Spectroscopic analysis of fire suppressants and refrigerants by laser-induced breakdown spectroscopy

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Laser-induced breakdown spectroscopy is evaluated as a means of detecting the fire suppressants CF_3Br, C_3F_7H, and CF_4 and the refrigerant $C_2F_4H_2$. The feasibility of employing laser-induced breakdown spectroscopy for time- and space-resolved measurement of these agents during use, storage, and recharge is discussed. Data are presented that demonstrate the conditions necessary for optimal detection of these chemicals.

OCIS codes: 140.3440, 120.1880, 300.6390, 300.0300.

1. Introduction

Certain halogenated hydrocarbons (halons), such as CF_3Br (Halon-1301) and CF_2ClBr are among the most effective fire suppressants. Unfortunately, the production of these bromine-containing fire suppressants has been banned by international agreement[1] because these substances have been implicated as contributing to stratospheric ozone depletion. Part of the ongoing effort of choosing a replacement suppressant is the determination of how a given suppressant is dispersed within a clutter-filled environment (such as the crew compartment aboard a military vehicle) and how the concentration of suppressant changes with time after the chemical has been released. Also, there is great interest in developing field sensors for monitoring unwanted release (leaks) of these chemicals.

Many candidate replacement suppressants are fluorinated hydrocarbons.[2] In an initial study we have used laser-induced breakdown spectroscopy (LIBS) to measure atomic-fluorine emission from candidate replacement suppressants (CF_4, CF_3H, CF_2H_2, and C_2F_5H).[3] These measurements were used to deduce limits of detection (LOD) for these compounds. The reasons for choosing LIBS for these measurements are that the technique allows laser delivery and collection optics to be fiber coupled to provide access to remote or hostile environments as well as that the data collection rate is determined by the repetition rate of the laser. This means that LIBS-based measurements of suppressant concentrations can be made rapidly and *in situ* during full-scale fire suppressant testing or for detection of leaks from storage containers. Although there are commercially available halocarbon (refrigerant) detectors that use detection techniques other than UV–visible plasma emission, there is still a need for a halocarbon sensor with certain desirable characteristics such as near real-time response, remote operation, and freedom from other chemical interference.

The research presented here extends our initial study in two important directions. First, it includes three important compounds not previously studied: Halon-1301; C_3F_7H (FM-200), a leading replacement candidate for fire suppression; and $C_2F_4H_2$ (HFC-134a), a common replacement refrigerant. Second, unlike in the initial study, in which we captured the LIBS spectra by using a monochromator–photomultiplier tube system, in this study we concentrate on using and systematically optimizing the photodiode array–spectrograph system for the purpose of utilizing it in real-world applications.

2. Background

LIBS is a well-established technique[4] and has been widely discussed in the literature. Briefly, a pulsed laser beam is focused to a fluence of approximately 10^8–10^9 W/cm^2 on or in the sample. In this focal region, dielectric breakdown of the sample occurs. Continuum absorption of the laser radiation by free electrons produced during the dielectric breakdown further ionizes and heats the sample, generating the

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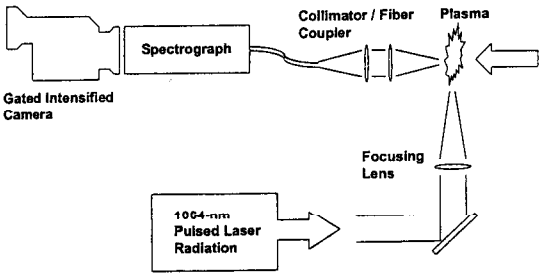

Fig. 1. Schematic of the instrumentation.

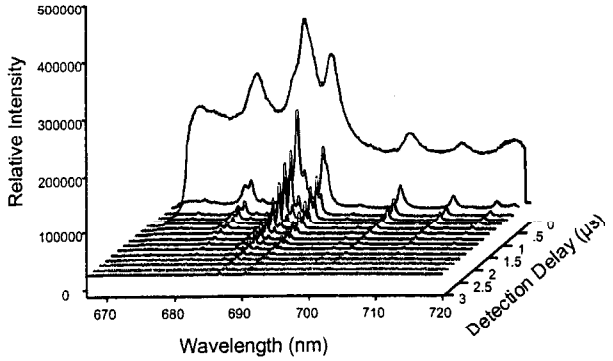

Fig. 2. Time-delay spectra: neat Halon-1301, integration time 0.2 μs, gate delay 0.0–3.0 μs in 0.2-μs steps.

plasma by cascade ionization. The emission of the atomic and molecular constituents, which are excited within the plasma, is collected with lenses or fiber optics, spectrally resolved, and measured with a photomultiplier or an optical multichannel analyzer. Typical LIBS plasma temperatures are in the 20,000–25,000 K range for gases at atmospheric pressure.[5]

Although LIBS is most commonly employed for solids analysis,[6,7] such as in measurement of metal contamination of soils, paint, metals, and steels, early studies[8] demonstrated the feasibility of the technique for detection of fluorine-containing species. Additionally, LIBS analysis of gaseous samples has been reported for the detection of chlorine, fluorine, sulfur, phosphorus, arsenic, and mercury in air.[9–11] Recently the authors' laboratory employed LIBS to determine limits of detection for a series of fluorinated methanes [CF_4 (Halon 14) CF_3H, CF_2H_2].[3]

In the research reported in this paper we used optical fibers to collect radiation emitted by the laser and then transferred it to the monochromator. Optical fibers have been utilized by other researchers for the remote analysis of metals in the environment.[12,13] These fibers have also been used in a probe arrangement for both transfer of the plasma generating pulse and the collection of emitted radiation.[14]

3. Experiment

A schematic of the experimental apparatus is shown in Fig. 1. Laser radiation at a wavelength of 1.06 μm is supplied by a Nd:YAG laser (Quanta-Ray DCR2A). The laser repetition rate is 10 Hz. The laser radiation is passed through a 25-mm-diameter plano–convex lens with a focal length of 50 mm and is brought to a focus 2 mm above the outlet port of the flow apparatus used to deliver the analyte. Plasma emission is collected with an $f/4$ quartz lens, collimated, and focused directly into a 1-mm-aperture bifurcated optical fiber bundle consisting of 10 individual fibers in a cylindrical shape at the light-collection point and a rectangular configuration at the other end. The output from the optical fiber bundle is spectrally resolved by a spectrograph (Jarell-Ash Monospec 27) and measured with an intensified photodiode array detector (Princeton Instruments IRY1024G). The grating is used in first order, and the effective resolution is ~0.7 nm. Single-shot spectra were obtained for each of these measurements. All spectra were obtained in a single-shot manner.

The sample delivery device was described previously.[15] The device consists of a 0.318-cm (O.D.) stainless-steel tube placed inside a 0.953-cm (O.D.) stainless-steel tube. Analyte gas is delivered by the center tube at a flow rate of 50 standard cubic centimeters per minute (sccm). The outer tube delivers argon gas flowing at 500 sccm. The argon gas is used as a sheath to confine the analyte to the focal volume of the laser. We mounted the sample delivery device upon a three-dimensional stage to adjust the location of the analyte stream relative to the laser focal volume. For the limit of the detection studies described here, the analyte sample was mixed with ultrapure nitrogen. Gas flows were controlled by mass-flow meters (Tylan). All gases were supplied by Matheson, Inc., and were used without further purification. The mass-flow controllers were calibrated with a wet test meter.

4. Results and Discussion

In general, initial laser-induced plasma emission consists of continuum radiation for several hundred nanoseconds.[4] This continuum emission is typically much more intense than atomic and molecular emissions, which occur sequentially from one to several microseconds following plasma formation. Figure 2 shows typical time-resolved laser-induced breakdown spectra for neat Halon-1301 with an argon sheath gas. Visible in this LIBS spectrum are emission lines from fluorine and argon.

Figure 3 illustrates the spectral emission from neat Halon-1301. This figure shows the bromine emission lines in the 460–480-nm wavelength region. All spectra obtained for the compounds of interest were identical except in this region. For these studies the fluorine emission line at 685.6 nm ($3S^4P_{5/2}$–$3P^4D^o_{7/2}$) is used for signal optimization and signal-to-noise ratio calculations. This line was chosen because it is the strongest fluorine emission line in this spectral region[3] and because it is free from interference from oxygen, nitrogen, and argon. For optimum sensitivity it is necessary to minimize contributions to the signal from the con-

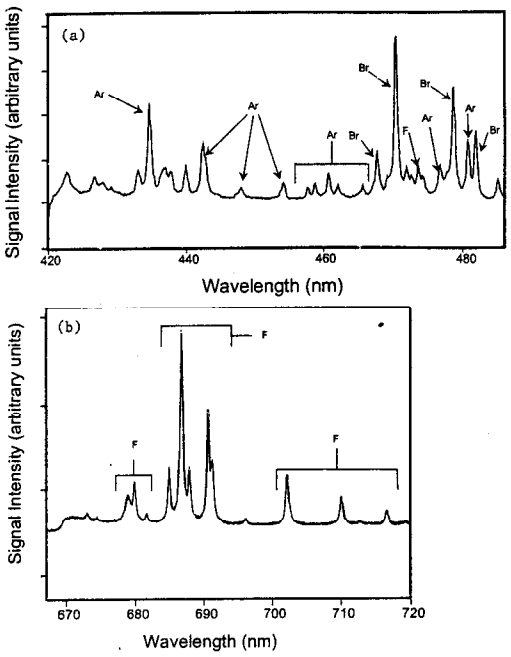

Fig. 3. LIBS spectra of Halon-1301.

tinuum radiation while maximizing the analyte signal-to-noise ratio. The factors that must be considered in achieving optimum balance are discussed below.

A. Optimization of Gate Delay

Previous studies of fluorine emission from halocarbons[3] delayed signal collection by 2 μs after the laser pulse. Because the time during which the diode array detector intensifier is on is termed the gate width, the delay between laser firing and collection of signal is called the gate delay. For these studies the signal-to-noise ratio for emission from the atomic-fluorine line at 685.6 nm was measured as a function of gate delay for an incident laser energy of 60 mJ per pulse. Integration time (i.e., the gate width) was 0.5 μs. Figure 4 shows that, for the compounds studied here, the optimum gate delay was 0.6 μs. The uncertainty of the data shown in Fig. 4 is approximately

Table 1. Dependence of Signal-to-Noise Ratio on Laser Energy for Atomic-Fluorine Emission at 685.6 nm

Energy (mJ/Pulse)	Signal/Noise
40	229
50	247
60	251
72	157
80	119
90	231
100	245
110	209
120	184

15%. We have found that the uncertainty level for all the data that we report in this paper is in the 15–20% range. The signal-to-noise ratios for all experiments were calculated from the average of five peak measurements and the rms noise from 20 blank measurements.

B. Dependence of Signal-to-Noise Ratio on Laser Power

We measured the emission intensity from a plasma occurring in a nitrogen–FM-200 gas mixture containing 4.23 parts in 10^3 (ppTh) of FM-200 at various laser pulse energy levels to determine the laser energy that maximized signal-to-noise ratio for emission from atomic fluorine at 685.6 nm. Table 1 shows that for FM-200 the laser pulse energies that yield the best signal-to-noise ratio for fluorine emission were observed at 60 and 100 mJ/pulse (Table 1). A pulse energy of 60 mJ/pulse was chosen for further optimization studies because we observed that at greater than approximately 80 mJ/pulse the plasma was breaking apart or segmenting. This phenomenon is well known in the laser breakdown field, where at a sufficiently high laser pulse energy the single microplasma converts into multiple spatially distinct microplasmas.

C. Optimization of Gate Width

To determine the optimum signal integration time (gate width) we measured the signal-to-noise ratio for atomic-fluorine emission at 685.6 nm as a function of

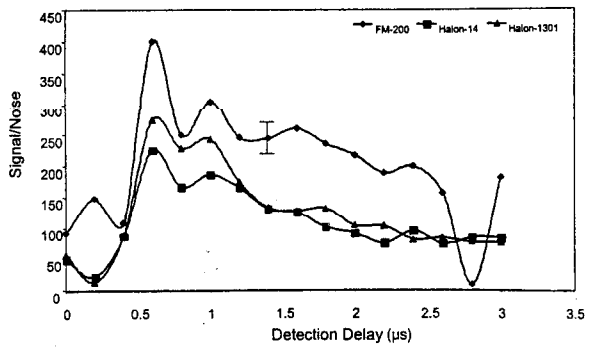

Fig. 4. Signal-to-noise ratio for atomic-fluorine emission at 685.6 nm as a function of gate delay for the gated, intensified diode-array detector used in these studies. For each of the compounds studied, optimum delay was determined to be 0.6 μs.

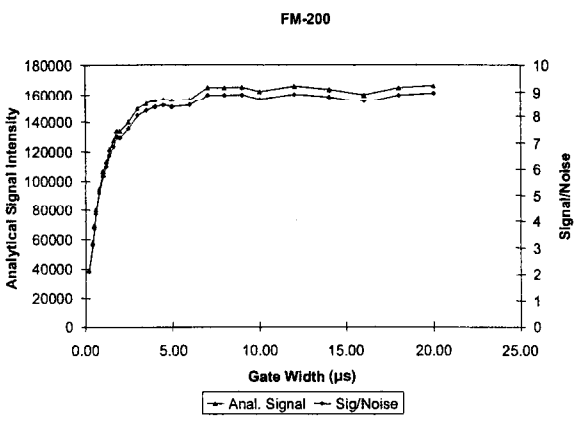

Fig. 5. Dependence of signal-to-noise ratio on integration time.

Table 2. Limits of Detection for Halon Alternatives Examined for This Study

	Halon-14[a]	Halon-1301[a]	FM-200[a]	HFC-134a
$y = mx + b$				
m (slope)	2.080	1.721	3.313	1.118
b (y intercept)	42,114	41,156	37,228	35,217
R^2	0.9990	0.9730	0.9842	0.9988
LOD (ppm)[b]	490	750	170	530

[a]$n = 5$.
[b]Twenty background measurements.

gate width for a plasma formed in 4.23-ppTh FM-200 in nitrogen. Laser energy was 60 mJ per pulse, and the gate delay was 0.6 μs. The gate width varied from 0.2 to 20 μs. Figure 5 shows that no further improvement in signal-to-noise ratio for fluorine emission was achieved for gate widths greater than 2.5 μs. Further studies indicated that the lowest (i.e., most sensitive) limits of detection were at a gate width of 0.5 μs.

D. Limit of Detection

LOD's were determined from the following equation:

$$\mathrm{LOD} = 3S_b/m, \tag{1}$$

where S_b is the standard deviation of 20 background measurements and m is the slope of the signal-intensity versus concentration-calibration curve. The LOD is the level at which it is possible to conclude that the analyte is present. From Table 2 we find that FM-200 exhibits the lowest limit of detection (170 parts in 10^6), whereas the highest is that of Halon-1301 (LOD, 750 parts in 10^6).

Figure 6 shows LIBS atomic-fluorine emission intensity at 685.6 nm versus concentration for all four compounds studied. Correlation coefficients for these calibration curves are listed in Table 2.

Figure 7 shows the single-shot LIBS spectrum of Halon-1301 (9.16 ppTh) measured over the spectral region from 670 to 720 nm. As we stated above, the spectra for all compounds were identical in this spectral region, indicating that identification of the parent molecule from LIBS spectra measured over this spectral region is not feasible, although such identification is not necessary for our applications. This spectrum indicates that the LIBS detector should be useful for real-time concentration measurements in full-scale fire-suppression tests for which the required sensitivities are in the 1–100-ppTh range.

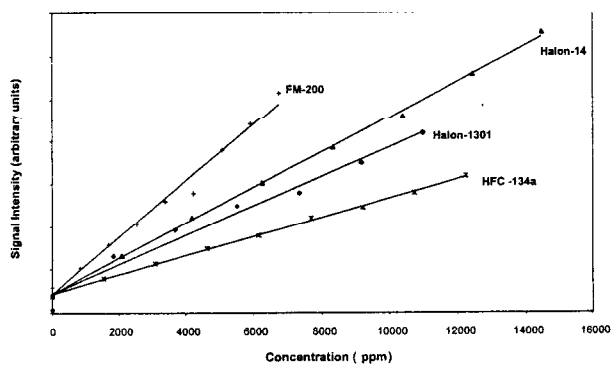

Fig. 6. Concentration versus LIBS atomic-fluorine emission intensity for the four compounds analyzed for this study; ppm, parts in 10^6.

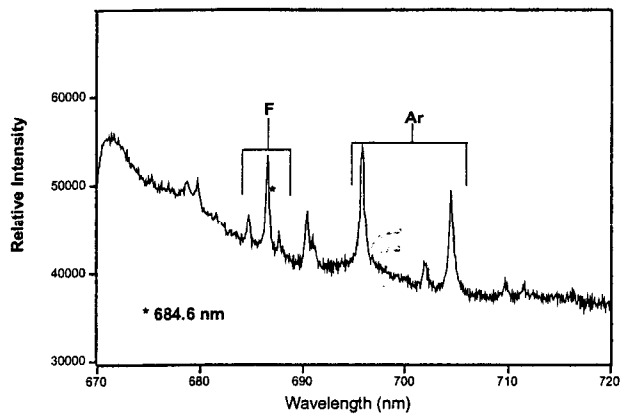

Fig. 7. Single-shot Halon-1301 spectrum: 9.17 ppTh, 0.6-μs detection delay, 0.5-μs integration time.

5. Conclusion

In this paper we have demonstrated the wide applicability of the LIBS technique to measure concentrations of a new generation of fire-extinguishing agents and refrigerants. To the best of our knowledge, we have presented the first quantitative LIBS spectra of CF_3Br (Halon-1301), C_3F_7H (FM-200) and $C_2F_4H_2$ (HFC-134a), all commercially and environmentally important compounds. Limits of detection for these halocarbons are somewhat greater (less sensitive) than those previously reported for fluorocarbons. We believe that this decrease in sensitivity is caused by the use of fiber optics to collect the LIBS radiation as well as by the use of a linear diode array to measure the LIBS emissions. This loss in sensitivity relative to lens coupled systems that use photomultiplier tubes for detection is compensated for by the ability of the present system to make measurements in hostile and remote environments.

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References

1. D. J. Wuebbles, P. S. Connell, and K. O. Patten, "Evaluating the potential effects of halon replacements on the global environment," in *Halon Replacements: Technology and Science*, A. W. Miziolek and W. Tsang, eds. ACS Symp. Series **611**, 59–71 (1995).
2. W. L. Grosshandler, R. G. Gann, and W. M. Pitts, eds., "*Evaluation of Alternative In-Flight Fire Suppressants for Full-Scale*

Testing in Simulated Aircraft Engine Nacelles and Dry Bays," NIST SP861 (National Institute of Standards and Technology, Gaithersburg, Md., 1994).

3. C. K. Williamson, R. G. Daniel, K. L. McNesby, and A. W. Miziolek, "Laser-induced breakdown spectroscopy for real-time detection of halon alternative agents," Anal. Chem. **70,** 1186–1191 (1998).
4. L. J. Radziemski and D. A. Cremers, "Spectrochemical analysis using laser plasma excitation," in *Laser-Induced Plasmas and Applications*, L. J. Radziemski and D. A. Cremers, eds. (Marcel Dekker, New York, 1989), pp. 295–325.
5. J. D. Simeonsson and A. W. Miziolek, "Time-resolved emission studies of ArF-laser-produced microplasmas," Appl. Opt. **32,** 939–947 (1993).
6. H. J. Hakkanen and J. E. I. Korppi-Tommola, "UV-laser plasma study of elemental distributions of paper coatings," Appl. Spectrosc. **49,** 1721–1728 (1995).
7. J. Belliveau, L. Cadwell, K. Coleman, L. Huwel, and H. Griffin, "Laser-induced breakdown spectroscopy of steels at atmospheric pressure and in air," Appl. Spectrosc. **39,** 727–729 (1985).
8. D. A. Cremers and L. J. Radziemski, "Detection of chlorine and fluorine in air by laser-induced breakdown spectroscopy," Anal. Chem. **55,** 1246–1252 (1983).
9. E. A. P. Cheng, R. D. Fraser, and J. G. Eden, "Detection of trace concentrations of column III and V hydrides by laser-induced breakdown spectroscopy," Appl. Spectrosc. **45,** 949–952 (1991).
10. M. Casini, M. A. Harith, V. Palleschi, A. Salvetti, D. P. Singh, and M. L. Vaselli, "Time-resolved LIBS experiment for quantitative determination of pollutant concentrations in air," Laser Part. Beams **9,** 633–639 (1991).
11. C. Lazzari, M. De Rosa, S. Rastelli, A. Ciucii, V. Palleshci, and A. Salvetti, "Detection of mercury in air by time-resolved laser-induced breakdown spectroscopy technique," Laser Part. Beams **12,** 525–530 (1994).
12. D. A. Cremers, "The analysis of metals at a distance using laser-induced breakdown spectroscopy," Appl. Spectrosc. **41,** 572–578 (1987).
13. K. Y. Yamamoto, D. A. Cremers, M. J. Ferris, and L. E. Foster, "Detection of metals in the environment using a portable laser-induced breakdown spectroscopy instrument," Appl. Spectrosc. **50,** 222–233 (1996).
14. B. J. Marquardt, S. R. Goode, and S. M. Angel, "*In situ* determination of lead in paint by laser induced breakdown spectroscopy using a fiber-optic probe," Anal. Chem. **68,** 977–981 (1996).
15. R. J. Locke, J. B. Morris, B. E. Forch, and A. W. Miziolek, "Ultraviolet laser microplasma-gas chromatography detector: detection of species-specific fragment emission," Appl. Opt. **29,** 4987–4992 (1990).