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LASER-INDUCED FLUORESCENCE ANALYTICAL TECHNOLOGIES–PHASE II

INTERIM REPORT
BFLRF No. 276

By

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Trade Names

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The U.S. Army has a large number of fabric-reinforced elastomer storage tanks, ranging in size from 100 to 200,000 gallons. These tanks are used for storing fuel and other liquids. An acceptable nondestructive inspection technique for determining the condition of these tanks does not exist. The objective of this project was to develop and fabricate a test device for evaluating degradation of elastomers using the technique of laser-induced fluorescence.

The present procedure used on these storage tanks is to discard them after they have been in storage for 5 years, even if they have never been in service. A method of nondestructive inspection is needed to inspect these storage tanks, as well as other elastomers in the military inventory.

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19. ABSTRACT

During previous work, it was discovered that the degradation of many polymers is strongly correlated to the laser-induced fluorescence intensity from those materials. Subsequently, Belvoir RDE Center, STRBE-VU, funded a research program to investigate the correlation of laser-induced fluorescence intensities with artificially induced degradation of polyurethane elastomers. As a consequence of the success of that project, this follow-on effort was initiated to develop a demonstration-prototype unit.

A demonstration-prototype unit has been designed, fabricated, and tested. It has been successfully demonstrated on a limited sample set. The unit was designed so that it could be used on many different materials, thus it has high sensitivity, wide dynamic range, and is very versatile. As with many first version prototypes, these features have been somewhat at the expense of increased size and weight. Further testing on a wide range of elastomers should be done to establish applicability to each material.

This innovative inspection technique can be used to save time, material, and money. Additionally, laser-induced fluorescence inspection techniques may be useful for a wide range of applications of interest to the military.

EXECUTIVE SUMMARY

Problem and Objective: The U.S. Army has a large number of fabric-reinforced elastomer storage tanks, ranging in size from 100 to 200,000 gallons. These tanks are used for storing fuel and other liquids. An acceptable nondestructive inspection technique for determining the condition of these tanks does not exist. The objective of this project was to develop and fabricate a test device for evaluating degradation of elastomers using the technique of laser-induced fluorescence.

Importance of the Project: The present procedure used on these storage tanks is to discard them after they have been in storage for 5 years, even if they have never been in service. A method of nondestructive inspection is needed to inspect these storage tanks, as well as other elastomers in the military inventory.

Technical Approach: During previous work, it was discovered that the degradation of many polymers is strongly correlated to the laser-induced fluorescence intensity from those materials. Subsequently, Belvoir RDE Center, STRBE-VU, funded a research program to investigate the correlation of laser-induced fluorescence intensities with artificially induced degradation of polyurethane elastomers. As a consequence of the success of that project, this follow-on effort was initiated to develop a demonstration-prototype unit.

Accomplishments: A demonstration-prototype unit has been designed, fabricated, and tested. It has been successfully demonstrated on a limited sample set. The unit was designed so that it could be used on many different materials, thus it has high sensitivity, wide dynamic range, and is very versatile. As with many first version prototypes, these features have been somewhat at the expense of increased size and weight. Further testing on a wide range of elastomers should be done to establish applicability to each material.

Military Impact: This innovative inspection technique can be used to save time, material, and money. Additionally, laser-induced fluorescence inspection techniques may be useful for a wide range of applications of interest to the military.

FOREWORD/ACKNOWLEDGMENTS

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The author would also like to acknowledge Mr. Bruce Reinhard, principal scientist, SwRI, for his help with the mechanical design work. The author may be contacted at Southwest Research Institute at (512) 522-3358.

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I. BACKGROUND

During previous work (1),* it was discovered that degradation of many polymers is strongly correlated to the laser-induced fluorescence intensity from those materials. Subsequently, Belvoir RDE Center, STRBE-VU, funded a research program to investigate the correlation of laser-induced fluorescence intensity with artificially induced degradation of polyurethane elastomers caused by hot water [160°F (71°C)]. The results of that work were reported in detail in the final report of that initial phase.(2,3) As a consequence of that project, a follow-on effort was proposed (4) to develop a demonstration prototype. That proposal is the basis for the present project.

II. INTRODUCTION

A. The Problem

The U.S. Army currently has a large number of fabric-reinforced elastomer storage tanks, ranging in size from 100 to 200,000 gallons, used for storing fuel or other liquids. These tanks must hold liquids for extended periods of time while exposed to the elements and then be folded and stored worldwide in crates for years before being needed again. The combination of heat and humidity is very deleterious to the materials used in the construction of these tanks. Although the tanks are drained after use and prior to storage, residual liquid usually remains in them. Exposure to the liquid can degrade the polymer after a long period of time and cause leakage. The current procedure is to discard tanks that have been stored for 5 years or more, even if they have never been in service. Nondestructive inspection techniques for determining the condition of these tanks are needed.

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* Underscored numbers in parentheses refer to the list of references at the end of this report.

B. Objective

The objective of this present project was to design, develop and fabricate a proof-of-principle demonstration-prototype unit for evaluating degradation (of material characteristics) of elastomers using the principle of laser-induced fluorescence. Previous work (2,3) has established this principle to be valid when applied to several types of nonblack opaque polyurethane materials, namely, Uniroyal "A" ester-based, Uniroyal "B" ester-based, Uniroyal "C" ether-based. and Goodyear nitrile-based. (Formulations may now be slightly different for these materials.) Also under consideration for evaluation were other materials that have not been tested to determine if laser-induced fluorescence correlates to any pertinent material characteristic. Preliminary measurements on samples from Belvoir RDE Center indicate materials designated as Bell Avon, Seaman Corp. (5) and B.F. Goodrich, Estane F (6) do fluoresce under 488-nm excitation (see below), but correlation with material characteristics has not been completely established over a wide range of materials or degradation parameters (see below).

It was decided (6) that the primary emphasis would be development of the demonstration-prototype unit (4); additional experimentation with laser-induced fluorescence techniques on fuel-degraded material would be held to a minimum under the present funding.

III. TECHNICAL APPROACH

A. Theory of Operation

1. Laser-Induced Luminescence

Laser-induced luminescence (LIL) is emission of light resulting from absorption of laser energy by a substance. Reradiated light contains a major component at the wavelength of the exciting laser light (reflected light); however, there are also many new wavelengths (luminescence) that are determined primarily by the electronic structure of the substance. Laser-induced luminescence includes both laser-induced fluorescence (LIF), which is fast luminescence occurring on time scales of the order of several nanoseconds, and laser-induced phosphorescence

(LIP), which is slower luminescence occurring on time scales as long as several seconds. The luminescence spectrum is not only a function of time, but also a function of the excitation spectrum. Fluorescence and phosphorescence have been studied for a number of years and have been used in numerous ways in the laboratory environment. Laser-induced luminescence is finding widespread use in many new and diverse applications; for example, it is currently being used to study energy redistribution collisions in vapors, for fingerprint detection, and to map flow fields in chemical lasers. In recent years, advances in laser technology have increased reliability and portability of lasers and also generally reduced costs; this is readily demonstrated by the wide use of helium-neon lasers in bar-code scanners found in many supermarkets.

In many applications, fluorescence dominates phosphorescence. Fluorescence is characterized by many spectra depending on the excitation wavelength. A fluorescent molecule emits a fluorescence spectrum after it absorbs radiation within its excitation spectrum. The spectral distribution of the fluorescent radiation is a physical and absolute characteristic of a given substance for a given excitation wavelength and is useful for qualitative considerations. Emission intensity of fluorescence at a given wavelength is useful for quantitative analysis with a given instrument after standardization. Quantitative measurements show that there is sometimes a very strong correlation between laser-induced luminescence and some physical characteristic of the material; many times this is because fluorescence reveals relationships between molecular functional groups, such as conjugation. (This is in partial contrast to infrared-absorption techniques, which are primarily used to reveal presence of individual molecular functional groups.) Because relationships between certain molecular functional groups are altered during degradation, laser-induced luminescence can be used to monitor these processes.

With the monochromaticity and power density available from lasers, transitions can be probed in molecules that are not normally thought of as fluorescent. For instance, chromophores that exhibit ultraviolet absorption can sometimes be induced to fluoresce with laser excitation in the visible region of the spectrum; representative examples include ethers (-O-), esters (-COOR), and nitriles (-CN). This effect can be very important from the viewpoint of practical implementation.

When laser-induced fluorescence is measured or visually assessed using optical filters instead of a narrow-bandwidth spectrometer, fluorescence signals of several wavelengths are measured simultaneously. Laser-induced fluorescence measured in this fashion is referred to as "integrated fluorescence" because the signal is related to the integral of the fluorescent-light intensity, weighted by the filter-detector response, over the wavelengths to which the system responds. Hence,

$$I(\lambda_e) = \int LIF(\lambda_e,\lambda)\, D(\lambda)\, f(\lambda)\, d\lambda \qquad (1)$$

where: $I(\lambda_e)$ = Integrated fluorescence for excitation wavelength λ_e,
$LIF(\lambda_e,\lambda)$ = Laser-induced fluorescence at wavelength λ when excited with wavelength λ_e,
$D(\lambda)$ = Detector response at wavelength λ,
$f(\lambda)$ = Filter response at wavelength λ.

Note that $LIF(\lambda_e,\lambda)$ is also a function of the penetration depths (absorption and scattering parameters) for both the excitation and detection wavelengths, as well as the quantum yield for fluorescence of the material.

2. Polymer Degradation

Polyurethanes are a broad class of chemically divergent polymers.(5) The two main subgroups are ether-based polyurethanes comprising flexible polyether segments joined by rigid urethane segments and ester-based polyurethanes where flexible aliphatic or aromatic polyester segments are joined by urethane links. The types and lengths of flexible and rigid segments in polyurethane determine if the resins are soft, rubbery, or glassy. Polyurethanes are widely employed as films, foams, moldings, and specialty items. In general, there are several mechanisms that initiate degradation in polyurethanes. **Hydrolysis:** In ether-based polyurethanes, only the urethane linkage undergoes hydrolysis, and quite severe conditions are required. In contrast, ester-based polyurethanes may undergo scission at either ester or urethane linkages; in fact, the ester group is an order of magnitude more sensitive to hydrolysis than the urethane linkage. Chain cleavage is accompanied by an increase in crystallinity, which accentuates changes in mechanical properties. **Thermal reactions:** At temperatures above 150°C, the urethane link cleaves to give a variety of reaction products. In the presence of oxygen, all polyurethanes oxidize, especially in the flexible segments. Ether segments are particularly prone to oxidation. **Photoreactions:** In general, all polyurethanes are light-sensitive to some degree, from either direct photoreactions or complex reactions involving free radicals. The wavelengths and power densities of the light involved are very important parameters in these processes.

B. Preliminary Laboratory Measurements

The following preliminary experiments were performed using standard laboratory equipment by methods previously described.(3) Briefly, data were obtained using 488-nm excitation and a Schott-glass OG530 blocking filter in front of an EG&G/PAR optical multichannel analyzer system model OMA-II.

1. Fuel Samples

Laser-induced fluorescence was measured from three neat-fuel samples contained in test tubes. With 488-nm excitation and 548-nm detection (at the peak of the fluorescence spectrum), the three fuels yielded the following relative intensities:

Referee diesel (AL-12329-F, MIL-F-46162B)	1603 counts
Referee diesel (AL-18135-F, MIL-F-46162C)	1325 counts
JP-8 Jet fuel (AL-18136-F)	80 counts.

Therefore, it can be seen that some fuels are relatively fluorescent.

2. Fuel-Degraded Samples

a. Seaman Corp. Sample in Diesel

The following experiments were conducted on elastomeric material samples supplied in November 1989 by Belvoir RDE Center. Samples manufactured by Seaman Corp. [0.075-in. (1.90-mm) thick] that had been treated in 160°F (71°C) diesel fuel for various time periods showed an increasing fluorescence with treatment time. For example, with 488-nm excitation and 577-nm detection:

0 days (Seaman Original Sample)	273 counts
28 days 160°F (71°C) diesel fuel (MIL-F-46162B)	909 counts
42 days 160°F (71°C) diesel fuel (MIL-F-46162B)	1228 counts
70 days 160°F (71°C) diesel fuel (MIL-F-46162B)	1418 counts.

(Note: These relative intensities should not be compared to the neat-fuels experimental intensities because the experimental parameters were different.)

b. Bell Avon Sample in Gasoline/Water

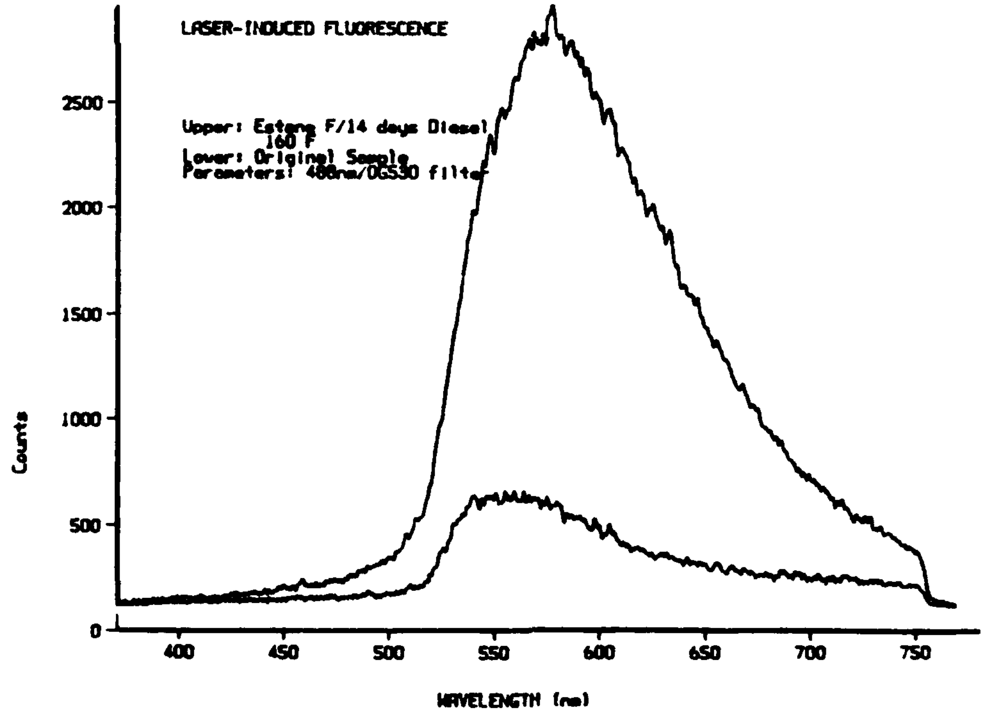
Bell Avon elastomeric-material samples [0.085-in. (2.16-mm) thick] treated with JP-8 showed similar results; however, the Bell Avon material that had been treated with unleaded gasoline showed a very intense increase in fluorescence in early stages of treatment, somewhat masking other effects due to degradation. It appeared that, if the samples were then aged in 160°F (71°C) water, the gasoline was increasingly washed out of the polymer matrix as a function of time, viz.:

0 days (Bell Avon Original Sample)	363 counts
14 days 160°F (71°C) gasoline	2402 counts
14 days 160°F (71°C) gasoline/14 days 160°F (71°C) water	1788 counts
14 days 160°F (71°C) gasoline/28 days 160°F (71°C) water	735 counts.

From the experiments described above, it can be concluded that in some cases, the increased laser-induced fluorescence intensity resulted from fluorescence of the fuel contamination itself, as well as from the degradation of the material. The degree of this effect is also a function of the type of material. These facts could be used to an advantage in detection and/or imaging fuel spills on the material.

c. B.F. Goodrich, Estane F Sample in Diesel

Fig. 1 shows the laser-induced fluorescence spectra from a sample of a polymer (B.F. Goodrich, Estane F) in its original state and after degrading in diesel fuel for 14 days at 160°F (71°C). From these spectra, it is apparent that fluorescence from the fuel-degraded sample is much more intense than that from the original sample. Further work will be required to determine if this effect is entirely caused by degradation processes or by fuel entrapped in the polymer matrix. (See Section III.E.3 below for measurements on these same samples made with the demonstration-prototype unit.)



(Note: the upper spectrum is from a sample that was artificially degraded in 160°F (71°C) diesel fuel for 14 days and the lower spectrum is the control sample. Tensile strength and elongation data from the degraded and control sample are 3500 psi and 470 percent and 3930 psi and 450 percent, respectively.)

Figure 1. Laser-induced fluorescence spectra from B.F. Goodrich, Estane F

3. Fluorescence Imaging Applications (Visualization)

Samples of fuel-degraded polymers were visually inspected through argon-ion laser-safety goggles under illumination from an expanded argon-ion laser beam (in a dark room). Possibilities for imaging fuel-degraded areas of larger samples were immediately obvious. Although these measurements were not quantitative, the polymers that were degraded with fuel were moderately to intensely fluorescent as compared to unexposed samples, depending on the polymer and the fuel. This concept could be used to detect fuel contamination or degradation of large areas; instrumentation could be built utilizing off-the-shelf solid-state video and image-processing equipment. If quantitative correlation of tensile strength with fluorescence intensity is not necessary, this technique can also be useful on a limited basis utilizing a long-wavelength ultraviolet mercury lamp. (These effects were demonstrated in the laboratory during the initial project meeting.)

C. Design Considerations

1. Introduction

Because this unit may be experimentally used on many different materials, the highest sensitivity, widest dynamic range of experimental parameters possible, ease of operation, and instrumental versatility are desirable features. As with many demonstration prototypes, these features may be at the expense of increased size and weight.

2. Components

Performance, cost, availability, ease of replacement, size, and weight were considerations for all major components. Several recent applications of fluorescence (8-11) were reviewed and considered during the design phase. Discussions of engineering trade-offs involved are summarized below and documented in more detail in the ordering documentation packages (Appendices A and B). A conceptual diagram of the unit is shown in Fig. 2. A brief discussion of the most important issues follows.

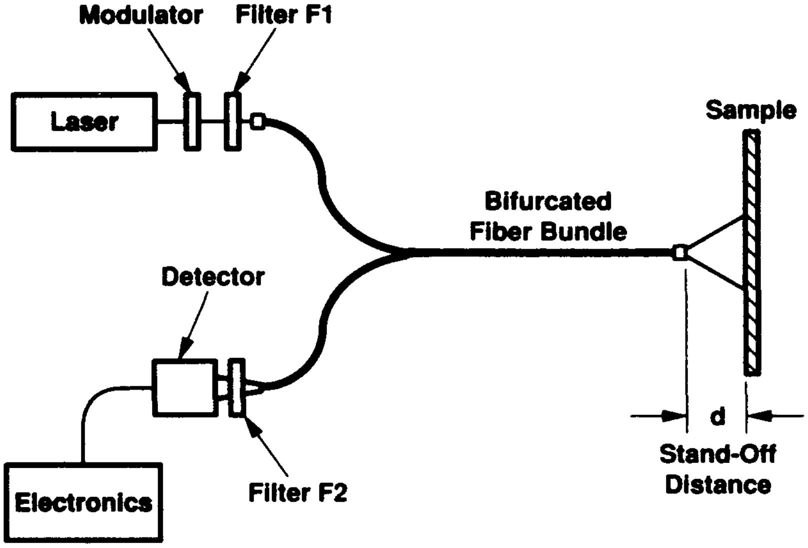


Figure 2. Conceptual diagram of the demonstration-prototype unit

a. Laser

Because the choices of laser parameters dominated most of the other decisions, these were considered first and in some detail. The optimum excitation wavelength for differentiation of degraded to nondegraded Uniroyal "B" material was found to be 488 nm (2) with approximately a factor of 10 worse performance using 363 nm or 633 nm. The power levels necessary for fluorescence measurements were relatively modest, with most of the experimental measurements being performed with only milliwatt-levels of optical power. For the present application, linearity has been confirmed to power densities of 20 mW/cm^2 (2); however, fluorescence quenching occurred when power densities were too high. (Measurements indicated that with 1.6 mW/cm^2, 488-nm excitation, fluorescence from Uniroyal "B" material decreased by a factor of two after 20 minutes.) Because there will be at least a factor-of-two loss through the laser-discharge filter, a factor-of-two loss through the fiber optics, and a factor-of-two loss in average power through the modulator, a laser power in the range of 10 mW offers the best compromise between power, availability, cost, weight, and safety. Because of the potential field application of this instrument, a rugged laser was necessary, i.e., integral mirrors and good thermal stability. The 488-nm wavelength necessitated an argon-ion laser, if only portable air-cooled lasers were considered.

Intensity stabilization and Gaussian-mode beam quality were necessary to allow the greatest system flexibility and measurement repeatability.

b. Fiber Optics and Optical Probe

Although single fibers are small and inexpensive, effective coupling of the laser energy into the fiber is difficult, and proper alignment is burdensome to maintain. For the present application, a commercially available bifurcated fiber-optic bundle offered the best compromise between size, cost, and ease of use.

The final design of the optical probe included an automatic spring-loaded mechanical shutter. This feature is both for laser safety and to protect the detector from overload if pointed directly at the sun or a very bright light source. The basic parameters of the final design are standoff distance: 25.4 mm, aperture: 7-mm diameter, and off-set angle (inclination): 10°. The diameter of the base was extended to 1.5 inch (38.1 cm) to add lateral stability. The probe was constructed from aluminum and anodized black.

c. Optical Filters

(1) Laser-Discharge Filter (Filter F1 of Fig. 2)

A laser-discharge filter is not necessarily needed if the fluorescence intensity is large; however, because some of the materials to be tested may have weak fluorescence, a laser-discharge filter was necessary because the discharge light may contain the same wavelengths as the fluorescent light.

(2) Blocking Filter (Filter F2 of Fig. 2)

The blocking filter separates reflected laser light from fluorescent light. In past work (2), it has been demonstrated that the differentiation capability can be enhanced somewhat by optimization of this filter. A Schott-glass OG530 filter was included in the primary design; however, it was mounted in such a way that it can be easily changed.

d. Detectors

Both a photomultiplier tube (PMT) and solid-state diode detector have been used in our previous work.(2) Because of the increased sensitivity available with a PMT system, it was felt to be the best choice for this application even though the system required a high voltage power supply. (There are three to four orders of magnitude difference in sensitivity at 600 nm.) However, the next-generation unit may well benefit from a solid-state detector.

e. Modulation/Demodulation Equipment

A modulation/demodulation technique was necessary because of potential interference to the signal by sunlight or room light scattered through the material and onto the detector. The most versatile technique for modulation is utilizing a mechanical light chopper with a commercially available lock-in amplifier system for demodulation. (The lock-in measures the signal developed across a load resistor.) Lock-in amplifiers are also currently available at plug-in card level; however, these do not permit the versatility required for the present project.

f. Packaging

Computer-aided design (VersaCAD) methods were used for the assembly and detail drawings of the component parts of the unit. Specialized mounting brackets, filter holders, optical-probe design, and other details are stored for future retrieval. In this way modifications can easily be documented. These drawings are available if additional units are desired. (Note: in the actual unit, the position of the modulator (chopper) and filter F1 of Fig. 2. are reversed and a small beam expanding lens follows the modulator.)

g. Safety Considerations

Safety issues that were considered include those associated with the photomultiplier-tube high voltage power supply, light chopper, and the argon-ion laser. A pair of laser safety goggles are included as a deliverable item. The photomultiplier-tube high voltage power supply that was specified has programmable automatic-trip circuitry that adds an additional safety factor, as well as built-in overload protection for the photomultiplier tube. The rotating chopper also presents a slight safety hazard, if the unit is operated with the top or sides removed. (Note: this chopper is enclosed in a housing.) Appropriate safety warnings and manuals are included with the operating instructions.

h. Modifications Made After "Breadboard" Measurements

During initial "breadboard" measurements, a slight problem of fluorescence from the fiber-optics bundle was discovered and subsequently investigated. (This fluorescence leads to an undesired zero-offset that will not, in theory, affect the technique, but will decrease the signal-to-noise ratio.) It was found that the source of this fluorescence was from both (1) the glass fibers themselves and (2) from the polymer compound used to "pot" the ends of the fibers together to form the bundle termination. Experiments with two other similar fiber-optics bundles, i.e., (1) a quartz bundle from a spectrometer (EG&G/PAR P/N K-0218) and a medical (endoscopic) bundle (Karl Storz P/N 26033A), showed a similar 488-nm laser-induced fluorescence, however, at lower intensity levels (significantly lower for the quartz bundle). A quartz bundle of similar dimension to the one specified for the present project is considerably more costly, e.g., $875 as compared to $167. This cost differential was the primary reason a glass bundle was originally chosen instead of one constructed from quartz. Future designs may benefit from a single large-diameter multimode quartz fiber (instead of a bundle), so that the potting compound issue could be avoided. However, a single fiber would still have to be mechanically protected, i.e., "armored."

A beam-expanding lens was placed between the laser and the input end of the fiber-optics bundle, so that the laser beam was expanded to fill the bundle as evenly as possible. In order to minimize the effect of the unwanted fluorescence, two other steps were taken: (1) the lens on the output end of the fiber-optics bundle was removed to eliminate back reflections of the unwanted fluorescence from the lens back into the bundle and (2) the angle of the fiber-optics bundle with respect to the sample was offset to reduce unwanted fluorescent light from bundle that reflects from the sample back into the detection fibers. The absorption of the laser light by the sample is a very slowly varying function of angle-of-incidence (refer to Fresnel's equations) and can be varied somewhat without significantly influencing total absorption. Additionally, the resulting fluorescent spot can be considered to be essentially a "Lambertian" source (equal radiance at all angles) and, therefore, the overall system response with-respect-to angle is a relatively slowly varying function. Several tests were conducted to confirm these concepts, and it was discovered that a slightly more intense signal can be obtained with the fiber-optics bundle at approximately an angle of 10° with-respect-to normal incidence. (Half-beam width of the emerging laser beam was approximately 7° for these measurements.) For example, for 0°, 10°, 20°, 30°, and 40°, the respective outputs (in volts) were 8.53, 8.82, 8.14, 7.33, and 6.83. If a limiting aperture is used, the effect is slightly increased because the spot size on the sample stays a constant, viz., 5.81, 6.81, 6.54, 4.30, and 3.05, respectively.

Three optical probe designs were fabricated. The first of these had a fixed stand-off distance of approximately 32 mm and 0° inclination (off-set angle). There were several aperture sizes, that could be interchanged. Because the aperture size was not critical, 7-mm diameter aperture was used for most measurements, and this size was adopted for the additional probes described in the following. The second optical probe had a variable stand-off distance so that various experiments could be performed with it. Since performance as function of the stand-off distance and the inclination angle were both relatively slowly varying functions, the final design for the third probe was chosen such that it was in the midrange of both parameter spaces. The final design has a 25.4-mm standoff distance and a 10° inclination angle.

i. Fluorescence Standards

Several options were considered for low-cost and rugged fluorescence standards. It appears that glass filters can be used as reasonable standards since manufacturing of these materials is well controlled, optical characteristics are well quantified, and laser-light absorption is high. Suggested standards are:

High fluorescence:	Corning 3-79 (uranium) glass
Low fluorescence:	Schott OG570 glass

These standards should be over black paper, so that fluorescence from the underlying material will not influence the measurements. Other standards could include dilute solutions, either in liquid or in a polymethylmethacrylate (PMMA) matrix (such as commercially available from Perkin-Elmer P/N C 520-7440, but somewhat expensive), white paper (fluorescence characteristics may not be well controlled), or various polymer samples.

D. Calibration

It should be noted that the unit cannot be calibrated to correlate laser-induced fluorescence with strength until the appropriate validation samples are supplied. That is to say, the present measurements on new samples can be accomplished, but the output will be laser-induced fluorescence intensity, not strength. The correlation cannot be established until samples are measured that have had strength measurements conducted on them. This may be appropriate for follow-on work. (For example, this was done for the materials "UA," UB," "UC," and "G" during the previous project.(2,3) These measurements have been duplicated with the present demonstration-prototype unit for material "UC", an ether-based polyurethane, see the "Operating Instructions" in the appendix for a discussion of this procedure.)

E. Typical Data from Demonstration-Prototype Unit

1. Coated Fabric Samples

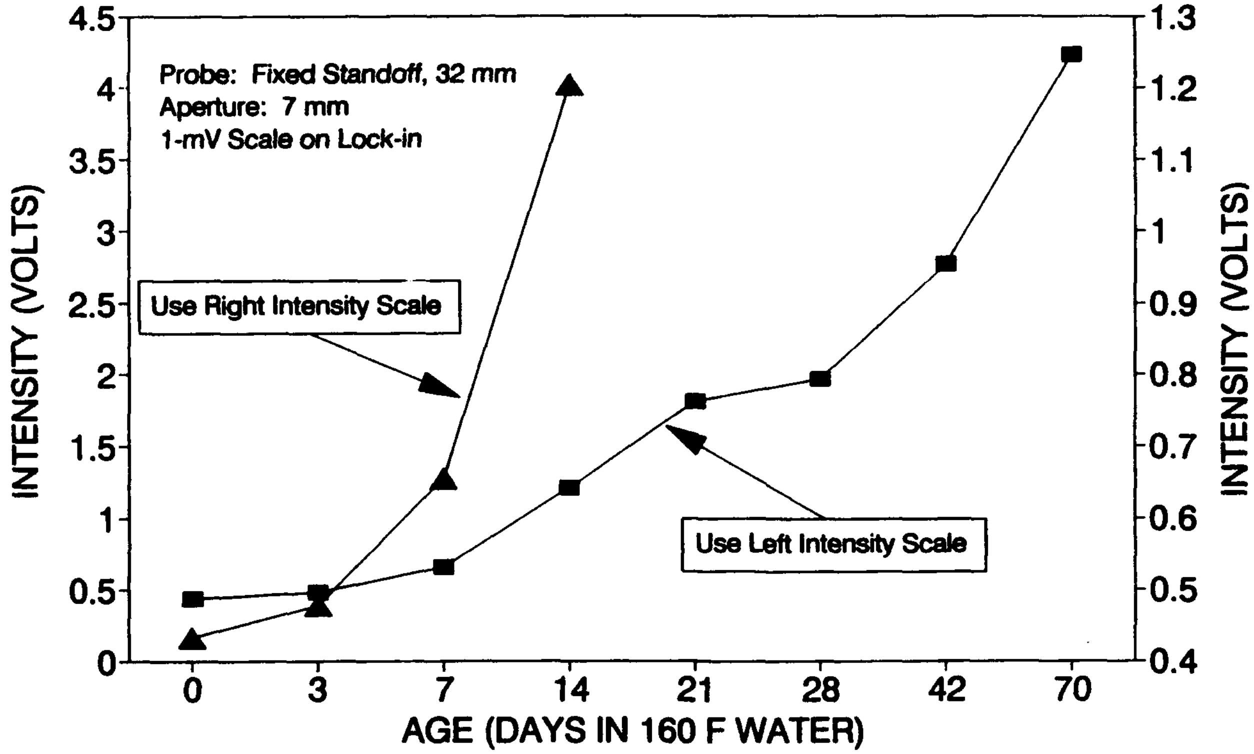
Samples of coated fabric were received (28 June 1991) from Belvoir RDE Center, along with some degraded coatings. Although these coated fabric samples were not aged, they have been used to determine the baseline fluorescence of these materials. Using the experimental parameters equivalent to those in the table included in the "Operating Instructions" of Appendix C of this report, but with a laser power of 5.1 mW, 7-mm diameter aperture, and a 32-mm standoff distance, the baseline fluorescence of the coated fabrics CF1, CF3, CF4, CF5, and unlabeled black sample were measured on the 1.0-mV lock-in sensitivity range. Additionally, the degraded samples of coating material C-10 were checked, and all yielded laser-induced fluorescence intensity signals on the 1.0-mV scale, except for the sample that had been aged 14 days in hot [160°F (71°C)] diesel fuel; that sample yielded a reading off scale, therefore the 10-mV range was used. These samples had been degraded with various combinations of hot water, JP-8, or diesel fuel. A 3-mm thick piece of Schott OG570 glass was used as a reference standard.

2. Material "UC" Samples in Water

Measurements using the demonstration-prototype unit with the final optical-probe design were accomplished on an ether-based polyurethane (sample from a previous project) and the results are shown in Fig. 3. (This material has previously been designated as "UC.") In comparison of different data, it must be remembered that the signal intensity will vary with optical-probe parameters (stand-off distance, aperture diameter, and inclination angle), laser intensity, lock-in amplifier sensitivity setting, high voltage power supply setting. A typical value for the standard deviation as a percentage of the mean for these data is in the range of 3 to 5 percent for repeated measurements on the same piece of material.

3. B.F. Goodrich, Estane F Samples in Diesel

The samples discussed in Section III.B.2.c. (B. F. Goodrich, Estane F) that were used to measure spectra (see Fig. 1) were used as samples for the demonstration-prototype unit. The laser-induced fluorescence intensity was 16.2 times more intense for the degraded sample. This larger intensity was expected based on the spectral differences; however, the exact ratio was not previously predicted since it depends on the "integrated fluorescence" as discussed in Section III.A.1.

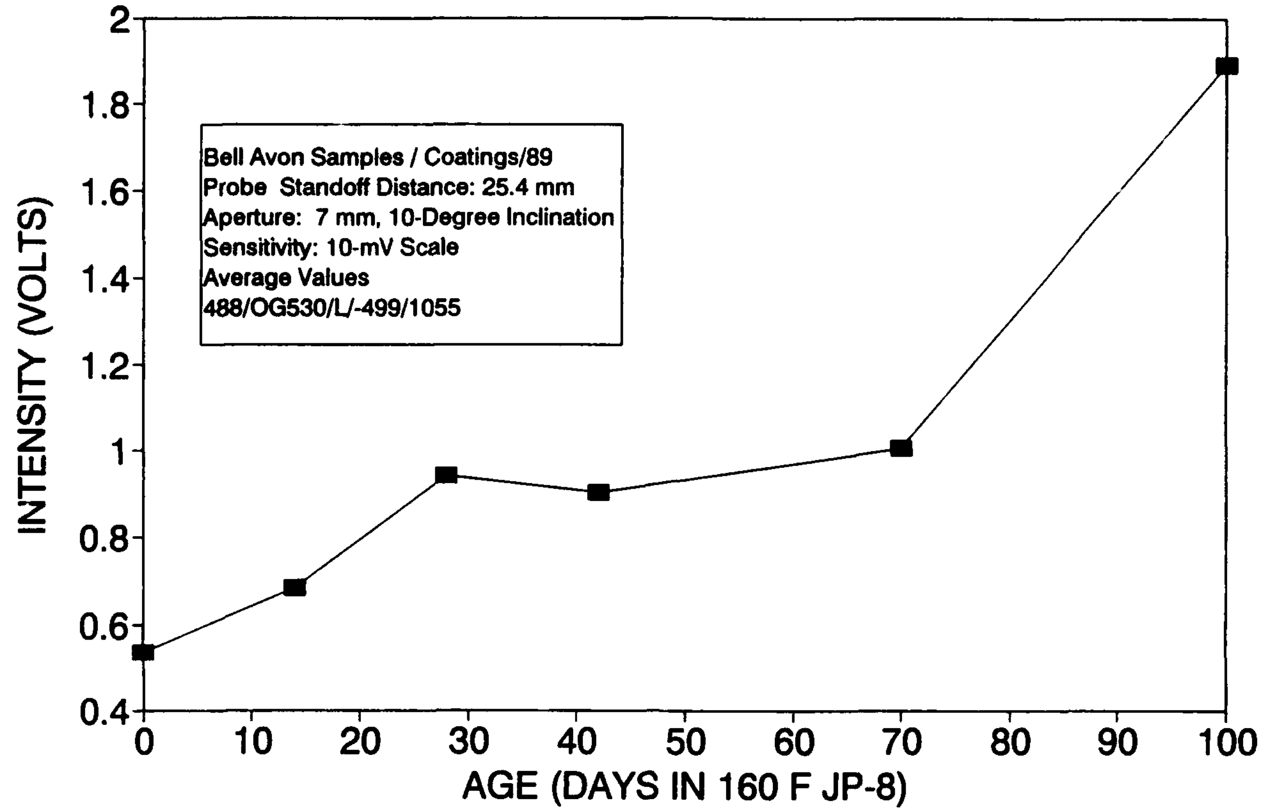


(This material has previously been designated as "UC." See text for pertinent experimental parameters.)

Figure 3. Laser-induced fluorescence intensity (obtained with the demonstration-prototype unit) as a function of age of an ether-based polyurethane material

4. Bell Avon Samples in Jet Fuel

Bell Avon samples degraded in JP-8 jet fuel at 160°F (71°C) were measured with the demonstration-prototype unit. See data in Fig. 4. These samples have been stored since late 1989 and therefore many be somewhat suspect. It appeared that a rather broad sample-to-sample variation was measured. If the highest and lowest readings are disregarded, the standard deviation for the readings from the degraded samples ranged from 11 to 58 percent of the mean. [For this graph, the data from the 7-day sample was not plotted, because it may have been inadvertently mishandled. (The average intensity from those samples was 1.4 V, clearly out of reasonable range.)]



(Pertinent experimental parameters are displayed in the inset.)

Figure 4. Laser-induced fluorescence intensity (obtained with the demonstration-prototype unit) as a function of age in jet fuel for a sample from Bell Avon

5. Coating Material in Water

Coating material C6 was also examined. The samples with 42 days in 160°F (71°C) yielded an average intensity 30 percent higher than from similar samples aged for 14 days. (Standard deviations as a percentage of the means were approximately 12 percent.)

F. Lessons Learned

1. The low-cost noncoherent fiber bundle is bonded together with epoxy, which has its own characteristic laser-induced fluorescence. This fluorescence introduces a small offset in the signal, which, although not a major problem, is somewhat undesirable.

2. Single fibers such as used with argon-ion lasers for surgery may be useful. These fibers would not be as rugged, but may be easier to obtain in long lengths.

3. The limiting factors on almost any fluorometric device is the background fluorescence (i.e., the fluorescence of the undegraded material). If the background fluorescence is too large (i.e., if the material has been colored with a fluorescent dye), then it may mask the effect due to degradation. If there is very little or no background fluorescence, then effects due to degradation may be so small that they are difficult to detect.

4. One problem with straight-on illumination (i.e., 0° inclination angle) is that the blocking filter may fluoresce if too much light is backscattered. (Note: this is partially countered by the inclination angle of the optical probe; but is only a minor issue on these polymer samples due to their relatively low specular reflectance.)

5. If material is degraded with fuel, some of the fluorescence may be due to the entrapped fuel itself. (The amount of fluorescence depends on the type of fuel.)

IV. CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions

A demonstration-prototype unit has been designed, fabricated, and tested. It has been successfully demonstrated on a limited sample set. The unit was designed so that it could be used on many different materials, thus has high sensitivity, wide dynamic range, and is very versatile. As with many first version prototypes, these features have been somewhat at the expense of increased size and weight. Further testing on a wide range of elastomers and degradation parameters should be done to establish applicability to each material.

B. Recommendations

Suggested follow-on tasks are as follows:

- Modifications or additions. During system checkout by Belvoir RDE Center, slight modifications may be desired, such as additional optical probes with different aperture diameters (for measuring very small samples).

- Construction of additional units. Additional units, if desired, could be constructed at a lower cost because the prototype design and engineering work has been done in the present project. (Slight modifications could be incorporated, such as utilizing different lasers.)

- Miniaturization. Engineering design and developmental work to make the next-generation unit smaller, lighter, and less expensive. (This could be accomplished by using a lower power laser or utilizing electronics with limited dynamic range.)

V. REFERENCES

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APPENDIX A

Major Parts List

Major Parts List

(Note: Prices as of approximately June 1990)

Laser: Cyonics Division of Uniphase, Model 2014-10SL, argon-ion, single-line 488 nm (10-mW nominal power), linearly polarized, cylindrical package, remote control with interconnect cable, cooling fan and air duct ($6015).

> *Alternates*: Omnichrome Model 532-15 or Spectra Physics Model 161C, but these units are not in cylindrical packages.

Laser Safety Goggles: Fred Reed Optical Laser-Gard Brand Model VL-A ($150) for argon-ion lasers.

> *Alternates*: Most optics supply houses.

Laser Line Filter: Edmund Scientific part number B30,708, 488 nm, 45 percent Transmission, 19 mm x 19 mm ($33).

> *Alternates*: Oriel Corp. at much higher cost.

Lock-In Detector: Ithaco Model 3921RM, 10 µV-1V, single phase, fundamental-only response, autophase servo system ($2055).

> *Alternates*: EG&G/PAR Model 5101; for future applications, Evans Electronics makes the necessary components on cards.

Load: Products for Research part number PR-202 ($67).

Photomultiplier Tube: Oriel Corp. part number 77341, 28-mm diameter, side-on, approximate cathode sensitivity at 600 nm: 20 mA/W, approximate cathode sensitivity at 700 nm: 10 mA/W (at -1000 V) ($270). (Note: delivered photomultiplier tube had a measured 3-nA dark current at -1000V bias and a measured response proportional to the voltage to the 7.4 power.) **Housing**: Oriel Corp. part number 70680 ($378) with 50-mm square filter holder Oriel Corp. part number 71260 ($186) and fiber-bundle flange Oriel Corp. part number 77817 ($53).

> *Alternates*: Hamamatsu part number R456 appears to be a direct replacement. Many other photomultiplier tubes can be substituted which will yield greater or lesser sensitivities than this tube. Some other suppliers considered: EMI-Gencom Inc., Burle Industries (previously RCA).

Spectral Filters: (50-mm square): Schott OG530 ($24), Schott OG570 ($24), Corning 3-79 ($25).

High Voltage Power Supply: (For photomultiplier tube): Stanford Research Systems (SRS) SRS PS310, 1.25 kV at 20 mA, with programmable current-limit and trip-range capabilities, voltage regulation better than 0.001 percent for ten percent change in line voltage, rack mount option, with SHV to MHV cable ($1285).

Alternates: Oriel Corp. Model 70705, EMI-Gencom Inc. Model PM28R.

Light Chopper: Oriel 75155, enclosed light chopper with reference output, 30 aperture blade ($1082).

Alternates: EG&G/PAR 197 at much greater cost. (Smaller custom-built choppers are a possibility from EG&G/PAR, but they do not usually fabricate less than ten at a time on special order.) Note: there are several other choices from SRS, PTI, or Scitec for open choppers, but cost difference is not significant.

Bifurcated Fiber Optic Bundle: Oriel 77533, numerical aperture 0.56, total length 914 mm ($167). **Accessories:** Oriel 77645, collimating beam probe with compound glass lens ($97), Oriel 77808, collimating beam probe connector ($12).

Alternates: Ealing Electro-Optics.

Equipment Rack: "Equipto" Rack, consisting of frame approximately 21-inches height of rack space, side panel, accessible top panel, bottom panel, recessed storage drawer and rear panel ($857).

Rolling Cart: Welded laboratory cart with wheels, Dennis Neukirch Co., P/N SH835 ($305).

Digital Voltmeter: Fluke Model 73 multimeter ($85).

Misc. Hardware: Switches, fasteners, wire, fan hardware, materials (aluminum and stainless steel approximately $100).

APPENDIX B

List of Sizes and Weights

List of Sizes and Weights

	Component	Weight, lb (kg)	Size, in. (cm)/Comments
1a.	Laser Head	7.5 (3.4)	15 × 3.5 (38.1 × 8.9) diameter
1b.	Air Duct and Fan	2 (0.91)	3.5 (8.9) diameter duct up to 36 (91.4) length
1c.	Controller	14 (6.4)	8.5 (21.6 width × 6 (15.2) height × 14 (35.6) depth/Not supplied with rack mount
2.	Lock-In Detector	15 (6.8)	17 (43.2) width × 4 (10.2) height × 14 (35.6) depth/Has standard-rack mount option kit
3.	HV Power Supply	8 (3.6)	8 (20.3) width × 4 (10.2) height × 16 (40.6) depth
4a.	Chopper Head	1 (0.5)	6 (15.2) width × 6 (15.2) height × 3 (7.6) depth/Rod mount
4b.	Controller	6 (2.7)	8 (20.3) width × 4 (10.2) height × 12 (30.5) depth/Not rack mounted
5.	PMT/Housing	1 (0.5)	7 (17.8) length, 2.5 (4.7) diameter, approximately 5 (12.7) depth/Rod mounted
6.	Miscellaneous	1 (0.5)	Optical filters, cables, etc.
7.	Equipment Rack	148 (67.3)	24 (61.0) width × 26.5 (67.3) height × 24 (61.0) depth/Includes drawer
8.	Rolling Cart	126 (57.3)	24 (61.0) width × 28.5 (72.4) height × 36 (91.4) length

APPENDIX C

Operating Instructions

(Including List of Pertinent Documents and Manuals)

OPERATING INSTRUCTIONS FOR THE LASER-INDUCED FLUORESCENCE DEMONSTRATION-PROTOTYPE UNIT (LASER FLUOROMETER)

by

Ralph H. Hill, Jr.
Southwest Research Institute
San Antonio, Texas

Presented in

Laser-Induced Fluorescence Analytical
Technologies—Phase II
Interim Report BFLRF No. 276
SwRI Project 02-1955-660

* * * CAUTION * * *

The laser contained in this unit is a Class IIIb argon-ion laser. The laser beam is completely enclosed during normal operation, and the optical probe is designed such that the laser beam should not be exposed to the user. If during servicing, or if the optical probe is removed from the fiber-optic bundle, or if the fiber-optic bundle is removed from the unit, Class IIIb laser radiation may be exposed and should be dealt with accordingly. This laser radiation can potentially cause eye damage if viewed directly. Additionally, specular reflections (mirror like) may be hazardous. A laser safety manual, "Laser Safety Guide," published by the Laser Institute of America, has been supplied as a convenience to the user. The laser manual also has an excellent section on laser safety.

Hazardous voltages also exist within the unit, therefore, care should be exercised during any procedure conducted with top or side panels removed. High voltages are not exposed; however, they do exist because of the high voltage power supply and photomultiplier tube.

Although enclosed within the unit and within a protective housing, the rotating chopper wheel is a potential hazard to fingers during adjustments with the top panel removed.

The laser plasma tube contains beryllia ceramic, which is hazardous when powdered and inhaled. If the laser tube is broken, wet the pieces and seal them in a plastic bag. (As per manufacturer's manual, defective laser tubes can be returned to them for proper disposal.)

These safety issues are also discussed in the individual manuals for each of the component units.

Disclaimer

The findings in this document are not to be construed as an official Department of the Army position unless designated by other authorized documents.

Trade Names

Use of trade names or manufacturers in this document does not constitute an official endorsement or approval of the use of such hardware or software.

Patent Rights

The concept for operation of the demonstration-prototype unit described herein is patented under U.S. Patent Number 4,802,762, assigned to Southwest Research Institute (SwRI).

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LIST OF ILLUSTRATIONS

LIST OF TABLES

NOTATION USED IN OPERATING MANUAL

All capital letters will be used when discussing an actual switch, button, or unit as labelled on the front panel, e.g., the ON switch or the SELECT button. A diagram of the unit is also supplied with the individual locations identified, see **Fig. A-1.** Letters/numbers in square brackets refer to those of **Fig. A-1,** for example, [1] indicates the location of the laser REMOTE INTERFACE.

OPERATING PROCEDURE

Step 1: Power. Plug the unit into a 115-Volt AC outlet with an earth ground conductor. The power cord is located on the back of the unit. The main power [MASTER POWER] ON/OFF switch is located on the lower left side of the front top panel. Turn to ON. This should immediately bring the power up on the laser REMOTE INTERFACE [1] and the laser fan motor should come on. (**Note:** letters/numbers in square brackets refer to those of **Fig. A-1**, for example, [1] indicates the location of the laser REMOTE INTERFACE.) Power to the individual units can then turned on. The LOCK-IN AMPLIFIER [2] is located on the middle panel (the ON/OFF switch is at the lower right; pull for ON). The HIGH VOLTAGE POWER SUPPLY [4] is in the lower panel (the ON/OFF button is in the lower right; push for ON). The CHOPPER CONTROLLER [3] is also in the lower panel (the ON/OFF switch is on the left side).

Step 2: Chopper Controller. The chopper frequency should be set at approximately 1,000 Hz. This can be obtained by having the frequency control in the HIGH position and turning the FREQUENCY adjust knob until a frequency approximately 1,000 Hz is obtained. Typically, values around 1,073 have been used for the experimental data. The setting is not critical since the lock-in amplifier will lock onto any frequency within the general range.

Step 3: Fiber-Optic Bundle. The fiber-optic bundle should be attached and the optical probe should be on the single end of the fiber-optic bundle. If this is not the case, see details below on how to replace or remove the fiber-optic bundle or optical probe. The standard optical probe is the black anodized conical-shaped one that has a 7-mm aperture and a 25.4-mm standoff distance with approximately a 10° inclination. One other probe is supplied, a black anodized one with 32-mm standoff distance. (This was used during the optical probe development.)

Step 4: Laser Remote Interface. To turn the laser on, push (touch) the ON button in the TUBE CURRENT section. After an approximate 40-second delay, the laser discharge tube power will come on. At this point, the laser is still in the IDLE mode. The digital liquid-crystal display has two functions, either as a CURRENT display, which will be in amps (A) or as a LIGHT display which will be in milliwatts (mW), selectable by touching the appropriate button in the DISPLAY section. The LIGHT display will show approximately 4.6 mW, or in the CURRENT display, approximately 4.01 A while the laser is in the IDLE mode. In the IDLE mode, the current is at the lowest available such that the laser will still lase; however, for adequate regulation, the laser has to be in the RUN mode. The button labeled RUN on the REMOTE INTERFACE box should be pushed. The laser power or current can be adjusted by using the adjust arrows on the REMOTE INTERFACE. The up and down arrows can be pushed until this situation is accomplished. In the LIGHT control mode at 5.1 mW, the current should be approximately 4.2 A; as the laser ages these values will change somewhat. (More current will be necessary for the same laser output power.) The INTERFACE LOCAL switch should be in the ON position, i.e., LOCAL operation. This accomplishes the laser portion of the turn-on procedure. No laser light should be visible due to the design of the optical probe. However, one can check to make sure the laser is on by aiming the optical probe at a convenient surface (for instance, the front of the laser cabinet), pushing the button on the optical probe and bluish light should be observable. **CAUTION: Do not look directly into beam.** Do not operate the laser at full power, this will prematurely degrade the laser tube; additionally, nonlinear effects may make the laser-induced fluorescence intensity readings unreliable. Recommended power is in the range of 5.1 mW.

Step 5: Lock-In Amplifier. The next step should be to adjust the LOCK-IN AMPLIFIER controls. Typical values for lock-in amplifier are shown in **TABLE A1.** This table can be used as a checklist. The SENSITIVITY controls [B] are located on the left side of the LOCK-IN AMPLIFIER panel. The 1-millivolt (mV) or 10-mV range is a reasonable setting to start with. Notice that there is also a MULTIPLIER setting dial (ten-turn potentiometer), typically set to 1.0. (The overall full-scale sensitivity corresponds to the range setting multiplied by the multiplier setting.) The input to the lock-in amplifier [A] comes from a BNC connector in the lower left portion of the lock-in amplifier; the input switch should be adjusted to the FLOAT position. The TIME CONSTANT on the OUTPUT section [C] should be set to a typical value of 1 second. Output POST FILTER button should be ON, which is the "in" position (1 second). On the REFERENCE channel [D] adjustment, the PHASE is not critical, a good starting point is 90°; however, is not very critical in the AUTOPHASE mode. If autophase locking does not occur, push the 180° phase button "in." Lock-in amplification should be in the fundamental mode F, which is with the white button in the "out" position. The fundamental mode operation means the lock-in detector will be operating the fundamental mode as opposed to the second harmonic (2F) mode. NOTE: When in the autophase mode, the red light emitting diode (LED) located directly above the AUTO button should be lit, which indicates autophase lock-on has occurred. Data should not be taken unless this is lit. (At this point in the procedure, this light will probably be off because the high voltage power supply has not yet been activated; therefore, no signal is present.) The UNLOCK light should not come on; however, if it does this indicates no reference signal may be present from the CHOPPER CONTROLLER. (Check to be sure CHOPPER CONTROLLER is on.) The LAMP switch [E] should be in the ON position, so that the indicator lamps can be seen. If this is turned off, none of the lamps or LEDs will be visible. Full-scale deflection of the output display meter corresponds to the sensitivity setting multiplied by the multiplier setting. Additionally, a full-scale deflection (100 percent) of this meter corresponds to 10-volt DC output on the output BNC connector.

TABLE A1. Typical Experimental Parameters

Optical Filters	Blocking Filters:	Schott OG530 3-mm thick, 2 each
	Laser Filter:	Interference at 488 nm
Fiber-Optic Bundle	Bifurcated at one end (Expanding lens in-line)	
Fiber-Optic Probe	Standoff distance 25.4 mm, 7-mm aperture, 10° inclination, conical	
Load Resistor	100 kΩ	
REMOTE INTERFACE (Laser Controller)	INTERLOCK LOCAL:	ON
	TUBE CURRENT:	ON, RUN
	MODE:	LIGHT
	Display (Selectable):	LIGHT (5.0 mW) or CURRENT (4.02 A)
CHOPPER CONTROLLER	1067 Hz (HIGH Range)	
HIGH VOLTAGE PS	Polarity:	"-" (Set on Back Panel. DO NOT CHANGE.)
	HIGH VOLTAGE:	ON
	RESET:	MAN
	VOLTAGE SET:	500 V
	VOLTAGE LIMIT:	1000 V
	CURRENT LIMIT:	02.00 mA
	CURRENT TRIP:	02.00 mA
	Display (Typical):	-499 V, 0.15 mA
LOCK-IN AMPLIFIER	SENSITIVITY:	10 mV, MULTIPLIER: 1.0
	INPUT:	FLOAT
	OUTPUT TIME CONSTANT:	1 sec
	OUTPUT POST FILTER:	IN (1 sec)
	OUTPUT ZERO OFFSET:	-0.03 turn, -0.017 V on DVM
	REFERENCE CHANNEL: AUTO (Autophase) In, LED lit indicates lock-on PHASE: Does not matter in autophase mode (see text) F (Fundamental) Out	
	LAMP:	ON
	OUTPUT Connector (BNC):	Full-scale deflection of meter corresponds to 10 VDC output

If digital output is desired, the digital voltmeter (DVM) which is supplied with the unit should be connected. Plug the BNC connector into the OUTPUT BNC of the lock-in detector and the other end (dual banana jack) plugged directly into the small DVM; turn the voltmeter ON. The voltmeter should be set to the DC voltage scale; 10 volts from the lock-in amplifier output corresponds to full-scale deflection.

Step 6: High Voltage Power Supply (HVPS). **NOTE: This unit is designed for negative high voltage operation. DO NOT CHANGE POLARITY. (This change can be done only from back panel of HVPS.)**

To activate high voltage output, push the HIGH VOLTAGE ON switch which is the black switch on the lower left of the high voltage panel. Typical reading at this point should be -499 volts (V) showing on the left red LED display. On the current scale of the high voltage power supply (right red LED display), a typical reading should be 0.15 mA. These parameters can be easily changed. Details for changing them are described in the power supply manual. Briefly, the power supply stores the settings that have been previously programmed and will automatically come up to the preprogrammed settings. Typical readings for the limit voltage are -1,000 V, limit current 2 mA, with a trip of 2 mA. In other words, when a current of more than 2 mA is being drawn by this power supply, the trip will switch to protect the power supply. These various trip and limit values can be reviewed by pushing the SELECT button on the front of the high voltage power supply module. It will cycle between SET VOLTAGE, VOLTAGE LIMIT, LIMIT mA, and TRIP mA.

At this point in the procedure, everything has been powered on and the unit should be ready for operation. With no sample being measured, the unit may still show a reading. (This is essentially the offset due to the fluorescence of the inside of the optical probe hood, fluorescence from the fibers themselves, fluorescence from the epoxy securing the end of the fiber-optic bundle, or possibly slight fluorescence from the Schott OG530 blocking filters.)

Step 7: Zero Offset. This can be done using a virgin sample or no sample. ZERO OFFSET is accomplished by adjusting the appropriate ten-turn potentiometer on the OUTPUT section [C] of the LOCK-IN AMPLIFIER. Note that it is important to record the zero setting procedure. In other words, if a virgin sample is used to set the zero, the fluorescence intensity from a test specimen will then be that **above** the virgin sample, which is different from the total fluorescence.

Step 8: Data Taking. A warmup time of 30 minutes is recommended if very accurate data are desired; however, data can be taken shortly after turn on. Hold the optical probe in one hand and firmly press flat against the sample. A small button on the end of the optical probe will become depressed and open up a small trap door in the probe, therefore allowing the laser beam to hit the sample and the resulting fluorescent light to be collected. The red LED above AUTO on the LOCK-IN AMPLIFIER should be lit. If not, this indicates that the lock-in detector is not locking onto the signal; a larger signal may be necessary. (This can be accomplished by increasing the LOCK-IN AMPLIFIER SENSITIVITY or increasing the laser intensity.) All settings should be recorded for future reference. Of particular importance are the laser power and current, photomultiplier (HVPS) voltage, LOCK-IN AMPLIFIER SENSITIVITY and ZERO ADJUST setting technique. Additionally, it should be noted which optical probe is in being used. A convenient method is to use **TABLE A1** as a checklist of the relevant parameters. Parameters that are most probable to be changed can be listed in an abbreviated format, such as shown in **TABLE A2.**

Note that the operation is similar to that of a standard commercial fluorometer with the SENSITIVITY setting corresponding to the "gain" and the ZERO ADJUST corresponding to that of the "blank" on a commercial unit.

If there is any writing on the sample, avoid making measurements directly over it, since the ink may be somewhat fluorescent or absorbing.

TABLE A2. Abbreviated List of Typical Experimental Parameters

Laser REMOTE INTERFACE

Power _______ mW
Current _______ A

HVPS _______ V

LOCK-IN AMPLIFIER

Sensitivity _______ × Multiplier _______

Zero _______ Method _______

Probe _______

CHOPPER CONTROLLER _______ Hz

Sample Designation _______

Calibration:

Comments:

Step 9: Turn-Off Procedures. Switch the individual power supplies off one at a time. This is desirable so that when turned back on, the initial surge will not overload the circuit breaker. Although the laser manufacturer claims that there is no need to run the fan on the laser after the laser power is turned off, a conservative user can turn the laser off and let the fan run a little bit longer by the following procedure: Push the IDLE button on the remote interface which brings the laser power down to minimum output. Then push the tube current button to OFF. This will turn the laser supply off; however, the fan remains operational. After a short period of time, the whole unit can be turned OFF using the main power switch.

DISCUSSION

Safety Features

The optical power levels emitted from the fiber-optic bundle are well below the values indicated on the REMOTE INTERFACE laser controller. This is because an interference filter is located on the output of the laser, which attenuates the beam approximately a factor of two. Additionally, the light chopper attenuates the laser beam another factor of two (on the average), since it is continuously chopping the laser beam on and off. Therefore, when the output meter reads 5 mW, only approximately 1 mW is actually emerging from the end of the fiber-optic bundle. This power level can be conveniently used to measure the fluorescence of commonly available objects. If activated on the skin on the palm of one's hand (1.0-mV SENSITIVITY on the LOCK-IN AMPLIFIER), an overload will probably occur to the lock-in amplifier because skin and biological tissues are relatively fluorescent and the overload (OVL) light on the lock-in detector will activate. If this occurs, the sensitivity can be changed by simply adjusting the SENSITIVITY level to 10 mV. On the 10-mV scale, however, the DC offset will be different than on the 1-mV scale. Therefore, care should be taken in comparing one scale reading to another. The optical probe assembly prevents room light from entering the photomultiplier tube and therefore prevents it from overload. During the time that the button is pushed, however, room light can enter the fiberoptic/photomultiplier system and damage may occur to the photomultiplier tube if aimed at intense sources of light such as directly at the sun while high voltage is on the photomultiplier tube. Therefore, this optical probe assembly acts both as a safety device for the user and a protection device for the photomultiplier tube. The design is such that room light should not be entering the sensor element while in operation, and therefore, it should not make any difference the room lights are on or not. However, subdued lighting is preferable because then there is no chance that large amounts of light will enter the system due to uneven material surfaces. Even if this does occur, however, it should not influence the measurements greatly because the lock-in amplifier only detects appropriately modulated light (at the chopper frequency) and the room light is modulated at 60 Hz and multiples thereof. A typical frequency like 1,072 is preferable because it is not an integral multiple of 60. The lock-in amplifier can slightly detect multiples of the primary frequency; however, these are very highly attenuated. (See lock-in amplifier manual for a discussion of harmonic detection.)

Reference Standards

Several materials are supplied as reference standards, including a 3-mm piece of Schott OG 570 glass, a piece of Corning 3-79 uranium glass, and several small pieces of polyurethane material. Several measurements taken during preliminary exercises used the OG 570 filter glass as a reference standard. Black paper was used as a backing for these measurements to prevent fluorescence of the underlying material from influencing the measurement. The calibration procedure is as follows: (1) put a piece of black paper on a flat surface, (2) with the reference standard on top of that, use the optical probe to make the measurement of the laser-induced fluorescence. A typical value (from 3-mm thick Schott OG570 glass on black paper) on the 1-mV scale is 32-percent full-scale deflection (or approximately 3.2 volt DC on the digital voltmeter). CAUTION: **the fiber optical bundle should be treated with some care; although the bundle has a metal armor shield, which makes it appear very rugged, inside is a fiber-optic bundle.** If these fibers are broken or cracked, they will remain broken or cracked and cause light scattering centers, which will decrease the overall efficiency of the bundle. Even if this happens, the calibration procedure should offset this effect in the measurement mode. However, as more and more fibers become broken, less and less laser and fluorescent light will be able to be transmitted through the bundle, thus degrading the overall performance of the unit.

Beam Quality Adjustment

The laser beam quality can be checked by depressing the button on the optical probe while pointing at a flat surface approximately 0.3 m away (such as the front of the control panel). This beam should appear relatively round and uniform. If it is not, the laser beam may be out of alignment as it enters the fiber. This misalignment can be adjusted by removing the top lid of the unit. As viewed from above, the laser is mounted in two mounting brackets with adjusting thumb screws. Slight adjustments of the laser beam direction can be made by slightly adjusting these screws. A small lens is in the beam path such that it slightly expands the laser beam impinging on the fiber-optic bundle face. During this alignment procedure, it should be noted that if the light chopper is off, one of its vanes may block the laser beam. There are two choices to remedy this situation: (1) turn the light chopper blade slightly until the laser beam goes through [make sure power to the chopper is OFF and the chopper wheel is not rotating] or (2) activate the light chopper to the ON position so that it is constantly spinning. It is not extremely critical how the beam quality appears as it leaves the fiber-optic bundle, because the laser light will induce fluorescence, which will subsequently be imaged back into the photomultiplier tube. However, if this beam quality is extremely uneven, then sampling over the surface will be limited. In other words, inspection will only occur where the laser beam hits the surface. Therefore, a round, uniform beam is desirable.

Fiber-Optic Bundle and Optical Probe Removal/Replacement

If the fiber-optic bundle needs to be removed from the unit, simply remove by loosening the thumb screws on the laser side [LASER OUTPUT] of the probe and small Allen screws on the photomultiplier tube end [PMT INPUT] of the bundle. When these are replaced, small misalignments will probably occur, and therefore the zero offset may be different than from previous measurements. This is the reason that making a calibration sample run against a standard is desirable.

Replacement is done, likewise, by tightening the small Allen screws and thumb screws. Theoretically, it should not matter where the two ends are placed. However, for most repeatable results, these should be maintained consistently in the same ports.

The optical probe can also be removed from the end of the fiber-optic bundle by loosening the two small securing Allen screws.

Optical Filters

The optical filters can be changed if desired by opening the small rectangular container [FILTER BOX] at the end of the fiber-optic bundle. The filters can be removed by pushing up with the plunger located on the bottom of the rectangular box. The standard operating configuration is two 3-mm thick Schott-glass OG 530 filters in this unit. Additionally, an interference filter is attached to the output end of the argon-ion laser. This filter is to remove unwanted discharge light from the laser output. However, because the interference filter attenuates the laser beam by approximately a factor of two, more power can be gained by removing this filter. The unit has been tested with and without the filter and only small differences in the performance can be seen. Because there is some discharge light in the red wavelength region of the spectrum, a slight advantage can be gained by filtering it out of the signal. (This discharge light introduces noise into the signal, and the detection system misinterprets it as fluorescent light.) However, if the unit is used for other applications such as visualization, more power can be obtained from the output of the fiber-optic bundle by removing this interference filter. It can be simply removed by unscrewing the two red thumb screws on the output end of the argon-ion laser and removing the interference filter assembly. This has been custom-made to attach on the front of the commercially obtained laser.

Laser-Induced Fluorescence Visualization

Laser-induced fluorescence can also be used for visualizing small degraded areas on polymers by observing (through laser safety goggles) the laser-induced fluorescence from an expanded laser beam through laser safety goggles. **The laser safety goggles are absolutely required for this mode of operation.** A set of laser safety goggles are supplied with the unit for this purpose. In this mode of operation, the fiber-optic bundle can be removed and the beam expanded directly from the assembly or the optical probe can be removed from the end of the fiber-optic bundle and the laser beam can then emanate directly from the fiber-optic bundle. In this mode, the laser power can be turned up to provide easier viewing; however, it is not recommended to run the laser at full power. The higher the laser power, the more potential safety hazard exists. Therefore, caution should be used when using the unit in this mode. Laser safety goggles for additional observers can be obtained from many suppliers. If the fiber-optic bundle or the optical probe has been removed from the unit, when it is being replaced, if any alignment problems occur, a small plexiglass alignment fixture has been constructed and delivered with the unit. This plexiglass fixture is simply placed over the collar on the laser beam output, and it makes a convenient target so that the laser beam adjusting thumbscrews can be adjusted until the laser beam hits the center of this target. This procedure is not as alignment critical as in some applications because the fiber-optic bundle is relatively large as compared to the sub-millimeter fibers used in fiber-optic communications. Alignment can also be done with the fiber-optic bundle in place by observing the resulting beam quality as it emerges from the bundle. This is most easily done with the optical probe removed and the beam directed onto a piece of paper.

Load Resistor

A 100-kΩ load resistor for the photomultiplier tube has been supplied with the unit. An additional small blue box with a 10-kΩ load resistor is also supplied. However, due to the wide dynamic range of the lock-in detector and the large range of powers available with the present laser, it is probably not advisable to change this resistor. However, in future experimental situations, this resistor network is available if necessary. By lowering the load resistor by a factor of 10, the output voltage also decreases approximately by a factor of 10. This would be advantageous on materials with very high fluorescence.

Laser Power Setting

The lifetime of an argon-ion laser is directly related to the tube current at which the laser is operated. Much longer tube life can be obtained by operating the laser at relatively low current levels. Additionally, in the present apparatus, a large dynamic range offered by the photomultiplier tube/lock-in amplifier system means that the laser does not need to be operated at high levels. Therefore, it is recommended that all measurements be taken at approximately 5-mW level output from the laser. It is, however, recommended that it be at least 5 mW so that the regulation range can be operational. In other words, if the operation of the laser is at the minimum power level possible, while in the light control mode, the regulation will not properly occur. For this reason, one should operate the laser slightly above the lower limit so that it can regulate both upwards and downwards in its range. Reasonable data can be obtained while the laser is in the CURRENT control mode; however, the LIGHT control mode is preferable for the present application since laser-induced fluorescence intensity is proportional to input light intensity.

Preventive Maintenance

Because this unit is constructed from commercially available subassemblies, it is not anticipated that any preventive maintenance will be required on the individual components. Manuals for each commercially obtained unit are also supplied. If problems should occur with any of these units, and they may be need to be replaced, the design is based on a standard rack mount concept and, therefore, replacement units can easily be obtained. If the optical surfaces become contaminated, they can be simply cleaned with distilled water or spectroscopic grade methanol and a cotton Q-tip swab. Critical laser mirrors are not exposed in this arrangement. However, if large amounts of dust and dirt accumulate inside the unit on the interference filter, it can be cleaned in like manner with distilled water or spectroscopic grade methanol and a cotton Q-tip. Solvents such as trichloroethylene should not be used on the fiber-optic bundle for they may dissolve the epoxy which holds the bundle together. Compressed air canisters, such as those obtained in commercial photographic accessory shops, are very convenient for blasting large dust particles off optical surfaces. This should be done prior to any other type of cleaning since it will remove the larger particles, thus preventing them from grinding and doing any physical damage to the optical surfaces.

Fuses/Breaker

If any of the fuses need replacement, the back panel can be easily removed to gain access to the fuses on each individual unit. If this is necessary, remove the power cord and unscrew the four Phillips-head screws. The storage drawer may also be pulled fully forward to give more room during fuse replacement.

A 20-Amp circuit breaker is also located on the back of the unit. If for some reason, the laser is operated at full power with all of the other units on, this breaker may trip. Since this is not the normal operating mode, this situation will probably not occur. (It is recommended that the laser be operated with as low current settings as possible, as described above.)

Rolling Cart

The unit as delivered is bolted onto a rolling cart. This was done primarily for convenience of the user. It is possible that the whole rack assembly can be removed from the rolling cart if desired; however, care should be taken if this is done so that the laser is not damaged due to extremely rough treatment.

Calibration

Samples of coated fabric were received (28 June 1991) from Belvoir RDE Center, along with some degraded coatings. Although the fabric samples were not aged, they have been used to determine the baseline fluorescence of these materials. A 3-mm thick piece of Schott OG570 glass was used as a reference standard.

It should be noted that the unit cannot be calibrated to correlate laser-induced fluorescence with strength until the appropriate validation samples are supplied. That is to say, the present measurements on the new samples can be accomplished, but the output will be laser-induced fluorescence intensity, not strength. The correlation cannot be established until samples are measured that have had strength measurements conducted on them. This may be appropriate for follow-on work. (For example, this was done for the materials "UA," "UB," "UC," and "G" during the previous project. These measurements have been duplicated with the demonstration-prototype unit for material "UC.") When these correlation measurements have been conducted, a look-up table can be used to correlate laser-induced fluorescence with material strength; an example of this procedure is given below.

Future Developments

Future generations of this device may not need an argon-ion laser or a photomultiplier-tube detector. Solid-state detectors, as well as solid-state lasers are beginning to show up in many applications. (See for instance, "Diode lasers produce blue-green light," *Laser Focus World*, Sept. 91, p. 9.) The main reason for using argon-ion laser and photomultiplier-tube techniques in this unit were due to the uncertainty in the actual types of materials to be tested. Low fluorescence materials and unknown materials that may be tested in the future need a wide dynamic range of both laser excitation and detection. If a similar unit were to be designed for a specific material, then both the excitation laser and the detection circuitry could probably be drastically reduced in size and complexity, if the operating range were to be known in advance.

It is expected that ambient temperature variations will slightly change the sensitivity of the photomultiplier tube. The next generation unit may contain a temperature sensor and microprocessor which will take this sort of variation into account. (This variation will be recorded in the present arrangement by a change in the calibration signal.) Additionally, a microprocessor could be used to make most or all of the adjustments described above.

EXAMPLE

With the experimental parameters of **TABLE A1**, data were taken on material "UC" (a polyether based polyurethane manufactured by Uniroyal). The results are shown in **Fig. A-2**. For this data, the zero was adjusted on the 10-mV SENSITIVITY with no sample and with the conical probe closed. Additionally, the 3-mm thick Schott OG570 glass over black paper gave a reading of 0.312 V on the DVM. From previously measured tensile strength and elongation data for artificially degraded material, **Figs. A-3 and A-4** were constructed. (Data from one sample was not plotted since strength and elongation data were not available.)

The next day, the unit was turned on and data were taken on piece designated as "UC42" (i.e., 42 days in hot water). This gave a reading on the DVM of 2.05 V. (The Schott OG570 glass over black paper gave a reading of 0.281 V.) Since the system response to the OG570 standard was slightly different, a calibration factor (0.312/0.281) = 1.11 was applied to the reading of 2.05 V to yield an effective reading of 2.26 V. This value was then used with **Fig. 3 and 4** to estimate a tensile strength of 2000 psi and elongation of 715 percent.

For quantitative measurements, similar calibration curves are required for each material of interest. However, qualitative degradation can be monitored without such data.

LIST OF MANUALS AND PERTINENT DOCUMENTS

1. "Laser Safety Guide," edited by James F. Smith (1991), Laser Institute of America, 12424 Research Parkway, Suite 130, Orlando, FL 32826-3274, 407/380-1553.

2. "Lasergard (Laser Goggles)", Glendale Protective Technologies, Inc., 130 Crossways Park Drive, Woodbury NY 11797, 516/921-5800.

3a. "Uniphase Model 2014 Air-Cooled Argon-Ion Laser System, Installation and Operation Manual," Cyonics, A Division of Uniphase, 163 Baypointe Parkway, San Jose, CA 95134, 408/433-3838. Note: this manual also contains safety information.

3b. "Preliminary Operating Instructions, Model 2014 (-10SL)," Cyonics, A Division of Uniphase, 163 Baypointe Parkway, San Jose, CA 95134, 408/433-3838.

3c. "2010 Series Air-Cooled Argon Ion Laser Systems," Cyonics, A Division of Uniphase, 163 Baypointe Parkway, San Jose, CA 95134, 408/433-3838.

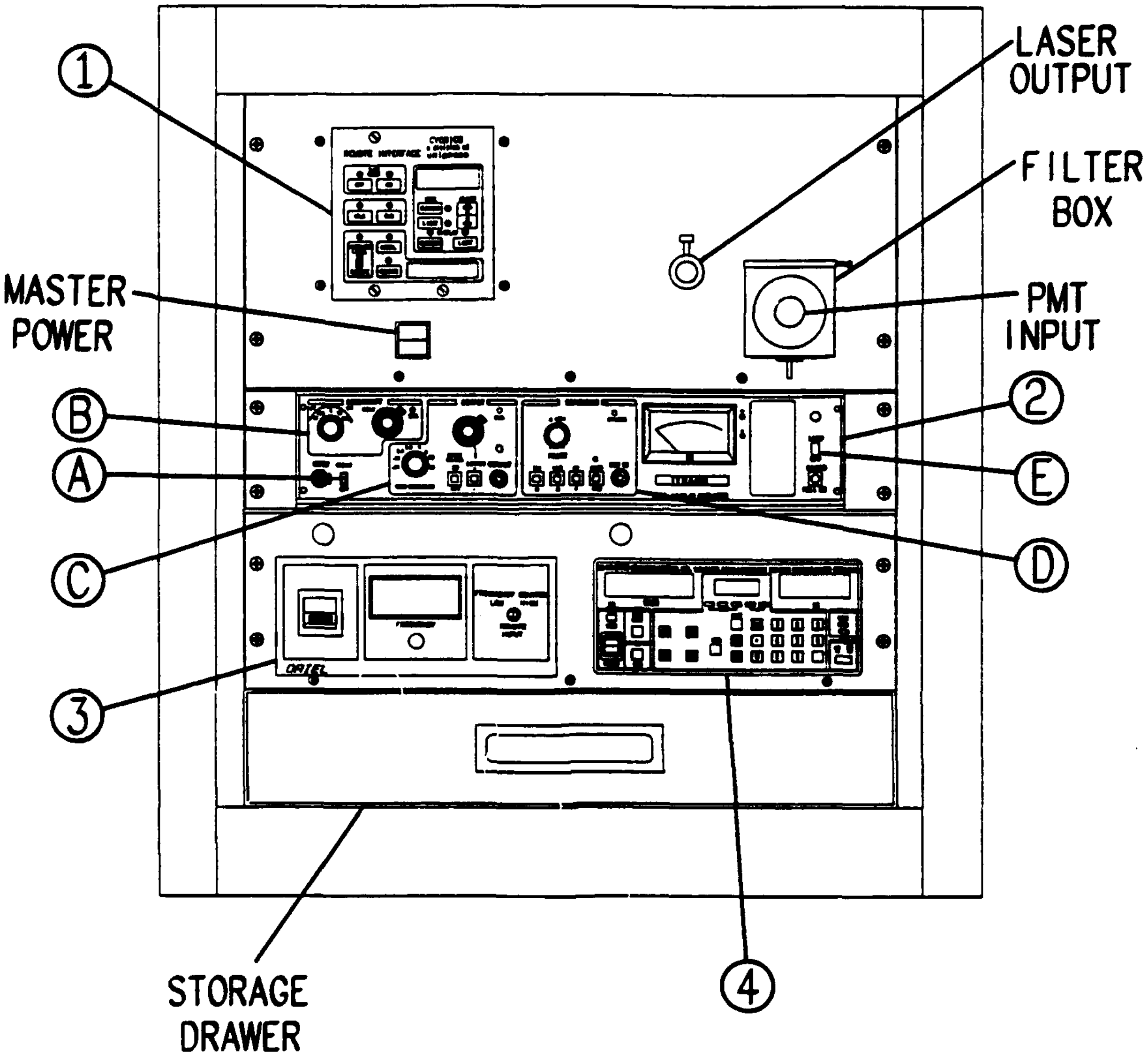
4. "Instruction and Maintenance Manual Ithaco Model 3921 Lock-In Amplifier," Ithaco, Inc. 735 West Clinton St, P.O. 6437, Ithaca, NY 14851-6437, 607/272-7640.

5. "Oriel Variable Frequency Open Chopper Model 75100/75102 Instruction Manual," Oriel Corp., 250 Long Beach Blvd., P.O. Box 872, Stratford, CT 06497, 203/377-8282.

6. "Series PS300 High Voltage Power Supplies, Models PS 310, 325, and 350," Stanford Research Systems, Inc., 1290 D. Reamwood Ave., Sunnyvale, CA 940789, 408/744-9040.

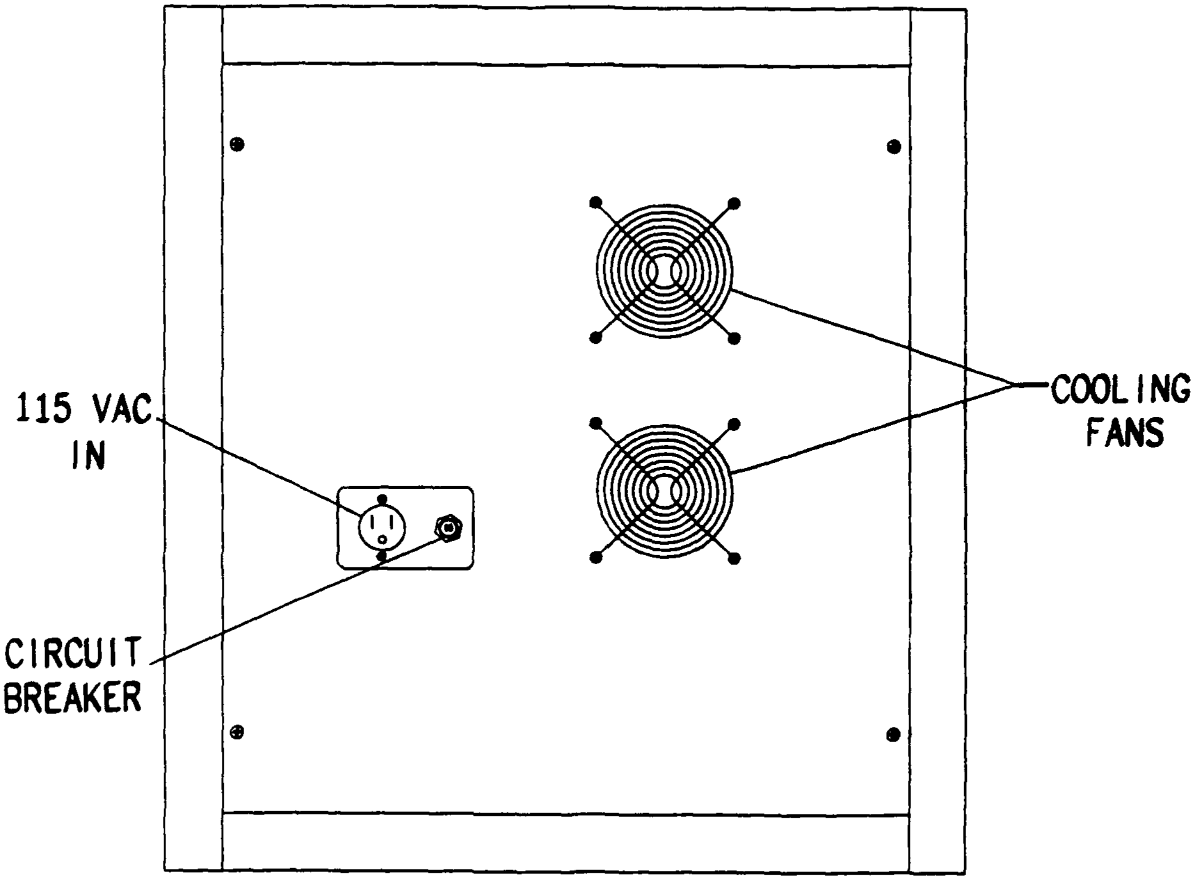
7. "Photomultiplier Tube Housings and Accessories," Products For Research, 88 Holten Street, Danvers, MA, 508/774-3250.

8. "Series 77/75/73/70/23/21 Series II Multimeter Users Manual," John Fluke Mfg. Co., Fluke Technical Center, 2104 Hutton Dr., Suite 112, Carrollton, TX 75006, 214/406-1000.



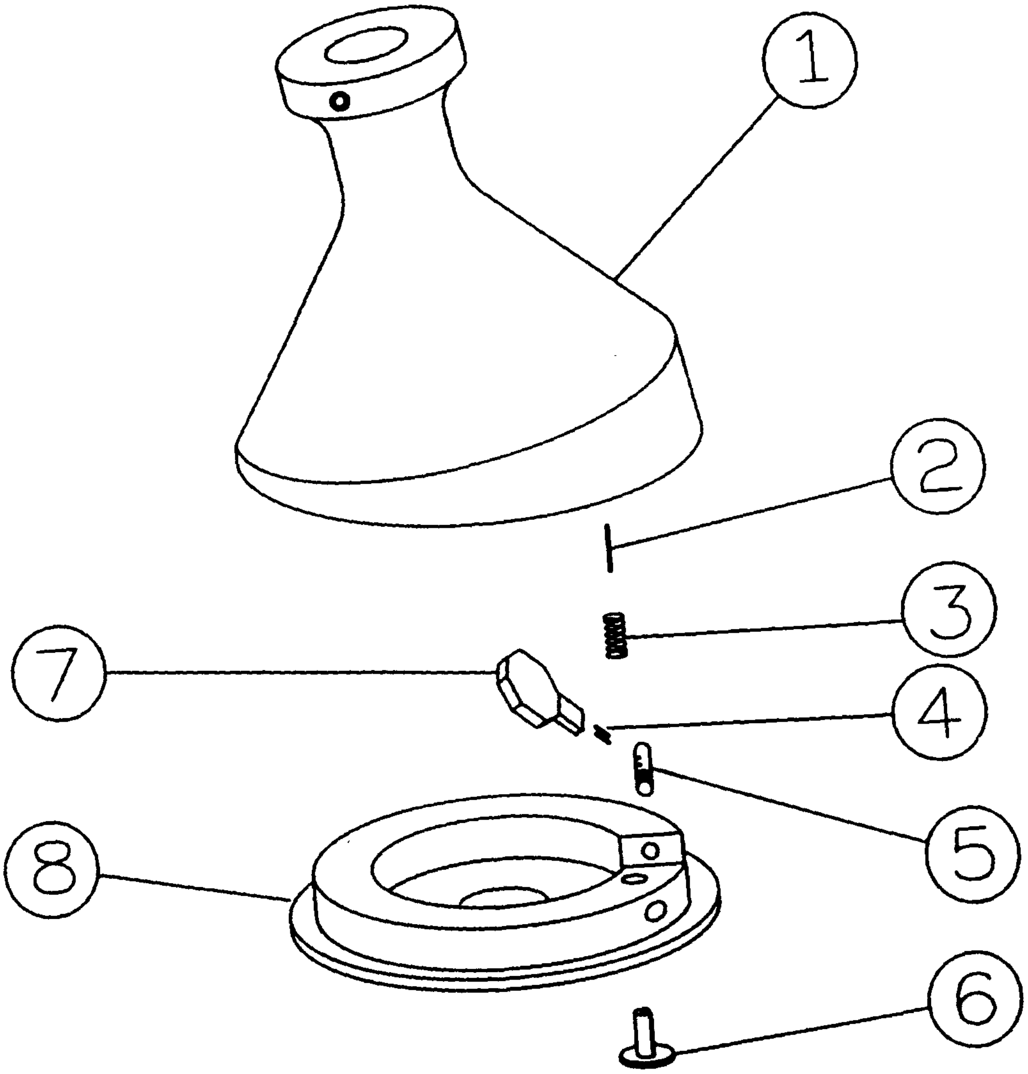
(Note: the bifurcated fiber-optic bundle is not shown; however, it attaches to the LASER OUTPUT and PMT INPUT ports of the unit. Major components depicted in this drawing are (1) REMOTE INTERFACE laser controller, (2) LOCK-IN AMPLIFIER, (3) CHOPPER CONTROLLER, and (4) HIGH VOLTAGE POWER SUPPLY. The LOCK-IN AMPLIFIER consists of the following subsections: (A) INPUT, (B) SENSITIVITY, (C) OUTPUT, (D) REFERENCE, and (E) POWER. Also shown are the MASTER POWER switch, FILTER BOX, and STORAGE DRAWER. The unit was delivered on a small rolling cart.)

Figure A-1a. Configuration diagram of the demonstration-prototype unit, front view



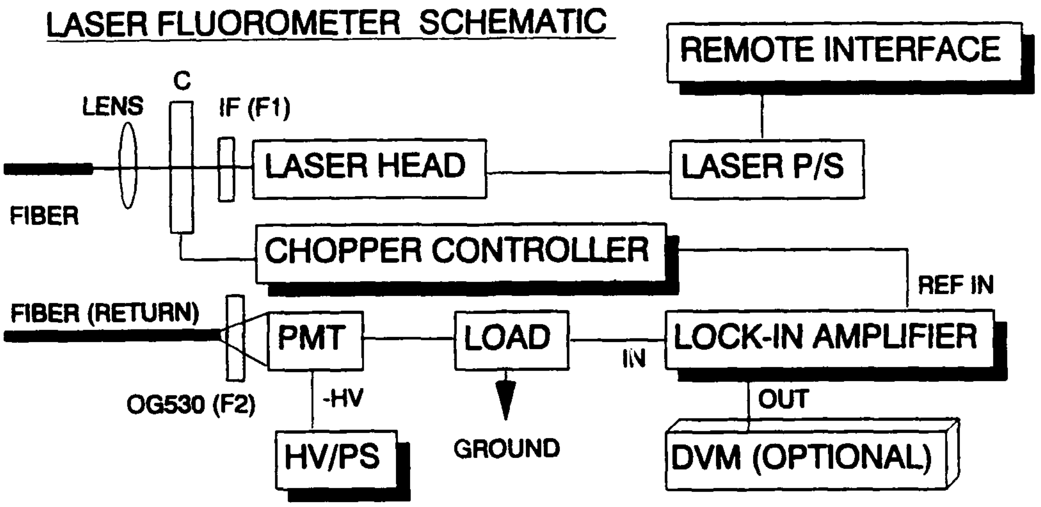
(Note: locations are shown for the 115 VAC INPUT, CIRCUIT BREAKER, and COOLING FANS.)

Figure A-1b. Configuration diagram of the demonstration-prototype unit, back view



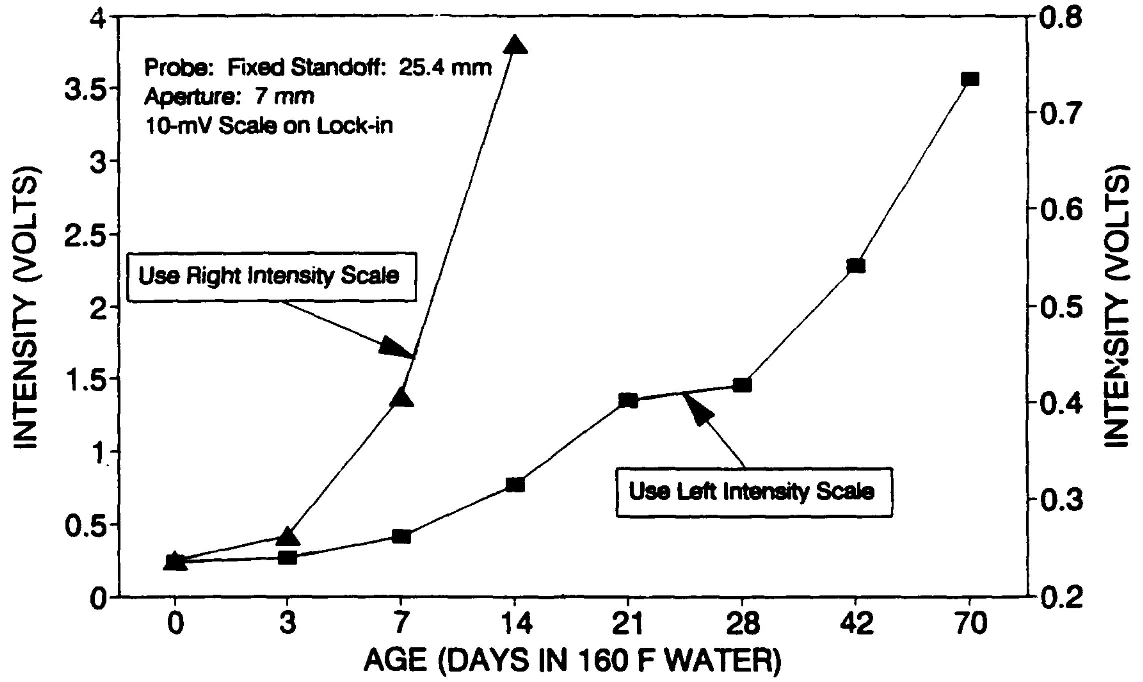
(Note that the fiber-optic bundle attaches into the hood assembly (1) and the material to be inspected is positioned below the aperture plate (8). When in operation, button (6) activates the trap door (7) to swing open during the measurement; otherwise, it is held in the closed position by spring (3).

Figure A-1c. Exploded view of optical probe assembly



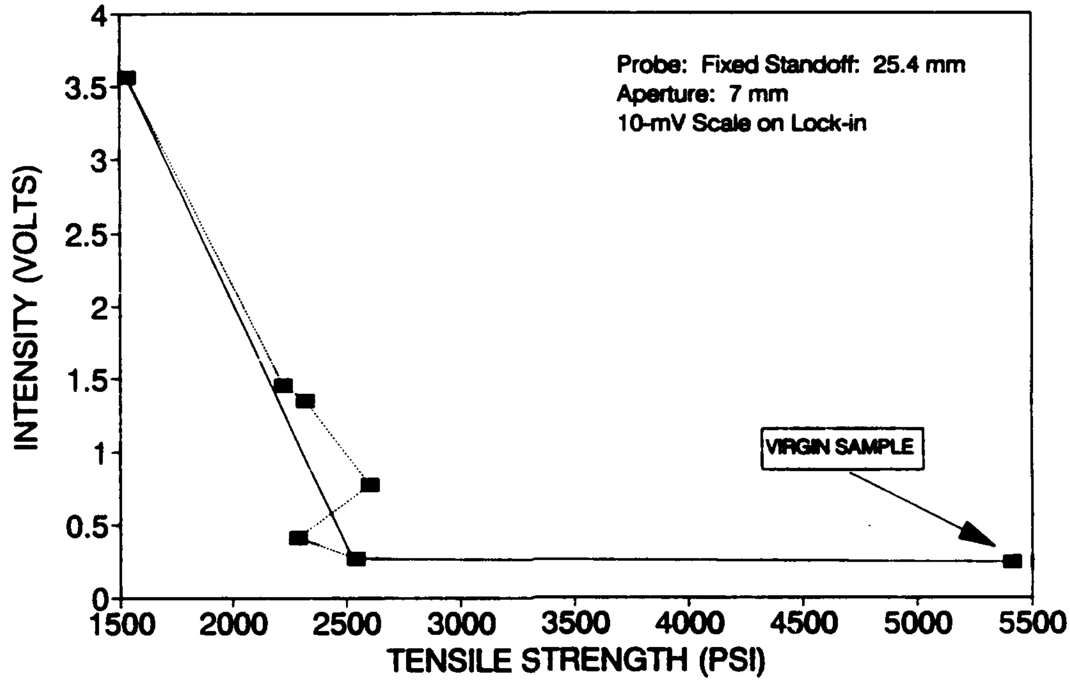
NOTES:
(1.) Shaded boxes indicate front panel instruments.
(2.) IF (F1) indicates interference filter.
(3.) OG530 (F2) indicates blocking filter.
(4.) C indicates chopper wheel.

Figure A-1d. Laser fluorometer schematic



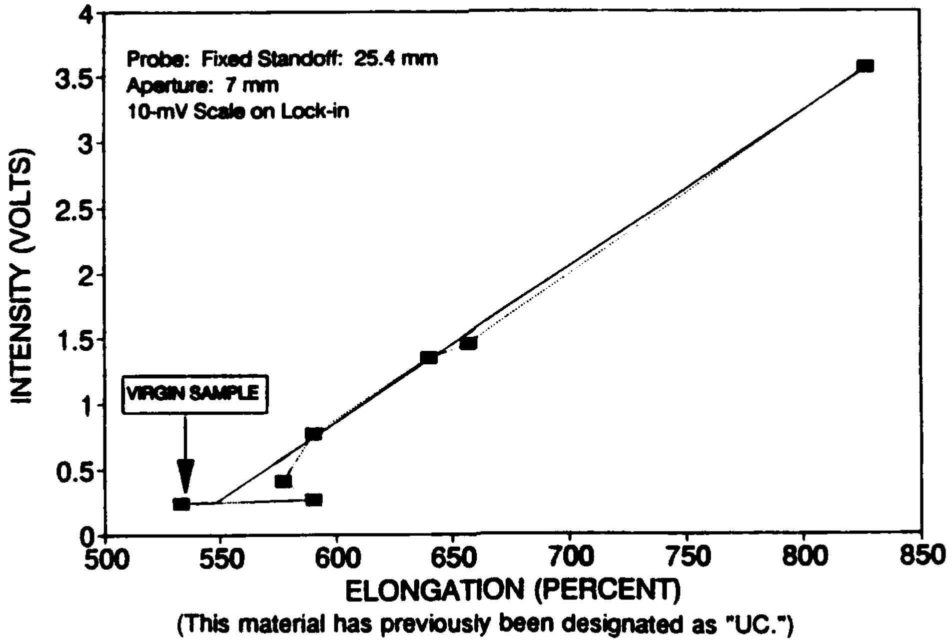
(This material has previously been designated as "UC.")

Figure A-2. Laser-induced fluorescence intensity (obtained with the demonstration-prototype unit) as a function of age of an ether-based polyurethane material



(This material has previously been designated as "UC.")

Figure A-3. Laser-induced fluorescence intensity (obtained with the demonstration-prototype unit) as a function of tensile strength of an ether-based polyurethane material



(This material has previously been designated as "UC.")

Figure A-4. Laser-induced fluorescence intensity (obtained with the demonstration-prototype unit) as a function of elongation of an ether-based polyurethane material

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