibit a tendency to form crystalline aggregates. Examples include polyolefins, polyesters, polyethers, polyamides, and cellulose. In these cases, the chains are packed in well-ordered, dense arrays within domains that are dispersed throughout a matrix of amorphous material. Both physical processing and chemical composition influence the exact characteristics ("morphology") of this microstructure.

Finally, polymers take a variety of forms in their end uses. These include yarns, films, foams, sheets, and molded solids. They can be combined with fillers, such as carbon black, carbon fibers, glass or metal fibers, and inorganic pigments. They can be compounded with additives to enhance fire resistance, to reduce static electricity, to modify mechanical properties, or to improve chemical stability.

Inasmuch as "compatibility" characterizes the interaction between a polymer and another chemical species, it is easy to see that this term must be described by a matrix of values rather than as a single measurable property.

## 3. Sorption and Diffusion

Polymeric materials show some capacity to accommodate foreign molecular species within their matrices. This phenomenon is called "sorption." The process by which foreign molecular species migrate into the matrix of a polymer is called "diffusion." Crank and Park [2] provide a good introduction to the rich literature on these phenomena.

Sorption is usually described by Henry's Law:

$$C_p = S C_e, \quad (1)$$

where  $C_p$  is the concentration of solute in the polymer,  $S$  is the solubility parameter, and  $C_e$  is the concentration of solute in the surroundings.

The value of  $S$  is influenced by the chemical affinity between the solute species and the host polymer, the morphology of the matrix, and the concentration of solute.  $S$  is usually a strong function of the temperature. In cases where the solvent swells the polymer, the solubility will also be influenced by the presence of crosslinks or fillers.

TABLE 3. FACTORS INFLUENCING COMPATIBILITY

Molecular Structure	Molecular Weight
Monomer Composition	Additive Content
Aromatic	Antioxidants
Aliphatic	Catalysts
Ethers	Plasticizers
Amines	Fire Retardants
Amides	Reinforcing Fibers
Imides	Physical Form
Esters	Sheet
Silanes	Fibers
Biological Substances	Films
Main Chain Linkages	Molded Parts
Aliphatic	Fabrication
Double Bonds	Thermoplastic
Ether Linkages	Thermosetting
Covalent Silicon	Transport Properties
Interchain Interactions	Diffusion Coefficient
Crosslinking	Solubility
Hydrogen Bonding	Morphology
van der Waal's Forces	Crystallinity
Side Groups	Amorphous Content
Alkyls	Solvent Effects
Aromatics	Chemical Composition
Aliphatics	Molecular Size
	Polymer-Solvent Interaction
	Reactivity

A large value of  $S$  should be considered *prima facie* evidence for incompatibility between a fire-suppression agent and a polymer, because a polymer matrix cannot absorb large amounts of a solute without undergoing some swelling with concomitant alteration in its properties. Even if the properties of the polymer were not degraded, it could prove to be difficult to remove the solvent from the part following

TABLE 4. RESULTS OF EXPOSURE TESTS (RESULTS IN PERCENTAGES)

	Reagent					
	halon 1301		halon 1211		TCTFE	
	dm/m <sub>o</sub>	dL/L <sub>o</sub>	dm/m <sub>o</sub>	dL/L <sub>o</sub>	dm/m <sub>o</sub>	dL/L <sub>o</sub>
Viton A	0.	0.	-0.11	0.	4.7	1.3
neoprene	0.06	0.	-0.4	0.	11.	3.3
urethane			1.7	0.	23.	5.0

TABLE 5. INCOMPATIBILITY RATINGS

	Reagent		
	halon 1301	halon 1211	TCTFE
	Viton A	1	1
neoprene	1	1	3
urethane		1	3

exposure. On the other hand, small amounts of solute can usually be removed, and their effects on the properties of the plastic part are usually negligible.

Crank and Park [2] illustrate experimental procedures for the direct determination of S. The practices used in such measurements have remained essentially unmodified for many years. If additional precautions are taken to measure the reagent concentration, the data from the low-level exposure tests described in Section C can provide S values for the specific conditions employed in the test.

Solubility is an equilibrium property. In practice this equilibrium may take considerable time to achieve, because the migration of solute into the polymer matrix is controlled by diffusion.

In simple cases, diffusion can be described by Fick's Law:

$$j = -D \frac{dC}{dx} \quad (2)$$

where j is the flux of the solute, C(x,t) is the concentration of solute at the point x at time t, and D is the diffusion coefficient. The requirement that matter must be conserved in this process leads to the diffusion equation

$$\frac{\partial C}{\partial t} = - \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right) \quad (3)$$

Crank [3] has discussed the solution of Equation (3) for a number of cases with varying degrees of complexity. There are a number of important cases for which Fick's law must be modified [3,4] and the mathematical description of the phenomenon rapidly becomes more complex, if not impossible.

D is yet another parameter that depends on the choice of polymer, solute, and measurement conditions. D is also sensitive to morphology and the presence of fillers. In some instances, D is also a function of concentration, although in most such cases Fick's law ceases to apply over an extended range of concentrations. In cases where sorption gives rise to significant swelling, Fick's law may be invalid even in a local sense and other approaches must be tried [5].

Diffusion is important in characterizing sorption because it establishes the time scale over which the process takes place. Diffusion thus controls the approach to equilibrium in solubility measurements. This is illustrated by the following result for a simple mass uptake experiment [2]:

$$\frac{M(t)}{M_{\infty}} = 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp \left( - \frac{D (2m+1)^2 \pi^2 t}{L^2} \right), \quad (4)$$

where  $M(t)$  is the total mass taken up in time  $t$  after exposing a solute-free slab of material with a thickness of  $L$  and a cross sectional area  $A$  to a solute whose concentration in the surroundings is  $C$ .  $M_{\infty}$  is the equilibrium solute uptake. Figure 1 is a plot of this result. The approach to equilibrium is asymptotic on a time scale controlled by  $L^2/D$ . Experiments of this kind can be used to estimate both  $S$  and  $D$ .  $S$  is given by

$$\frac{M_{\infty}}{C \cdot A \cdot L}$$

and  $D$  is obtained by fitting the mass vs. time data to Equation (4).

Other solutions of the diffusion equation can be used to estimate the depth to which a solute will penetrate into a plastic within a given amount of time.

The existence of sorption and diffusion implies that containers made from plastics will exhibit some tendency to lose their contents into the surroundings. This phenomenon is called "permeation." It has been a serious concern in applications of plastics in packaging [6], transportation [7], and environmental protection [8].

Under steady-state conditions, the flux,  $j$ , of solute across a slab of polymer of thickness  $L$  with a solute concentration  $C$  on one side into a volume devoid of solute on the other side is

$$j = \frac{CP}{L} = \frac{CDS}{L} \quad (5)$$

The permeability coefficient,  $P$ , is the product of the diffusion coefficient and the solubility parameter. Polymer-solute pairs that possess large permeability coefficients would be defined as

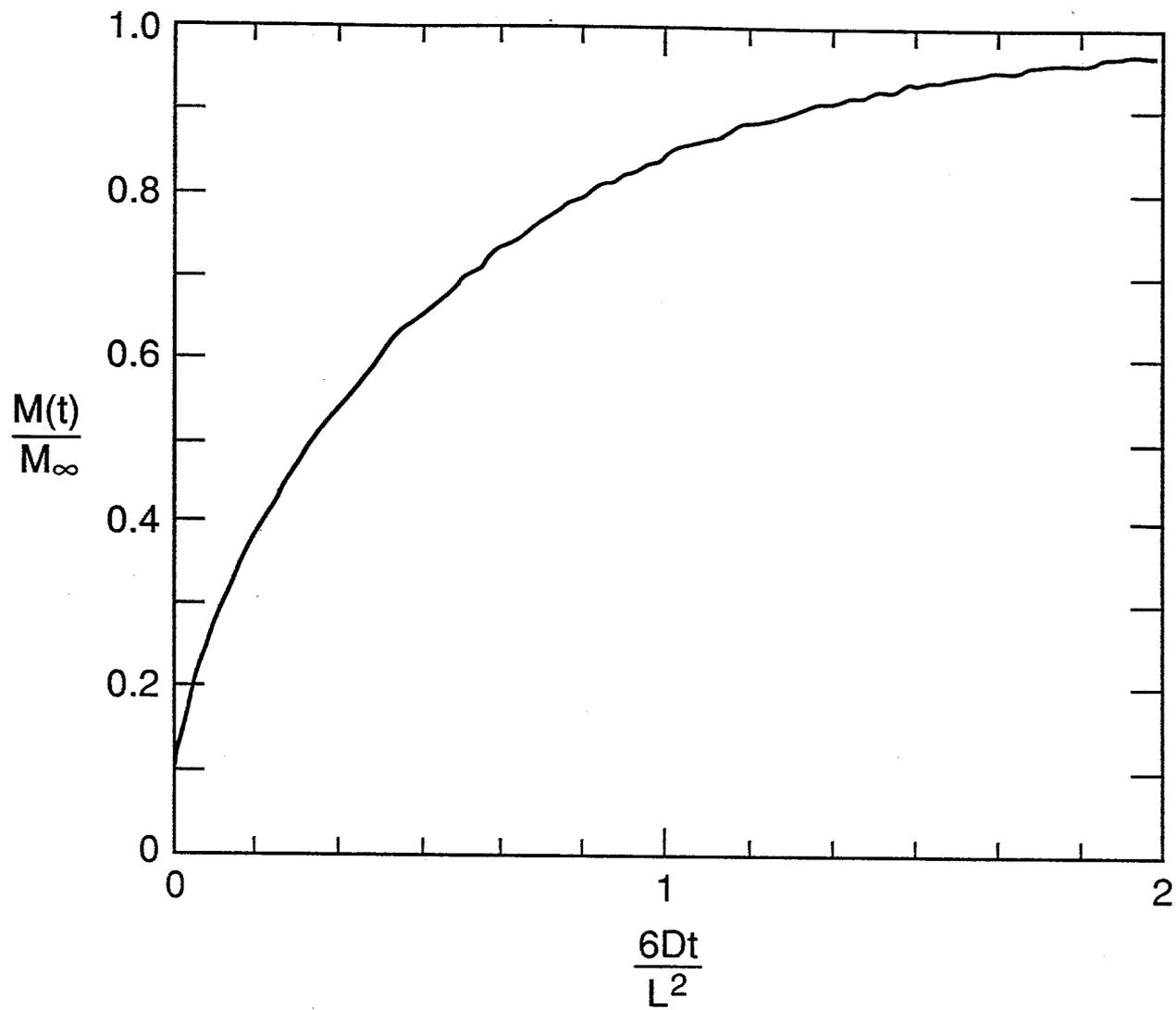


Figure 1. Results of Sorption Experiment

"incompatible" under the terms of this study, although this is not necessarily true for cases in which the permeability arises from a very large value of the diffusion coefficient while the solubility remains low (as, for example, is the case with helium gas in most polymers).

#### 4. Sorption Properties as a Screening Criterion

Failure modes of polymers exposed to solutes include:

- swelling - changes in the dimensions of polymer chains required to accommodate the presence of solute molecules perhaps leading to loss of mechanical integrity;
- chemical modification - direct chemical attack leading to chain scission or oxidative degradation;
- changes in mechanical properties - loss of stiffness as a consequence of swelling, embrittlement as a consequence of extraction of plasticizing agents, loss of tensile strength, and enhanced creep rupture; and
- stress cracking - interactions with molecules at pre-existing stress concentrations leading to rapid crack formation and propagation.

Since the above modes of failure are strongly mediated by sorption and diffusion, these phenomena provide a suitable basis for identifying undesirable interactions in a screening program.

Compatibility with polymers has been important in the application of halons only to the extent that it plays a role in the proper selection of materials for seals and gaskets in storage and discharge systems. In these situations, the interaction between polymer and solute takes place at high solute concentrations, the parts are under considerable mechanical stress, and the exposure persists for a long time. The consequences of failure in these applications are so catastrophic that there is no room for guesswork. Each polymer-solute pair must be carefully evaluated under realistic conditions of exposure. Screening procedures for such applications employ high concentrations of solvent, often at high pressures. The identification of an acceptable agent is so difficult that it is presumed that fully suitable seals (perhaps even metal-to-metal seals) will be created once the most suitable agents are identified.

Similarly, interactions between plastics and solutes in cases where the plastics are directly involved in a fire are so complex as to defy quantitative description of any kind. Data from screening procedures of the kind described here are of no value in such cases.

Once the high-level exposure and the direct fire involvement scenarios are excluded from consideration, one is left with a scenario where damage to a plastic artifact occurs from contact with a fire suppression agent even though the artifact itself is not directly involved in the fire. Exposures arising from testing, training, and accidental discharge are examples of this. Indeed the amounts of agent released by these means constitute the bulk of the total [9]. It is desirable to limit losses of expensive electronic equipment and other hardware from such causes. The currently employed halon fire suppression agents have been found to be sufficiently benign toward plastics that such damage has not been a concern in the past. The concentrations are low, the exposures are brief, and temperatures are not excessive.

It is, however, conceivable that some future fire suppression agents will be more aggressive toward plastics because of chemical differences. It is, therefore, reasonable to provide some means of establishing comparative rankings among such agents.

## 5. Mechanical Properties

The mechanical properties of plastics may also change as a consequence of exposure to chemical reagents. Tensile modulus, tensile strength, flexural modulus, and related properties, such as hardness, are influenced by the chemical environment in which plastics are used [1]. While tests for these properties are important in assessing the suitability of plastics for their intended use, such tests require large amounts of reagent, some of them take a long time to perform, and others require expensive equipment. Tensile creep-rupture testing [1,10] is an additional alternative method, but it is not clear how it can be adapted to use reagents in the vapor form or liquids under high pressure.

Post-exposure measurements of mechanical properties may yield valid results in cases where the reagent is not volatile. This is what du Pont did in evaluating potential replacements for CFC refrigerant gases [12]. Hardness tests [11] are quick and simple to perform, but yield limited information. It would appear to be preferable to use a tensile test like ASTM D 639 [13], which yields complete stress-strain curves. The specimens would have to be cut to the proper shape for testing before exposure to the reagent and the effects of desorption during the tensile test would be difficult to control.

## B. EXISTING TEST METHODS

Test methods that address incompatibility exist in the current literature. ASTM D 543, "Standard Test Method for Resistance of Plastics to Chemical Reagents" [14], is one example and ASTM D 471, "Standard Test Method for Rubber Property - Effect of Liquids" [15], is another. These procedures can be paraphrased as follows:

- Immerse suitably shaped specimens in a liquid reagent contained in an appropriate vessel. Suspend them so as to avoid contact with the walls of the vessel.
- At the end of a suitably chosen time period, remove any excess reagent, place the specimen in a tared weighing bottle, and determine its mass.
- Examine the specimen for changes in appearance.
- Perform any required measurements of mechanical properties (tensile characteristics, flexural properties, hardness, etc).

The tests are simple to conduct and the results are easy to interpret. To the extent that the test conditions mimic the exposure conditions, these tests can be expected to yield valid performance data. The final determination of the suitability of a material is, however, usually based on evaluation of prototype components made from the plastics.

The amounts of reagent required to conduct these tests are small, typically on the order of a few milliliters per test. Most applications of these test methods call for long exposures, sometimes upwards of 30 days. This is determined by the use to which the plastic is being put. For example, in the packaging industry the main interest is in the shelf life of a product and its container.

ASTM D 543 lists a wide range of agent types for which this method is thought to be applicable. There is nothing to indicate that, with proper modifications to allow for testing in the vapor phase, there should be a problem in carrying out or interpreting the results of this test on fire suppressants.

The method described above requires substantial modification to be used to test polymer-reagent pairs like those addressed in this study. First of all, the currently-used halons and at least some candidate fire suppression agents, are either vapors at standard laboratory temperatures or are liquids likely to have high vapor pressures. Provision must, therefore, be made for testing in sealed containers and for introducing the agent into the container in vapor form.

E. I. du Pont de Nemours and Co. has reported a study of compatibility between a series of elastomers and two halogenated reagents used as refrigerants [12]. They describe their procedure as follows:

"Clean and dry elastomer specimens (60 x 7 x about 2 mm) were checked for length ( $\pm 0.01$  mm), weight ( $\pm 0.0001$  g), hardness ( $\pm 2$ ), appearance, and elasticity (by hand). Each Pyrex tube (11 mm I.D. x 140 mm) was charged with one elastomer and 3 ml of refrigerant and then sealed. The tubes were stored, horizontally, at 25, 80, and 141°C. After 27 days, the elastomers were measured while still in the sealed tubes. The tube contents were examined and rated for the noted changes. Each tube was then chilled to just below the refrigerant's melting point and opened. Within three minutes, the specimen surface was flushed briefly with isopropanol and Freon TFR and, when the surface first appeared dry, was placed in a sealed, pre-tared vial and weighed. Immediately afterwards, the hardness and elasticity were determined. These data are referred to as 'temporary' data.

After storing the elastomers horizontally in open vials in air at 25°C for 14 days, the properties mentioned above were redetermined (the 'final' changes)."

In presenting its conclusions, the Du Pont report uses an index of (in)compatibility based on changes in two quantities: the hardness and the length. An incompatibility rating based on multiple properties has the advantage that a combination that exhibits a significant change in only one property is less likely to escape notice.

The method for arriving at the incompatibility rating is as follows. The two test results are plotted against one another on a diagram as shown in Figure 4. One constructs the set of curves to enclose regions that describe qualitative levels of interaction between a polymer and a solvent. The polymer-solvent pair is then assigned the classification of the region within which the combined result falls. The graphical origin (0,0) in the diagram indicates where there is no change in the polymer as a result of exposure to the solvent. Areas of the diagram that lie farther from the origin imply alteration of the properties of the polymer upon exposure to the solvent.

The Du Pont method is appropriate for the case of refrigerants and elastomers because the exposure is long term at high concentrations and because hardness is a meaningful parameter in this limited range of applications, where elastomers are used as seals and gaskets. The sealed glass tube is the simplest way to contain the reagent at the high pressures that are developed.

The data contained in the Du Pont Product description sheet for halon 1301 [18] were obtained many years ago using similar test procedures. Product literature for halon 1211 from the Mond Division of Imperial Chemical Industries Ltd. [19] gives application recommendations without providing quantitative data.

The first problem that is encountered when extending this approach to a broader range of polymers is the inapplicability of Shore A hardness [11] as a mechanical property, because it is not defined for polymers in the form of fibers or films. Alternative mechanical properties, such as stress-strain curves or flexural moduli are expensive to measure, especially if one attempts to do so with the polymer exposed to the reagent.

This immersion of a sample in a sealed tube test with neat liquid for 27 days represents much more severe exposure than plastics would experience in an incidental fire suppression scenario. The manipulations

involved in filling and sealing the tubes add to the cost of testing, and the protracted durations of exposure contribute to delays in screening decisions.

Research methods for obtaining solubility data of handbook quality for use in a database to establish fundamental physical and chemical mechanisms require elaborate apparatus to ensure good control of the reagent concentration:

- careful temperature control,
- delicate and expensive equipment, such as electronic microbalances or quartz springs, and
- skilled operators to conduct the measurements.

It is not known how many institutions would be able to conduct such measurements on a large number of polymer-reagent pairs.

## C. SCREENING METHOD SELECTED

### 1. Rationale

An engineering method, of which the sealed tube test is probably the simplest and most direct, is the most reasonable solution to generating data for incompatibility screening. The method chosen is in the spirit of ASTM D 543, ASTM D 471, and the Du Pont method. The data taken are the mass gain and the swelling of the polymer, each measured using the standard procedures in the ASTM methods. Triplicate samples should be exposed. The results of the mass uptake and swelling are plotted against one another on a diagram like the one in Figure 4. An incompatibility rating is assigned according to the region in which the measurement pair falls. From there, a number of minor modifications to the published procedures are introduced.

### 2. Modifications

For the purposes of this study, the sealed tube test described in Section B was modified in the following ways:

- A re-usable test vessel is used. Figure 2 shows the main features of this device.
- The specimen is tested at 25°C in contact with the reagent vapor at a partial pressure of slightly less than one atmosphere (gaseous reagents). If the test chemical is a liquid, the sample tube is partially filled with the liquid, with the remainder of the sample exposed to the saturation vapor pressure of the reagent. To the extent that these concentrations are the highest that would be experienced in an incidental exposure scenario, they represent "worst cases."
- The specimens are strips 140 to 150 mm in length and 12 to 15 mm wide, cut from sheet materials. A one percent linear swell gives rise to a change in length of somewhat more than 1 mm, which is easily measurable with a scale held against the outside of the test vessel.
- A valving manifold is used to introduce gaseous reagents into the test vessel at known pressure and to allow removal of atmospheric gases by evacuation. Figure 3 is a schematic layout of this apparatus. The valving manifold was assembled from standard brass swage-lock

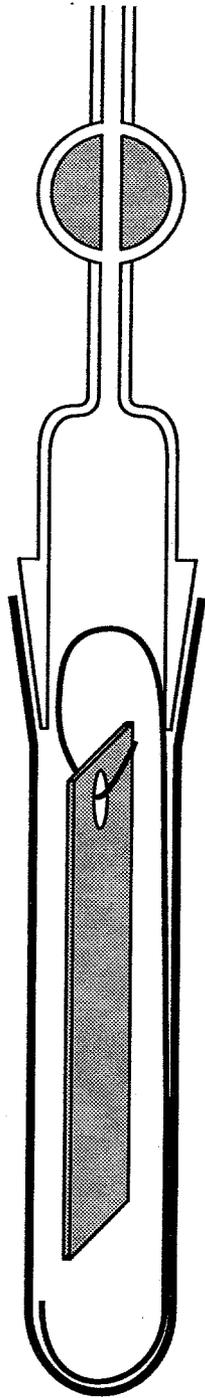


Figure 2. Test Vessel

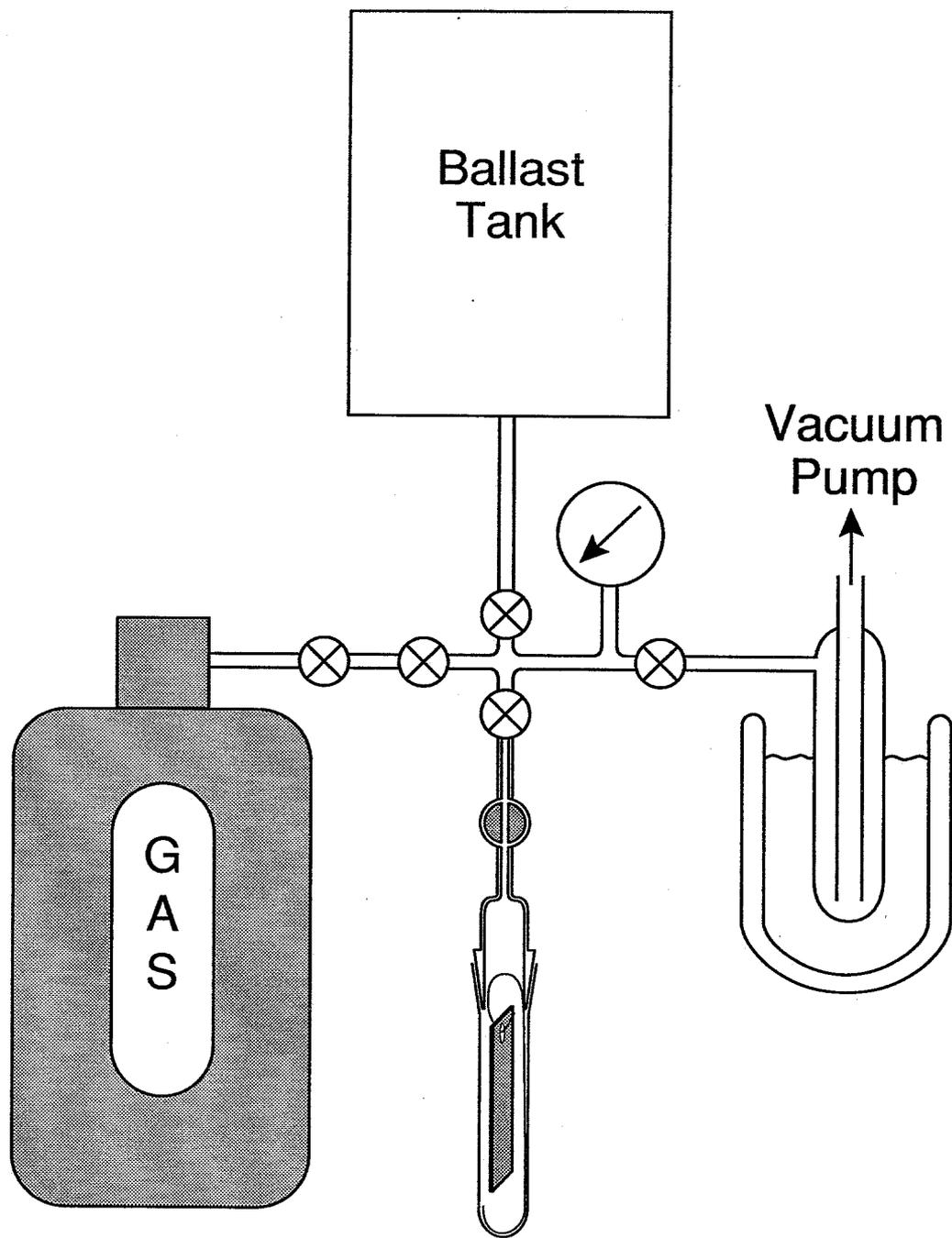


Figure 3. Piping Layout for Gas Transfer

tube fittings. An electronic capacitance manometer is provided as a means of measuring reagent pressure. A liquid nitrogen cold trap is intended to minimize contamination of the vacuum pump oil. A 1-liter stainless steel sample bottle is used as a ballast reservoir to facilitate control of the final pressure in the test vessel.

- The specimen is exposed for 24 hours. While this may not be long enough to attain complete equilibrium for reagents with low diffusion coefficients, it is much longer than would be experienced in an incidental exposure scenario. This duration is a compromise between a worst case and one that is convenient for conducting the test.

#### D. CRITERIA

The selected test method yields numerical data for mass uptake and linear swell. Qualitative data on changes in appearance or pliability of the specimen can also be observed.

The key to deriving Performance Classes from the two measurements is the construction of the Classification Diagram. We propose the use of the Diagram in Figure 4, although (as will be seen below) there is some variability in its make-up. The qualitative nature of this Diagram makes the use of broad Performance Classes especially pertinent in this screen.

The desired regions in such a diagram correspond to effects on the polymer of the chemical, relative to those for halons 1301 and 1211. It is gathered from past experience that fire suppression using these halons poses no serious compatibility problems with exposed plastics.

- |          |   |
|----------|---|
| Class 1: | Effects less severe than or equally severe to those from exposure to halons 1301 or 1211. It is expected that such changes would not result in permanent damage to plastic parts.   |
| Class 2: | Effects more severe than those from exposure to halons 1301 or 1211. Alterations of polymers to the extent implied by this rating may be a cause for concern. Further investigation of the polymer-reagent pair is needed.      |
| Class 3: | Effects significantly more severe than those from exposure to halons 1301 or 1211. Alterations of polymers to the extent implied by this rating may be sufficient cause to preclude the exposure of the plastic to the reagent. |

The shapes of the regions are defined on the basis of experience. The asymmetry of the curves reflects the fact that shrinkage and mass loss are usually manifestations of chemical changes or extraction of additives, whereas mass uptake and swelling represent the interaction between polymer and solvent. Therefore, "negative" values of these parameters are serious warnings of incompatibility.

The magnitude of the regions in Figure 4 were approximated based on the performance of these polymers when exposed to halons 1301 and 1211. As listed in Table 4, the mass gains range from -0.4 to 1.7 percent. Since this is an approximate test, we presumed that double the maximum gain would be of little consequence. As discussed in Section E.3., the small negative values were considered unimportant, so no negative space is included. While no swelling was measured, we presumed that a small, reversible swelling (<2 percent) would be unimportant. These values defined the Class 1 region. The Class 2 envelope was selected at about double the Class 1 positive values, with a slight allowance for shrinkage or mass loss.

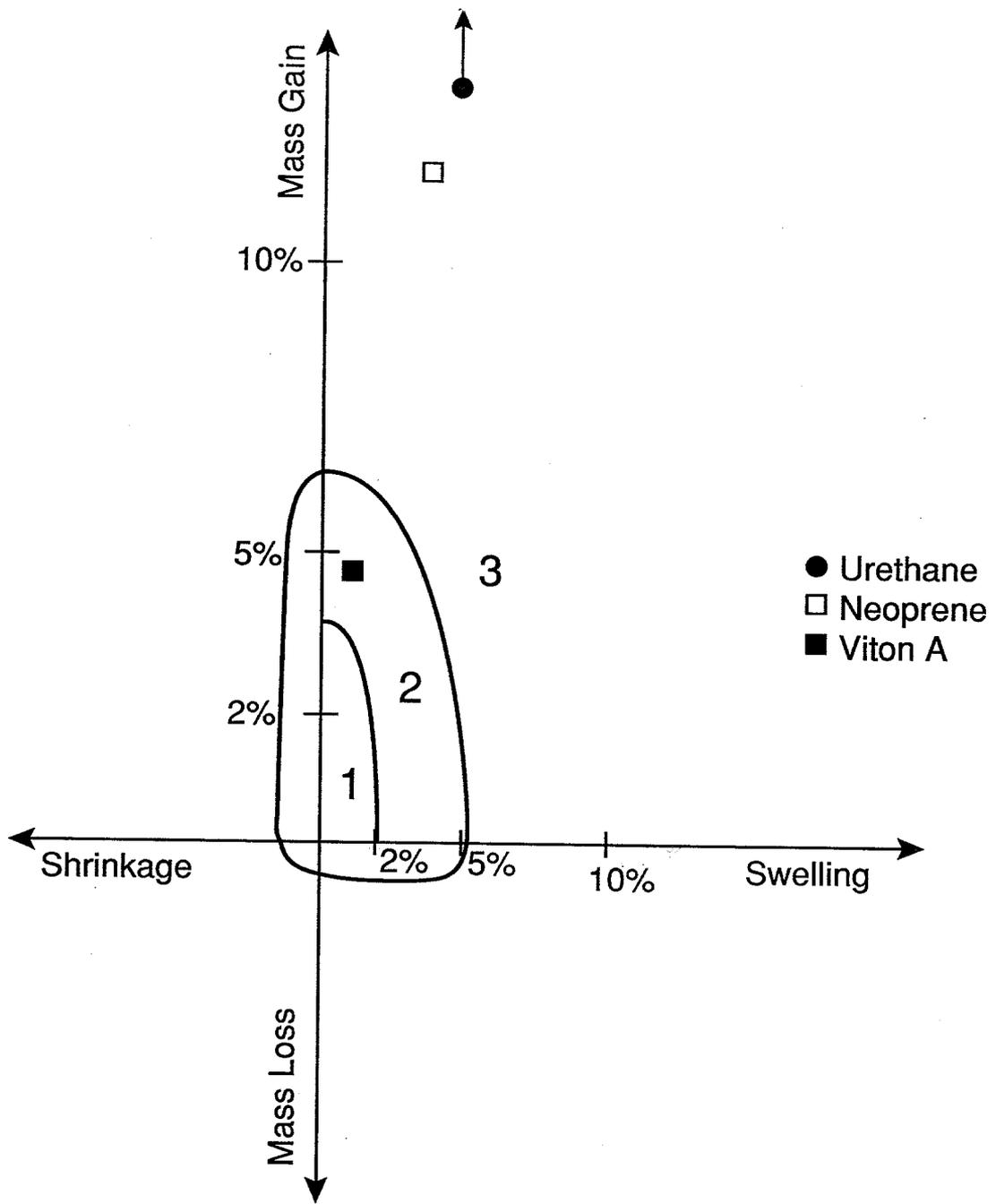


Figure 4. Assignment of Compatibility Rating

The numerical values that mark the boundaries will vary from one application to another. Some non-critical uses, such as for upholstery fabrics, would not be compromised if the material absorbed considerable amounts of solvent or if it swelled considerably. Other parts, such as circuit board components, might have to be replaced if the absorption of minor amounts of solvent led to stress-cracking.

Clearly, there is a degree of approximation involved in this Diagram. This reflects the qualitative nature of the interpretation of this type of testing. The scheme developed here was derived solely for screening replacements for halons 1301 and 1211. It should not be extended to other uses without considerable refinement.

## **E. PERFORMANCE DATA**

The screening method was examined with a limited number of tests conducted at NIST. The particulars of these tests and the results obtained are given below.

### **1. Chemicals Selected**

The reagents chosen were halon 1301, halon 1211, and trichlorotrifluorethane (TCTFE). TCTFE was chosen because it was likely to be a reasonably effective swelling agent on the basis of its molecular weight, boiling point, and vapor pressure.

The polymers chosen were three elastomers: a neoprene, a Viton A, and a urethane. The product data sheet for halon 1301 gives values for neoprene and Viton A that can be compared with the results of these experiments. The urethane was added when it became apparent that the exposure conditions were too mild to induce changes in the neoprene and the Viton. Since these experiments were designed only to evaluate the operation of the test method procedures, it was not deemed necessary to cover a complete spectrum of possible behaviors.

### **2. Results**

The results of the exposure tests on the three polymers are given in Table 4. The mass and length changes are expressed as percentage changes  $100 \times (m_f - m_o)/m_o$  and  $100 \times (L_f - L_o)/L_o$ , where  $m_o$  and  $m_f$  are the initial and final masses and  $L_o$  and  $L_f$  are the initial and final lengths of the test specimens.

### **3. Analysis**

Table 4 shows that the two halons do not interact appreciably with the neoprene or the Viton. The small negative mass changes indicate that sorption and desorption of water vapor or other atmospheric constituents may be interfering with the measurements in cases where sorption of the reagent is small. Sorption on such a small scale is probably not of concern in any case. The results from TCTFE provide clear-cut indications of sorption and swelling and indicate this reagent is considerably more aggressive toward the plastics tested than are the two halons.

## **F. EVALUATION OF SCREENING METHOD**

These results demonstrate, on a very limited scale, that a sorption test of the kind proposed here is capable of providing data that allow chemical reagents to be distinguished from one another. The Classification Diagram is quite approximate and is application-dependent. If this method is to be applied as part of a screen for determining compatibility of plastics with replacement fire suppression agents, additional

work should be done to identify a proper set of polymers to be used in the testing and a more rigorously-determined Classification Diagram.

The selection of polymers can be enhanced as more data becomes available. As additional rows and columns are added to Table 5, it should become possible to devise a spectral ranking wherein the column order is defined by the aggressiveness of the agent and the row order is defined by the sensitivity of the polymer. The correlations exposed in such a spectral ranking could even lead to methods for estimating compatibility based on group contributions, as is currently practical for solvency properties [20,21]. Salame [22] devised a scheme for predicting permeability in polyethylene based on group contributions in the early 1970's, but this scheme has not seen further development. Polymer compatibility is, however, a sufficiently serious continuing concern in all areas of polymer engineering that a method of estimating properties from  $n + m$  measurements rather than from  $n \times m$  measurements would be of great benefit.

It may even be possible to establish a more fundamental basis for this approach if one uses suitably-define "solubility parameters." The survey presented by Grulke in the Polymer Handbook [20] provides an introduction to these ideas. The "coherent energy density" is another fundamental thermodynamic concept that is closely related to solubility parameters. Barton [21] has written an excellent review of work in this area up to about 1980.

The concentration levels, temperatures, durations, and similar elements of the screen testing that are specified in the protocol adopted for regulatory purposes should be re-examined in the light of field experience with fire suppression agents and plastic artifacts. It may prove desirable, for example, to conduct testing above ambient temperature if the applications involve vehicles, cargo containers, and the like. The maximum ambient temperature in such situations is commonly regarded as somewhere in the neighborhood of 60° C.

## G. LABORATORIES/COST

An informal survey of laboratories known to perform plastics testing as determined from the directory listings of the American Council of Independent Laboratories [16] and the ASTM [17] revealed that there are an ample number of organizations who would be capable of performing testing of the sort described herein.

As noted in Section F, before proceeding with the screening of candidate suppressants, a set of target polymers must be selected and the Classification Diagram constructed. This is still a research area and requires an experienced polymer scientist.

The tests themselves are inexpensive; run in triplicate, the cost is estimated to be about \$200 per polymer-reagent pair plus the cost of the chemical. Each of the triplicate samples requires about 10 ml of liquid or about 25 ml of vapor at 1 atm.

## H. CONCLUSIONS

We have developed a screening procedure involving the immersion of polymer samples in the gaseous or fluid phase of a candidate fire suppressant. The measured changes in mass and length are combined to indicate the performance of the chemical relative to halons 1301 and 1211.

The final selection of polymer families to be employed in the screening should be made after the field of candidate agents is narrowed. The criteria for selecting polymer families in the screen should include their engineering importance and their expected sensitivity to candidate agents. The screening criteria are polymer application-dependent and involve expert judgment in their selection.

The Performance Classes from this screen are less objective than in the other screens. We suggest that this screen should be undertaken after narrowing the field of candidate agents to those with adequate performance on the basis of fire suppression efficiency, ozone depletion and global warming potentials, and toxicity as is suggested in Section 11 of this report. The tests described herein are simple and inexpensive enough that carrying them out will not appreciably delay decisions on the final suitability of agents.

The data derived here for incidental exposure must not be used to make decisions regarding materials suitability for use within storage systems for fire fighting agents. The consequences of failure in such systems are severe enough that they require the assurance that can only be gained from testing of the actual system. The number of plastics components in such systems is very limited, so that it is practical to test each component under conditions that simulate actual use.

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# SECTION XI

## USE OF SCREEN TESTS

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## SECTION XI

### USE OF SCREEN TESTS

#### A. INTRODUCTION

The purpose of these screen tests is to obtain information for deciding which alternative chemicals or chemical families to pursue further. This must be done quickly, inexpensively, and often with little agent. For this use, accurate indicators are critical; precise numbers are not. The nine procedures described in Sections 2 through 10 represent our best judgment for obtaining this kind of data. However, because of the restrictive criteria for developing them for screening, they should not be used for regulatory purposes or for materials specification without further scrutiny.

Before performing each of the screens, a search of the relevant literature may provide some insight into the expected behavior of the candidate agents. However, in our experience, some misleading and erroneous results have been found to be cited in the literature. These could lead to rejecting some potentially successful candidate chemicals. To prevent this from happening, and to provide needed information for further development, we urge cautious use of structure-activity relationships and recommend performing the appropriate screens.

#### B. MODES OF SCREEN TEST USE

In the process of searching for alternative fire suppressants, there are two different manners in which this set of screens will be applied. In this section, we will define these and then present examples of their use. It should be emphasized that both applications require some expert judgment to make accurate decisions.

##### 1. Research information

In this context, chemicals are not rejected. Rather, the need is to develop a uniform database of properties of many different chemicals. All chemicals are subjected to all screens as rapidly as possible. The data is collated in such a form that simple searches provide useful information. The full matrix of data becomes a source of ideas and principles for the technical community as it applies expert judgment in the search for new fire suppressants. A chart showing how one might develop this set of data is shown as Figure 1. Table 1 summarizes the resources required.

##### 2. Production Screening

Here, one has in mind certain criteria for unacceptable performance. The objective is to identify rejectable chemicals rapidly. Therefore, a hierarchical sequence of testing is used to kick out the least desirable chemicals first. The expert judgment that had been applied to setting up the Performance Classes is now combined with further expertise in selecting the rejection criteria. The partial set of data is recorded mainly as a reminder of why a chemical was found wanting. Later, if the criteria change, the remainder of the screens may have to be performed.

###### a. Summary of Performance Classes

To better visualize how a testing sequence might look, it would first be useful to summarize the performance classes which have been proposed for each of the screens. The details are given

TABLE 1. TIME, COST, AND AMOUNT OF AGENT REQUIRED

Screen	Elapsed Time (days)	Cost (\$) <sup>1</sup>	Amount (moles) <sup>2</sup>
Residue Level	½	50	0.02
Fire Suppression Efficiency	½	400	0.5
ODP/GWP	4	10,000	0.3
Toxicity	7½	1,500	2
Long-term Storage Stability	2	150	0.1
Metals Corrosion	7½	200	1
Electrical Conductivity	½	100	0.1
Plastics Compatibility	1½	200 <sup>3</sup>	0.1
TOTALS	24	≈13k	≈4

<sup>1</sup> These cost figures are the maximum for each screen.  
<sup>2</sup> These amounts are the maximum values, generally for liquids; gaseous agents will require less.  
<sup>3</sup> Involves considerable professional time beyond testing operations and interpretation.

in the individual sections. In all cases, the "best" (but not necessarily the only acceptable) performance corresponds to Class 1.

Residue Level

- Class 1: No measurable residue, indicating a pure chemical of at least modest vapor pressure.
- Class 2: Less than less than 1 percent residue, representing the presence of a small amount of impurity.
- Class 3: Over 1 percent residue; not a clean agent.

Fire Suppression Efficiency

- Class 1: At least as effective as halons 1211 and 1301; quenches the test flame at less than 3 percent by volume.
- Class 2: Not as effective as halons 1211 and 1301; quenches the test flame at 3 to 6 percent by volume.

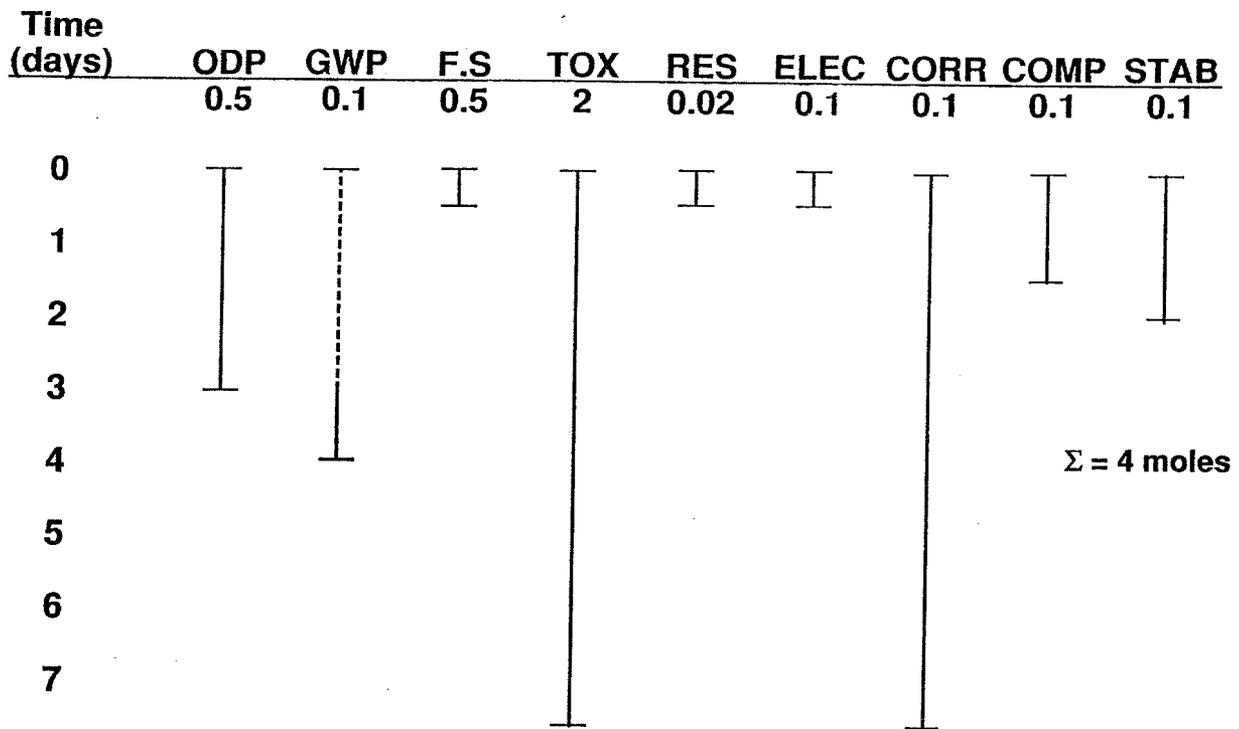


Figure 1. Possible Research Screening Procedure

- Class 3: Much less effective than halons 1211 and 1301; quenches the test flame at 6 to 12 percent by volume.
- Class 4: Not a chemical fire suppressant; requires at least 12 percent by volume to quench the test flame.

#### Ozone-Depletion Potential

Note that the contribution to stratospheric ozone depletion depends on both the ODP value and the mass released into the atmosphere. The latter must be considered in making decisions to proceed further with a chemical.

- Class 1: ODP is zero; contains no Cl, Br, or I.
- Class 2: ODP is low; tropospheric lifetime less than 1 year.
- Class 3: ODP is moderate; tropospheric lifetime between 1 and 10 years.
- Class 4: ODP is comparable to current halons; tropospheric lifetime greater than 10 years.

#### Global-Warming Potential

Note that the magnitude of contributions to global warming are still being determined and that there are immense contributions from sources other than fire suppressants. Again, the mass released into the atmosphere must be a factor in any judgment.

- Class 1: Weak absorbers and/or lifetimes less than 30 years.
- Class 2: Strong absorbers with lifetimes greater than 30 years.

#### Acute Inhalation Toxicity

- Class 1: Low toxic potency; all animals survive double the suppression concentration for 30 minutes with no lasting ill effects.
- Class 2: At least moderate toxic potency; some or all of the animals die or show ill effects.

#### Stability Under Long-Term Storage

- Class 1: Fairly stable; no measurable degradation observed after accelerated exposure (2 days at 170°C).
- Class 2: Less stable; measurable degradation observed after accelerated exposure (2 days at 170°C).

- Class 3: Not stable; significant (> 10 percent) degradation and/or tends to produce toxic by-products.

#### Metals Corrosion

- Class 1: Corrosion not observed on any of the test metals after 7 days of immersion in the test chemical [corrosion rates generally less than  $1 \times 10^{-6}$  mm/year].
- Class 2: Corrosion observed on some, but not all, metals after 7 days of immersion in the test chemical, and the corrosion rates are generally in the range from  $1 \times 10^{-6}$  to  $1 \times 10^{-4}$  mm/year.
- Class 3: Corrosion observed on all metals after 7 days of immersion in the test candidate, and/or the corrosion rates are greater than  $1 \times 10^{-4}$  mm/year.

#### Electrical Conductivity

- Class 1: Conductivity not a threat to electrical circuitry; agent is a gas below 20° C or a liquid with conductivity less than  $10^{-11} \Omega^{-1}$  cm.
- Class 2: Potential conductivity threat; liquid conductivity is greater than  $10^{-11} \Omega^{-1}$  cm.

#### Compatibility with Plastics

- Class 1: Effects less severe than or equally severe to those from exposure to halons 1301 or 1211; no expected permanent damage to plastic parts.
- Class 2: Effects more severe than those from exposure to halons 1301 or 1211. Further investigation of the polymer-reagent pair is needed.
- Class 3: Effects significantly more severe than those from exposure to halons 1301 or 1211. Alterations of polymers to the extent implied by this rating may be sufficient cause to preclude the exposure of the plastic to the reagent.

#### **b. Production Screening Strategy**

Before embarking on production screening, one should design a plan, a Decision Tree for Screening. This could take several forms and might or might not differ from the plan for obtaining research information shown in Figure 1.

If there were no other constraints, then one would perform the tests consecutively. The most critical property would be measured first. If acceptable results were obtained, then the second most critical property would be measured, and so on, until the least critical property were completed. For this series of tests, Table 1 shows this would take 24 days.

In our program, there are at least three likely constraints: shortages of time, money and chemical. Consecutive testing is unreasonable, since it uses the maximum amount of time and might emphasize tests that are more expensive and/or use a lot of the chemical.

Table 1 summarizes the approximate demands of the screen procedures in terms of time to perform the measurements, the cost of doing so, and the anticipated needed amount of chemical. These data, the performance classes summarized above, and the priorities/constraints of the situation form the basis for constructing a Decision Tree for Screening.

**c. Strategy Illustration**

As an example, consider a likely situation. There is a modest amount of the several chemicals to be screened, but funds and time are tight. The premium, then, is on doing a few, short, important tests first. Since our program is aimed at finding clean agents, and since screening for residue level is quick and inexpensive, it would be performed first. Atmospheric impact (ODP and GWP), fire suppression efficiency, and toxicity are next in importance. The other properties are only important if these four produce desirable results. These value judgments lead to a Decision Tree for Screening such as the one shown in Figure 2.

The "first round" screen is rapid. If the chemical is a gas at room temperature, it automatically goes into Class 1 with no testing. Even if it is a liquid, it takes only ½ day, \$50, and 2 ml of sample.

The "second round" screening for ozone depletion potential and fire suppression efficiency requires up to 3 days, up to \$8,000, and a mole of chemical. The cost and time are considerably reduced if the reaction rate data for the ODP calculation are known or can be estimated.

Toxicity and global warming potential follow as a "third round." This is logical, since the agent concentration for toxicity testing depends on the fire suppression efficiency results, and the GWP determination uses much of the data from the ODP determination. Note that this Tree makes immediate use of the within-exposure toxicity results. This allows the results of this round to require less than 1 day. It will cost less than \$4,000 and use about 2 moles of suppressant.

The other screens, shown at the bottom of Figure 2, and the remainder of the toxicity screen can be accomplished in about 8 additional days at a cost of less than \$1,000 and one mole of agent.

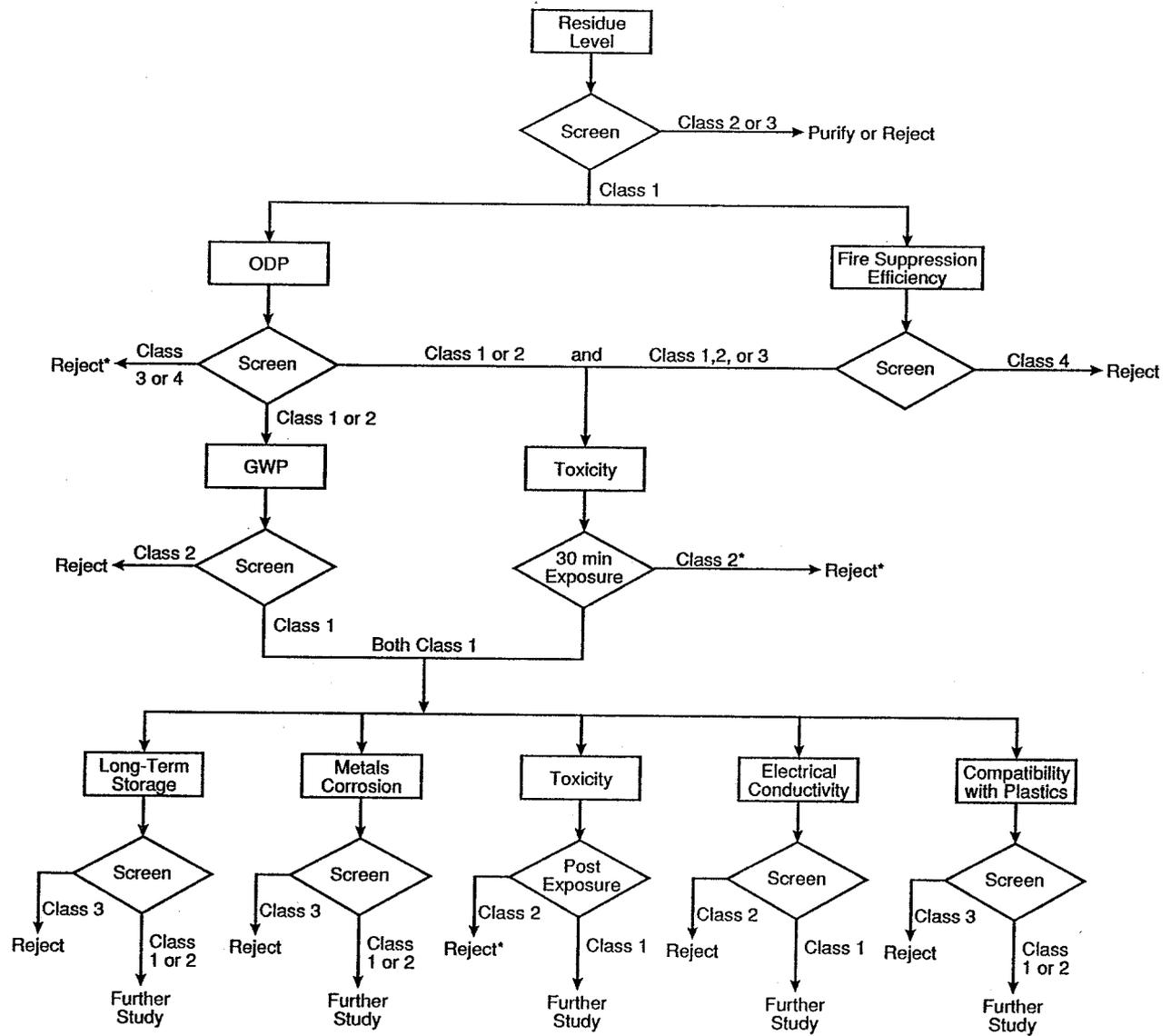
Figure 2 summarizes the successive investment for this example of a Decision Tree for Screening.

**d. Rejection of Chemicals**

Now, using the same Tree, let us look at possible use of the performance classes in making decisions as to whether to proceed with a chemical or not.

First, only the pure chemicals are to be examined. (It is recognized that during mass production, other chemicals from the synthesis process may remain and that other contaminants may accrue during transfer.) The residue screen and several of the last round of screens are somewhat sensitive to impurities. The ODP, GWP and electrical conductivity measurements are extremely sensitive. Therefore, it is essential that the chemical be purified before screening begins. This might involve considerable laboratory effort.

If the residue level screen results in a rating other than 1, then the candidate should be eliminated from further consideration, since the purpose of the project is to find clean agents. Continuing on, if the fire suppression results are in Class 4, then the agent is comparable in efficiency to the fully-safe perfluoroalkanes. Since the latter have already been tested extensively for health and materials safety, one might only pursue this agent further if it has desirable fluid mechanical properties.



\*If exposure risk is minimal, consider for further study

Figure 2. Possible Decision Tree Production Screening

If the ODP screen places the agent in Class 3 or 4, then the agent also should be rejected. This is because the expected production level of fire suppressants is expected to be sufficiently large that an ODP this high will be regulated under future versions of the Montreal Protocol. Therefore, such a chemical could be no more than a short-term or special use replacement. If the ODP places the candidate agent in Classes 1 or 2, then continue the evaluation for GWP.

The contribution of fire suppressants to global warming is still a subject of intense debate. Some hold that the anticipated production levels are sufficiently low that even Class 2 agents from the GWP screen should be considered for further study. In the absence of firm commitments from the regulatory community, chemicals should not yet be rejected for poor GWP values.

If the ODP screen shows the agent to be in Class 1 or 2 and the fire suppression efficiency screen results in a classification of 1, 2, or 3, then the toxicity screen should be performed. If any animals die within the initial 30-minute exposure, then generally the risk of human fatalities is too high and the chemical should not be pursued further. (There may be, however, applications in which the risk of exposure to humans is minimal. Then the candidate could be considered for further study.) If no animals die, then the fourth level of screens should begin.

The first of these involves continued observation of the animals in the toxicity screen. If any animals die during the post-exposure period, then further study is only warranted for those applications where the risk of people's exposure is minimal.

The other four screens, long-term storage, metals corrosion, electrical conductivity, and compatibility with plastics, should be performed during the toxicity post-exposure period. The long-term stability and metals corrosion screens reflect the degree of interaction with the interior of the storage vessel and distribution system. A Class 1 result for stability and a Class 1 or 2 for corrosion is desirable. However, if the chemical does poorly here and performs well in all of the other screens, then special storage cylinders and plumbing might well be worthwhile. The electrical conductivity and plastics compatibility screens measure interactions with products near the fire. Since one can rarely specify a limited set of products for all rooms protected by a widely-used suppressant, a Class 1 rating is needed here. (In a sense, any other classification reflects an unclean agent. Unless the user is willing to replace a potentially costly array of electronic and structural items, only Class 1 behavior is acceptable.)

This Decision Tree for Screening is intended as an example, albeit for a situation that is likely to arise. Different constraints on time, chemical, and funds will result in variations of it. However, it is our recommendation that enough resources be available to pursue at least the equivalent of the first two rounds of the screening procedure before making decisions to study a chemical further.

**SECTION XII**  
**CONCLUSIONS**

## SECTION XII

### CONCLUSIONS

Nine screening procedures have been defined for characterizing potential candidates for replacing the currently-used halogenated fire suppressants. These screening procedures have shown that they are able to distinguish between gases and liquids of varying degrees of performance. The results of this study leads to the following conclusions:

- We have constructed a battery of screening tests to guide the search for alternatives to the current halogenated fire suppressants. Some are based on standard ASTM procedures, some involve modifications of standard tests, and some are extensions of non-standard practices. These screens can be used to decide whether to pursue a particular chemical further.
- The full battery of tests requires about 4 moles of chemical and can be performed in about 8 days for less than \$15,000. Lower costs would result for concurrent testing of a large number of chemicals. Sequences of testing, potentially conserving resources, can be constructed, as described below.
- The tests are straightforward to conduct. Where a standard method has been modified or a non-standard method is recommended, operating procedures are described. Multiple laboratories are available for performing each of these tests, but few can perform them all.
- High purity of the samples of chemicals to be tested is critical.
- There are different uses for these tests, e.g., research or production. This report contains examples of testing sequences for each of these. A well-conceived plan is especially important for production testing.
- The interpretation of the data from this battery of screens requires the expertise of knowledgeable experts in each of the fields described. Weak performance in any given area may not be the basis for eliminating any material from further consideration.
- Classes of performance have been determined for ease of interpretation. These relate to the current values placed on halons 1211 and 1301.
- These tests should only be used to make decisions on proceeding to investigate a chemical further. In that further study, most of these tests should be superseded by different uses of the apparatus or by different methods altogether.
- Neither the methods or the performance classes are appropriate for specification or regulation at this time.



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11. ABSTRACT (A 200-WORD OR LESS FACTUAL SUMMARY OF MOST SIGNIFICANT INFORMATION. IF DOCUMENT INCLUDES A SIGNIFICANT BIBLIOGRAPHY OR LITERATURE SURVEY, MENTION IT HERE.)

The current halogenated fire suppressants, halons 1301 and 1211, are among the compounds whose production is restricted by the Montreal Protocol of 1987. The objective of this project is to facilitate identification of alternative chemicals by developing quick, inexpensive screening procedures for characterizing nine critical properties: fire suppression efficiency, ozone depletion potential, global warming potential, residue level, toxicity, long-term storage stability, metals corrosion, electrical conductivity, and compatibility with plastics. We have constructed and exercised such a series of tests that can be used to make decisions to pursue particular chemicals further. The procedures are straightforward to conduct, require about 5 moles of chemical, and can be performed in about 8 days for less than \$15k. Lower costs would result for concurrent testing of many chemicals. The results are reported in classes that relate to the performance of halons 1211 and 1301. Examples of testing sequences are provided. Interpretation of the results requires expert judgment since weak performance in a test may not be the basis for rejecting a chemical. These methods and performance classes have been developed for screening purposes only and should not be used for final selection, procurement or regulation without more extensive evaluation.

12. KEY WORDS (6 TO 12 ENTRIES; ALPHABETICAL ORDER; CAPITALIZE ONLY PROPER NAMES; AND SEPARATE KEY WORDS BY SEMICOLONS)

compatibility with plastics; electrical conductivity; fire suppression efficiency; global warming potential; halons; long-term storage stability; metals corrosion; ozone depletion potential; residue level; screening procedures; toxicity

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