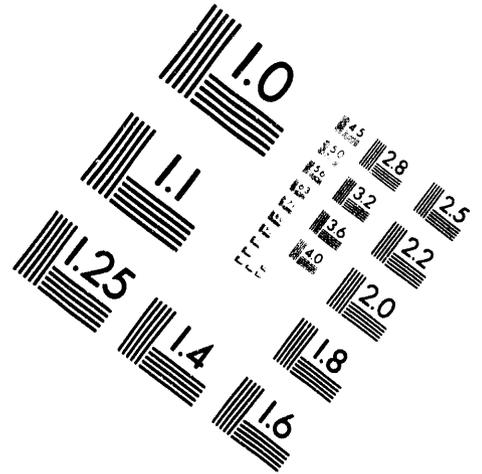
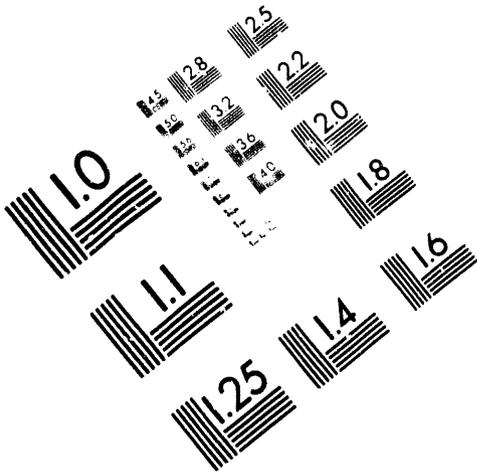




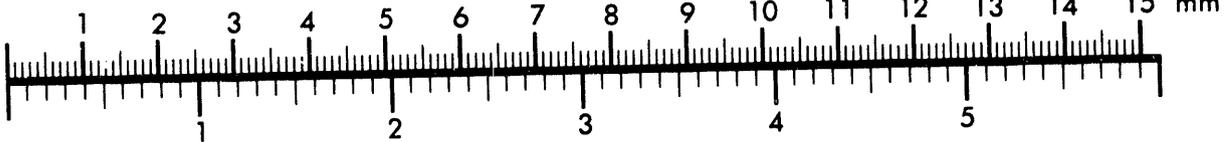
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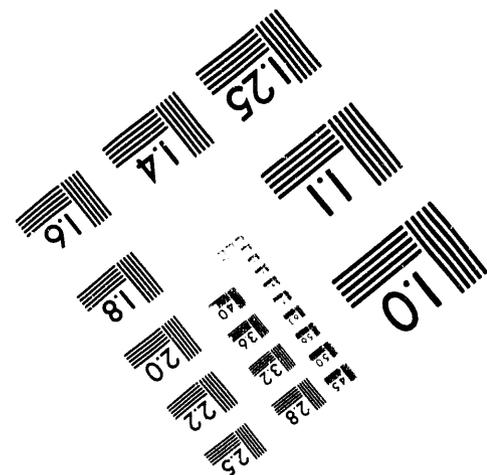
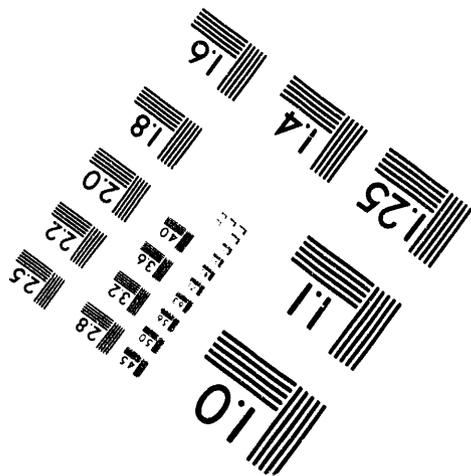
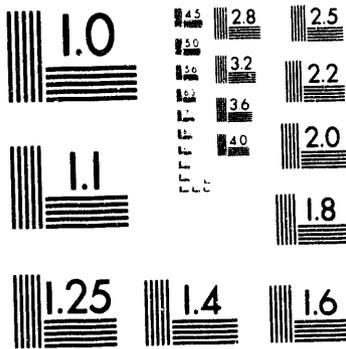
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## Testing of CFC Replacement Fluids for Arc-Induced Toxic By-Products

**W. Ray Cravey  
Dave A. Goerz  
Ruth A. Hawley-Fedder**

June 1993

Lawrence  
Livermore  
National  
Laboratory

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# Testing of CFC Replacement Fluids for Arc-Induced Toxic By-Products \*

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## Microwave & Pulsed Power Thrust Area Technical Planning Document

PPTA-93-119

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## I. Executive Summary

We have developed a unique test-stand for quantifying the generation of perfluoroisobutylene (PFIB) in chlorofluorocarbon (CFC) replacement fluids when they are subjected to high electrical stress/breakdown environments (see Figure 1). PFIB is an extremely toxic gas with a threshold limit value of 10 ppbv as set by the American Conference of Governmental Industrial Hygienists. We have tested several new fluids from various manufacturers for their potential to generate PFIB. Our goal is to determine breakdown characteristics and quantify toxic by-products of these replacement fluids to determine a safe, usable alternative for present CFC's.

## II. Introduction

Restrictions on the use of chlorofluorocarbons (CFC's) worldwide, nationally, and at Lawrence Livermore National Laboratory (LLNL) will have an enormous impact on industry and government laboratories. Worldwide usage of CFC is estimated at 750,000 metric tons<sup>1</sup>, of which 15% is used in the refrigeration industry! Although several replacements for existing CFC's do exist, many of these replacements are toxic,<sup>2</sup> flammable, or highly expensive. In addition, two replacements, although not toxic, have been identified as ozone depletion agents, and their use will be phased out in the near future.<sup>3</sup>

We are studying several new replacement fluids for CFC's that would have similar electrical and thermal characteristics. CFC's are currently used as high voltage electrical insulators and dielectric coolants for the high-average-power modulators used to drive the copper vapor lasers at the Atomic Vapor Laser Isotope Separation (AVLIS) facility at LLNL. Several substitutes have been suggested to replace these fluids. But a stumbling block associated with these replacements is the potential to generate toxic gases, such as PFIB, when the fluids are subjected to high electrical stresses and/or breakdowns.

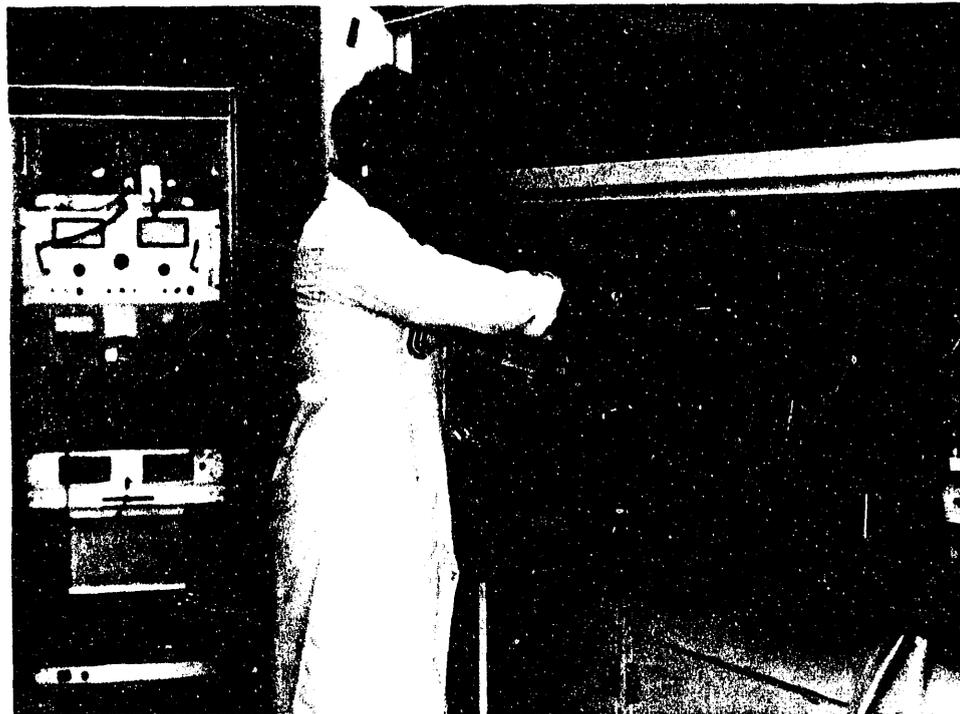


Figure 1. Replacement Fluid Test-Stand.

### III. Recent Progress

Over the past year, we developed and constructed a test stand suitable for evaluating new CFC replacement fluids. Our test stand provides a wide variety of test parameters including the electrical breakdown conditions associated with industrial refrigeration systems. Work is now proceeding on the compressive data collection and analysis that is necessary to quantify the toxic by-product production for given breakdown conditions. Initial results from tests conducted on fluids suggested as replacements for AVLIS modulators, show a linear trend in PFIB generation with respect to arc energy. We have also received funding from the Superconducting Super Collider (SSC) for analysis and testing of the cooling fluid used in their low-energy booster (LEB) cavities. A more descriptive summary of our progress is given in the subsequent sections.

#### CFC Replacement Fluid Test-Stand

We have identified three electrical breakdown/stress environments that may contribute to PFIB production in CFC replacement candidates for various applications: AC breakdown; high DC field stress; and pulsed breakdown. Our test-stand was designed to simulate all three of these environments. A block diagram and description of the operation of the test-stand is given in Figure 2.

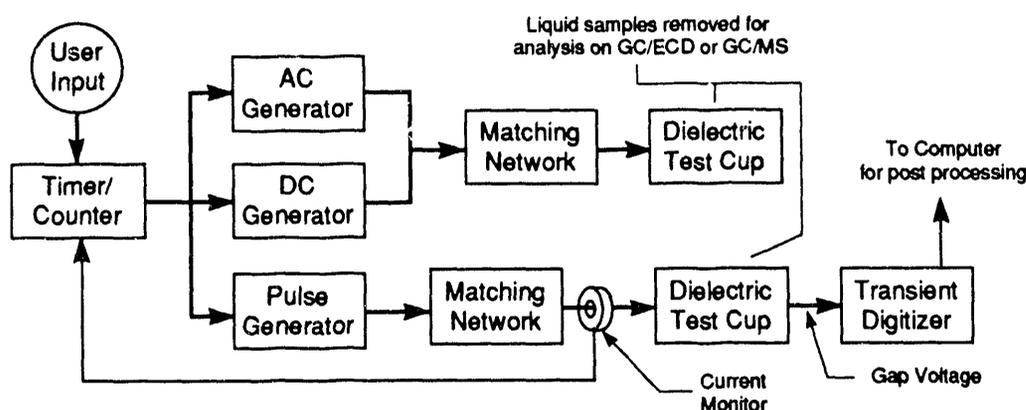


Figure 2. Block diagram of CFC replacement fluid test-stand. The user sets the time or number of pulses for the desired test: AC, DC, or pulse. The output of the corresponding generator is fed through a matching-network into the dielectric test cup. The test cup houses the gap electrodes and contains the fluid under test. Samples are removed from the test cup and analyzed on a gas chromatograph (GC) or GC mass spectrometer, to quantify the amount of PFIB that was produced, if any. The voltage across the gap and the coinciding current are digitized and recorded on a computer. There they are analyzed, and the power and energy are determined.

An important test that has application in the refrigeration industry is breakdown due to high AC voltages. We have the capability of producing 60-Hz AC, high voltage breakdown conditions with voltages ranging from 0 to 40 kV, and any desired gap spacing across the test cell electrodes. Our capabilities allow us to simulate the inside environment of the ordinary refrigeration compressor/motor assembly.

High DC field stress occurs in many situations where there are high voltages present. Electrical arcing is not associated with these conditions; however, there can be extremely high fields and corona onset. With our system, we are able to generate these high pre-breakdown fields in the fluid-under-test for any preset time limit. After the given time limit, the fluid is analyzed for PFIB formation.

Pulsed breakdown environments are produced with many high voltage modulators. Typically, these modulators are used for powering radar, lasers, and accelerator cells. We have a wide range of pulsed conditions that can be produced with our present test-stand. In addition to being able to produce the pulsed conditions mentioned, we have implemented a complete electrical diagnostic system for measuring the breakdown voltage, discharge current, arc power, and energy that are associated with each pulse. Through the use of the data that is recorded by the diagnostics, we are able to correlate the quantity of PFIB produced with the pertinent control variables, such as voltage, current, pulse-width, pulse repetition frequency (prf), and energy.

### Experimental Results

Measurements have been made on a candidate replacement fluid for the copper vapor laser modulators. The fluid was subjected to a 30-kV pulse at a pulse repetition rate of 75 Hz, with a full-width half-maximum of 100  $\mu$ s. A 10-mil gap spacing with brass electrodes conforming to ASTM standards<sup>4</sup> was used for testing. The dielectric test cup was filled with 85 ml of the fluid under test. Samples were taken from the dielectric test cup before exciting the fluid, at 20 kV, 40 kV, and 100 kV pulses. Between each sample interval, the voltage and current waveforms were recorded, and the instantaneous power and energy were calculated for the arc. A typical data set is illustrated in Figure 3.

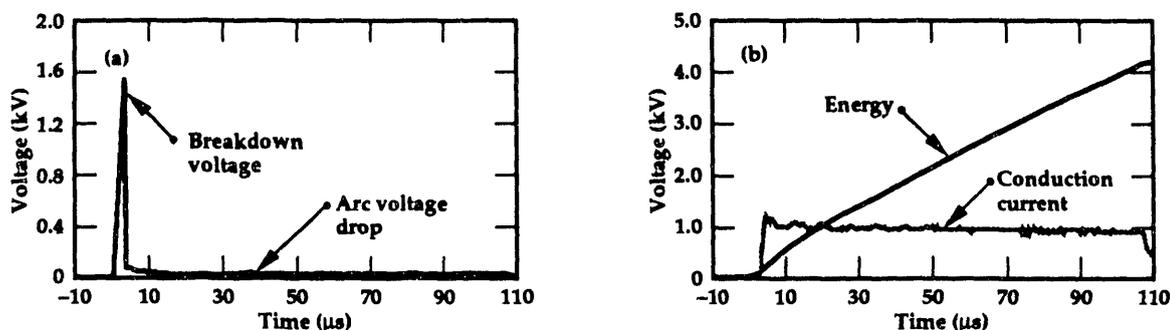


Figure 3. Typical data for (a) voltage and (b) current waveforms.

There are two loss mechanisms associated with the arc discharge: resistive/inductive phase<sup>5</sup> losses and conduction loss. The resistive/inductive phase losses are produced during the time the voltage collapses across the gap and the current begins to rise. During this phase, there is a power and energy loss associated with the instantaneous current rise and voltage collapse. The faster the voltage collapses, the less appreciable the losses are. The second loss mechanism, which appears to be the most dominant in this experiment, is the loss associated with the voltage drop across the arc itself. The forward drop of the spark gap was observed to jump between 40 and 60 volts. The maximum output current is 1 amp for the present configuration, limited by the output transformer.

The samples were analyzed on a dual-column gas chromatograph equipped with an electron capture detector. Results from the analysis are shown in Figure 4. The reduced data shows a clear trend with respect to energy. We would like to predict the amount of PFIB that is formed for higher energies, by using the data we collect on the test-stand. Initial data shows good agreement. The calculated field for the breakdown voltage is much lower than what was expected based on the published fluid characteristics. Further investigation showed that the breakdown level is much higher at lower prf due to fluid recovery. Although this is no surprise, it is a key variable in the pulsed breakdown of these fluids.

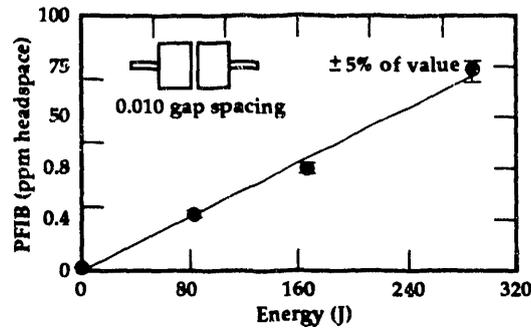


Figure 4. Preliminary data set for pulse breakdown-induced PFIB generation. The fluid sample was pulsed with a 30-kV, 1- $\mu$ s pulse at a prf of 75 Hz. This data was generated with brass electrodes and a 10-mil gap spacing in the dielectric test cup. The energy per pulse is 4 mJ.

### Superconducting Super Collider Tests

We have established a working agreement with SSC and received funding to evaluate the amount of PFIB that is potentially produced in their LEB cavities. Also, we are providing measurement capabilities and chemical analysis for quantifying PFIB in samples they provide. The first sample generated by SSC was subjected to 60 kV for 20 hours of operation. A two dimensional electrostatic model of the LEB cavity was created to examine the electric field enhancement due to the shape of the structures, and the maximum electric field in the fluid was calculated to be 83 kV/cm. The samples were analyzed, and no PFIB was measured above the 60 ppbv detection limit. SSC personnel reported that during their operations, there were no detectable breakdowns.

### IV. Resources

In addition to the unique test stand for characterizing CFC replacement fluids, LLNL has many additional capabilities that are being utilized including:

1. A dedicated toxic gas handling facility for working with highly toxic gases in a safe manner.
2. State-of-the-art analytical services for both physical and chemical characterization of materials including instrumentation for major/minor and trace level analysis for both organic and inorganic materials.
3. Extensive computer simulation capabilities needed to model various system geometries such as electrical feed-throughs in refrigeration compressors.
4. A ceramic test cell under development which will allow testing at pressures as high as 500 psi and temperatures above 300° C.
5. An extensive on-site library and access to a wide range of on-line literature search systems with databases relevant to various aspects of identifying replacement compounds for chlorofluorocarbons (CFC) and material compatibility.
6. Unique high-voltage, impulse generators and fault current simulators to induce breakdown conditions in heavy electrical equipment.
7. Scientific personnel with extensive experience in liquid breakdown physics and organic analytical chemistry.

## V. Future Work

Our plans for the next fiscal year are focused on three key areas.

- (1) We are currently working to generate a comprehensive and complete data set for various arc-induced breakdown conditions for various fluids. The last year was dedicated to developing the needed test-stand and diagnostics as well as chemical and analytical techniques. Now that the testing facility is in place, we will fill in our data set and analyze the results for PFIB generation trends, with respect to parameters such as energy, power, and prf.
- (2) In addition to the continued testing of the replacement fluids, we propose to test, in cooperation with 3M, a fluid contamination detection system. The system uses a UV source (not specified) and detector to measure the transparency of the fluid. Initial tests have been conducted by 3M, which show that the fluid's transmission changes by as much as 20% when the fluid is subjected to high thermal stress. We will test various detector configuration and breakdown parameters to decide if the detector can be used as a reliable means to signal the possibility of PFIB contamination in hostile working environments.
- (3) The third area that we believe we can positively impact is the refrigeration industry. In the majority of industrial refrigeration systems, the refrigerant is circulated through the compressor motor, for cooling and lubrication.<sup>7</sup> In large systems, the voltage level can exceed 1000 volts, leading to the occasional and often catastrophic electrical breakdown of the fluid. Our test-stand is capable of reproducing these breakdown conditions in the laboratory where a comprehensive analysis can be performed. Furthermore, we have the capabilities to do a comprehensive evaluation, including full scale compressor testing with electrically induced motor burnout and complete assessment of toxic and corrosive effects of by products.

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