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LASER MICROPLASMA-GAS CHROMATOGRAPHY DETECTOR.
II. DETECTION OF SPECIES-SPECIFIC FRAGMENT EMISSION

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OCTOBER 1990

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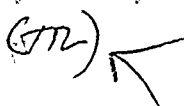
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13. ABSTRACT (Maximum 200 words) Characteristic laser-produced microplasma emissions from various simple carbon-containing vapors entrained in a He carrier gas have been observed and compared. A focused ArF (193 nm) excimer laser is used to induce microplasmas with modest pulse energies (15 mJ or less) in the effluent region of a gas chromatography (GC) capillary column. Strong atomic (C, H, O, Cl, and F), as well as molecular (C ₂ ⁺ , CH, and CCl) emissions are observed with very high signal-to-noise ratios. A plasma emission survey indicates that different classes of molecules show unique spectra which make it relatively easy to distinguish one chemical class from another. These results suggest that a laser microplasma gas chromatography detector (LM-GCD) should offer additional discrimination/resolution for unknown sample gas mixture analysis. In addition, the LM-GCD exhibits a significant advantage over certain other GC detectors, like the widely used flame ionization detector (FID), by readily detecting non-responsive gases such as CO, CO ₂ , CCl ₄ , and freons. (72) 				
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I. INTRODUCTION

Pulsed lasers have been used to produce microplasmas via laser-induced breakdown almost from the time of their invention. Virtually all of the reports in the intervening years involve the use of the ruby, Nd:Glass/Nd:YAG, or CO₂ lasers.¹⁻³ More recently, a specific technique called LIBS (laser-induced breakdown spectrometry) was developed for the purpose of chemical (elemental) analysis of aerosol and gas samples.^{4,5} In the last few years a new approach for laser plasma formation in gases has been developed which utilizes ultraviolet lasers and is based on atomic and molecular resonances in the microplasma formation processes.^{6,7} Attributes of this approach include efficiency with respect to the amount of incident laser energy that is required to form microplasmas, i.e., a lower threshold for breakdown, as well as a much higher degree of control over the intensity of the microplasmas, especially near the threshold region. This latter effect allows for the formation of much weaker microplasmas using UV resonant lasers than that possible with visible/infrared non-resonant lasers. As such, the weaker (lower temperature) microplasmas contain a relatively larger fraction of molecular fragments and, conversely, a smaller fraction of atoms and ions.

We recently reported our first results of the use of resonant laser-produced microplasmas for chemical analysis in a study which was aimed at ascertaining the utility of the laser microplasma approach for potential use as a detector for gas chromatography.⁸ Very simply, an ArF excimer laser beam (193 nm) was focused at the orifice of a gas chromatography (GC) capillary column through which a high purity He carrier gas flowed continuously. Utilizing modest laser pulse energies (ca. 10 mJ), microplasmas were formed when a small amount of analyte sample was injected into the carrier gas flow and were not produced in the He carrier gas by itself. Resonance in the formation of free electrons in the laser focal volume was accomplished by the coincident absorption of photons from the broadband excimer laser by carbon atoms at 193.1 nm ($2p^2\ ^1D_2 \rightarrow 2p3s\ ^1P_1^o$).⁸ Microplasma formation was detected using photoacoustic, optogalvanic, and photometric emission spectroscopy. Photometric detection was found to be the most sensitive method of the three techniques and thus offered the greatest promise for further development.

In this paper we report further work on the development of this technique which involves a survey of spectrally-resolved microplasma emissions for a variety of carbon-containing sample gases which are meant to represent different types of chemical groups. The results indicate that there is significant group-specificity in the emission spectra which should make it possible to increase the chemical selectivity/resolution of a gas chromatograph based on microplasma emission analysis using the LM-GCD technique.

II. EXPERIMENTAL

The apparatus and techniques used for the study of the dispersed emission of electronically excited fragments formed within the microplasma of various gaseous flows are essentially identical to those previously employed by Morris, et al.⁸ A schematic illustration of the experimental arrangement is presented in Figure 1A. The excitation

source is a Lumonics Model TE 861M-3 pulsed, broadband ArF (193 nm) excimer laser, which is equipped with unstable resonator optics. The laser pulse duration is approximately 15 nsec and, for this study, pulse energies of up to 15 mJ are used. The laser is operated at a repetition rate of 15 Hz. The laser pulses are focused through a 25 mm diameter, 50 mm focal length UV grade fused silica lens. The focus of the beam is directed to a position approximately 0.5 mm above the outlet of a 5 meter, 544 micron diameter fused silica "Megabore" column obtained from J & W Scientific which is normally used in the HP Model 5890A gas chromatograph. Since the purpose of this present study is to characterize microplasma emission from individual analytes and not analyte mixtures, the GC column was removed from the GC and used separately for experimental convenience. The laser energy is monitored by a Scientech laser power meter which also serves as a beam stop.

The LM-GCD comprises two separate components, specifically the sheath gas and column effluent. To prevent the mixing of room air with the GC effluent gases, the column outlet, illustrated in Figure 1B, is encircled by a 3/8" diameter helium sheath with a flow rate of approximately 200 ml/minute. The use of a sheath gas is unique to the LM-GCD. One important reason for separating room air and the GC effluent gases is to prevent a condition of breakdown in 100% of the laser shots. This is particularly important when using the LM-GCD for maximum sensitivity where broadband, rather than wavelength-specific, detection of weak microplasma emission signifies the elution of a small quantity of the analyte molecules.⁸ The room air-induced breakdown is due to the ease with which molecular oxygen is ionized by the ArF excimer laser via the resonant two-photon absorption through the intermediate Schumann-Runge (S-R) bands.⁹ Although absorption by laboratory air will clearly deplete the laser radiation in the O₂ S-R band wavelength region, at short distances from the laser (approximately 0.5 meter in our case), this effect is minimal.⁹ Another reason for excluding room air from the laser focal volume is to prevent the contamination of the microplasma emission by gases which are not components of the original sample. Centering of the column outlet within the sheath gas is accomplished by the utilization of a wire mesh which also allows for the unrestricted flow of the sheath gas.

The column effluent gas is composed of carrier gas and analyte vapor. The helium carrier gas (Spectra Gases 99.999%), after successive filtering and drying, flows to the atmosphere through the Megabore column at a rate of roughly 20 ml/minute. Gaseous samples were introduced into the carrier gas prior to the Megabore column at a typical flow rate of also about 20 ml/minute resulting in approximately 10¹³ analyte molecules present in the laser probe volume (10⁻⁶ cm³). Backing pressures and flow controls were adjusted to maintain similar concentrations in the effluent of the capillary column for the different sample gases. Alternately, liquid phase compounds (for most samples the vapor pressures at 298 K are in the 100 torr range) were inserted into the column by flowing the carrier gas over the neat liquid. This resulted in small variations of sample vapor concentrations in the probe volume between the different liquids. The difficulty of maintaining similar concentrations for the different liquid samples precluded the quantification and absolute comparison of the emission results.

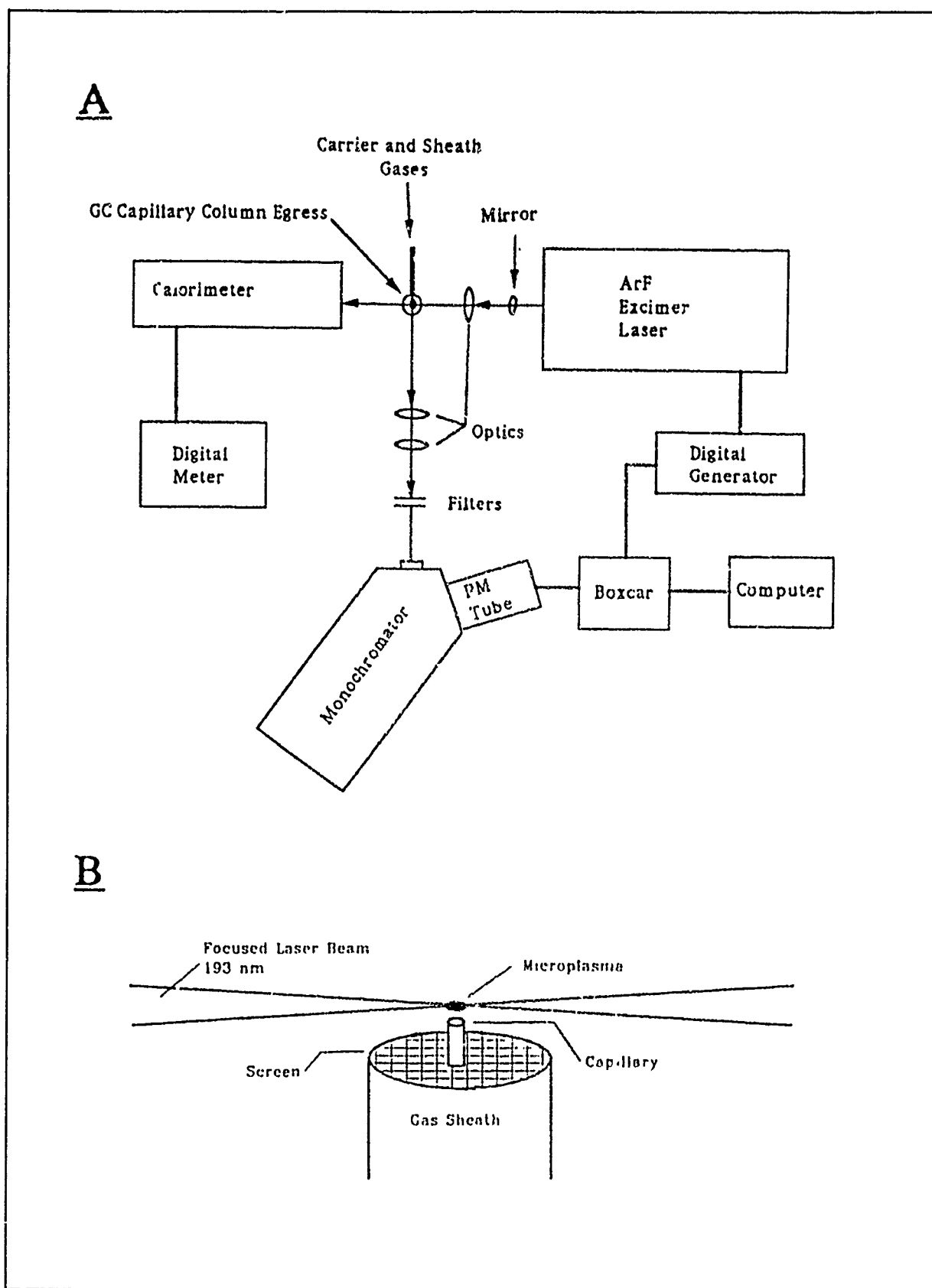


Figure 1. (A) Schematic of Experimental Apparatus. (B) Schematic Enlargement of Laser Interaction Region with the Effluent Gases from the Capillary Column.

A two-lens collection system, perpendicular to the direction of the laser excitation source, focused the emission originating within the microplasmas onto the entrance slit (width = 250 microns) of a 0.25 meter McPherson monochromator equipped with a Hamamatsu 955R photomultiplier tube (PMT). The signal from the PMT was processed with a Stanford Research Systems boxcar integrator with a gate width of 100 nsec. The output of the boxcar was then recorded utilizing a Zenith 80286-based computer. The spectra were acquired in three segments of approximately equal wavelength span. This was necessary in order to minimize the drop in ArF laser energy, and thus the signal level, over a prolonged spectral scan. This behavior, unfortunately, is quite characteristic of older excimer lasers such as ours. Typically these scans encompassed the following regions; 190-400 nm, 400-600 nm, and 600-850 nm. Consolidation of these three spectral regions into one spectrum was accomplished through use of the 1-2-3 Access System from Lotus Development Corporation. It should be noted that prior to acquiring the longer wavelength scans (>400 nm), a filter (GG-400) was inserted into the dispersed emission beam path in order to eliminate appearance of short wavelength emission in second order of grating from being recorded.

III. RESULTS AND DISCUSSION

To demonstrate the versatility and general nature of the LM-GCD, a number of different carbon containing compounds were examined. Figures 2, 3 and 4 present representative emission spectra originating from the electronically excited fragments formed within the various microplasmas. Additionally, Table 1 provides a detailed assignment of the major peaks observed in each respective spectrum. The relative intensity values are uncorrected for the monochromator/PMT instrument response function and the wavelengths listed represent actual readings from the monochromator mechanical dial (accuracy ± 0.5 nm).

Figure 2 displays the emission spectra obtained from the microplasmas generated in a flow of carbon monoxide (CO) and methanol (CH₃OH), top and bottom, respectively. Both CO and CH₃OH exhibit strong atomic carbon and oxygen emissions. CH₃OH, however, displays the additional emissions attributed to the atomic H α and H β transitions. It is noteworthy to consider that had a conventional flame ionization detector (FID) been utilized, only the presence of CH₃OH would have been discernible. The non-combustible CO would have remained undetected. The carbon dioxide (CO₂) microplasma emission spectrum was found to be very similar to that of CO (see Table 1). It should be noted that all of the spectra acquired for Table 1 display high signal-to-noise ratios for most atomic and molecular emissions. In addition, it was determined that the broad band appearing at 387 nm in this and all subsequent spectra is attributed to second order ArF laser scattering.

Figure 3 shows the emission spectra acquired from electronically excited fragments produced in a microplasma generated in a flow of propane (CH₃CH₂CH₃) and benzene (C₆H₆), top and bottom, respectively. It is immediately apparent that the only feature common to both compounds is that ascribed to the emission of atomic carbon (844.8 nm). Two additional lines observed in the propane spectrum are those of H α and H β .

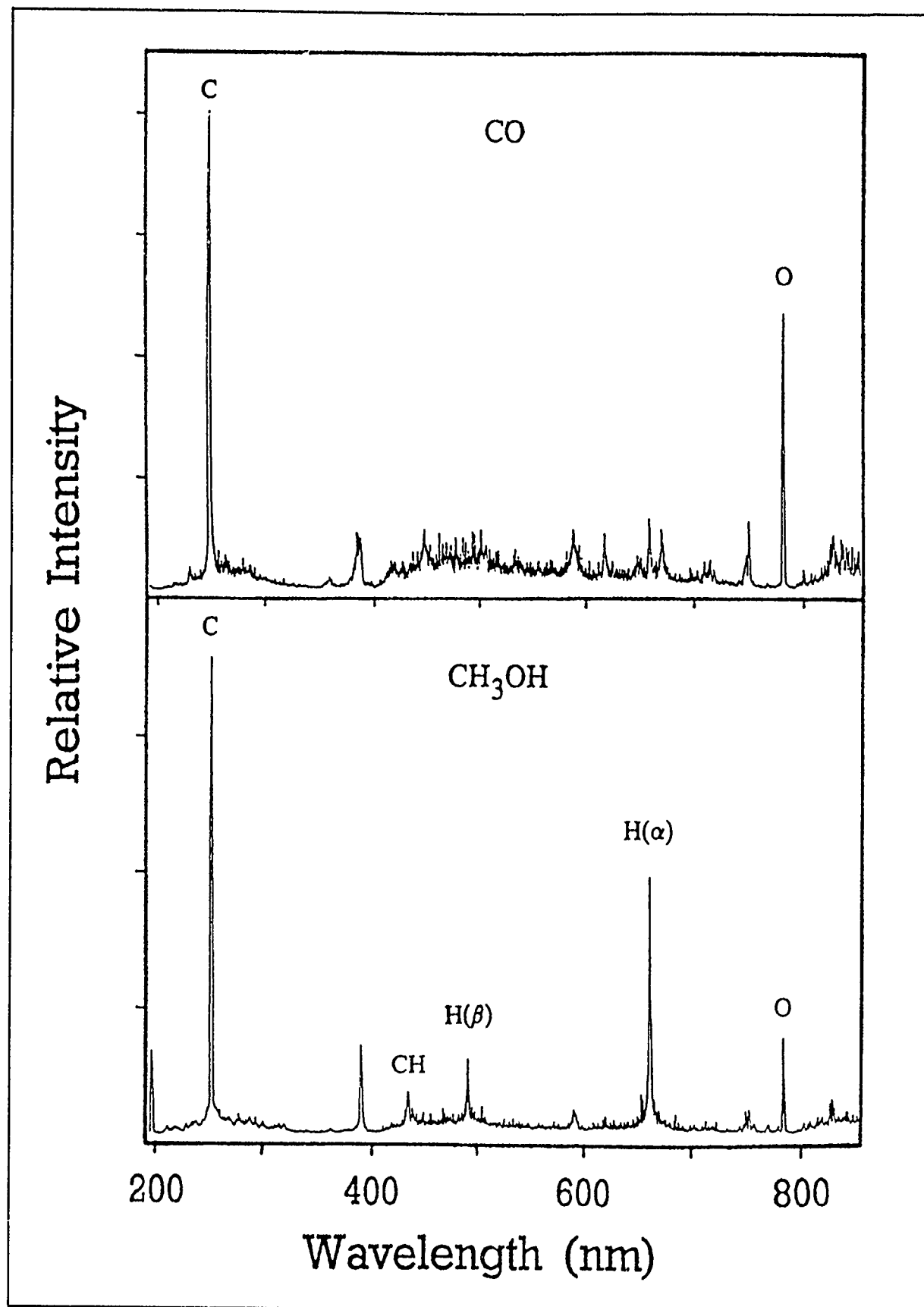


Figure 2. ArF Laser-Produced Microplasma Emission Spectra for CO and CH₃OH

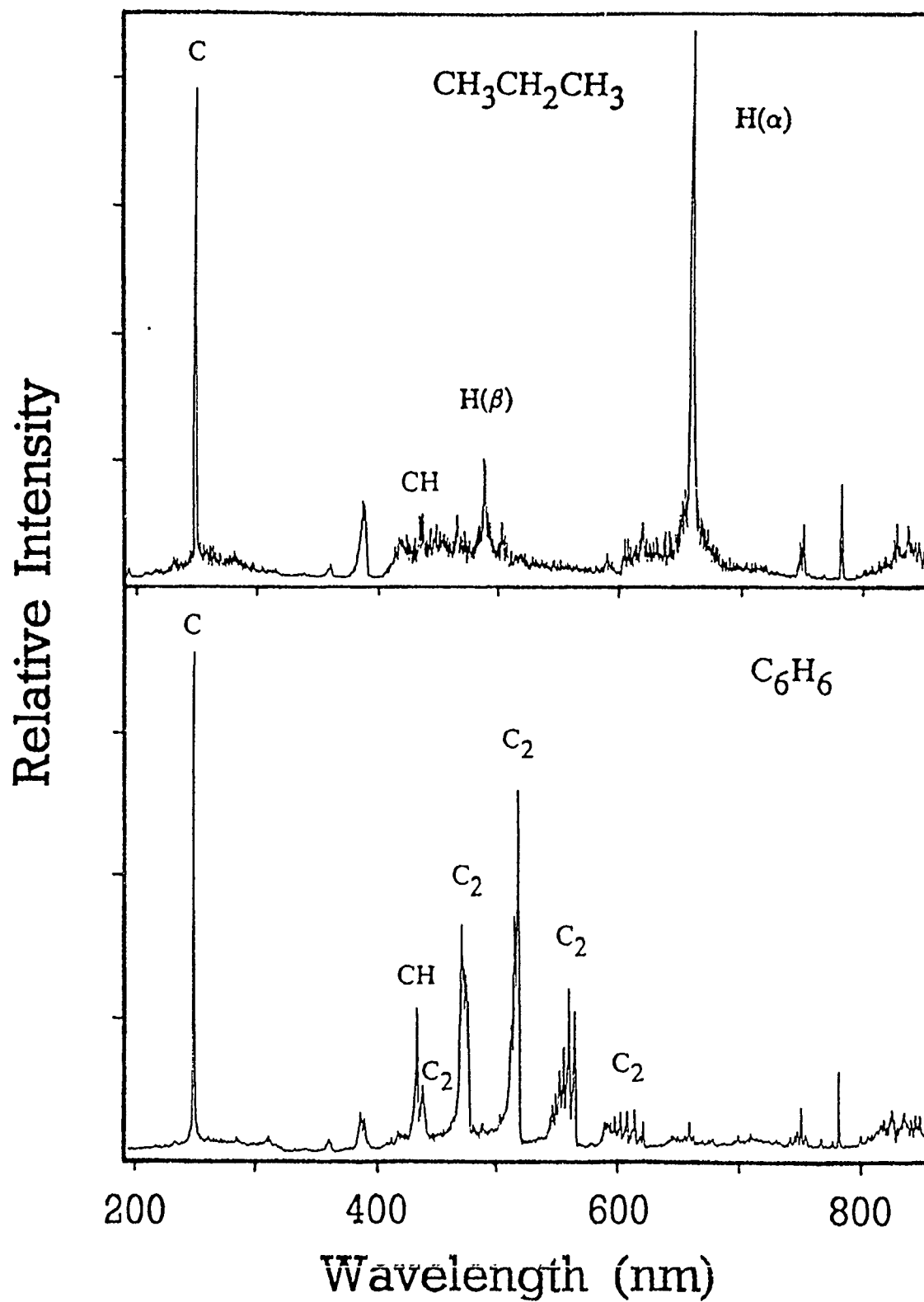


Figure 3. ArF Laser-Produced Microplasma Emission Spectra for Propane and Benzene

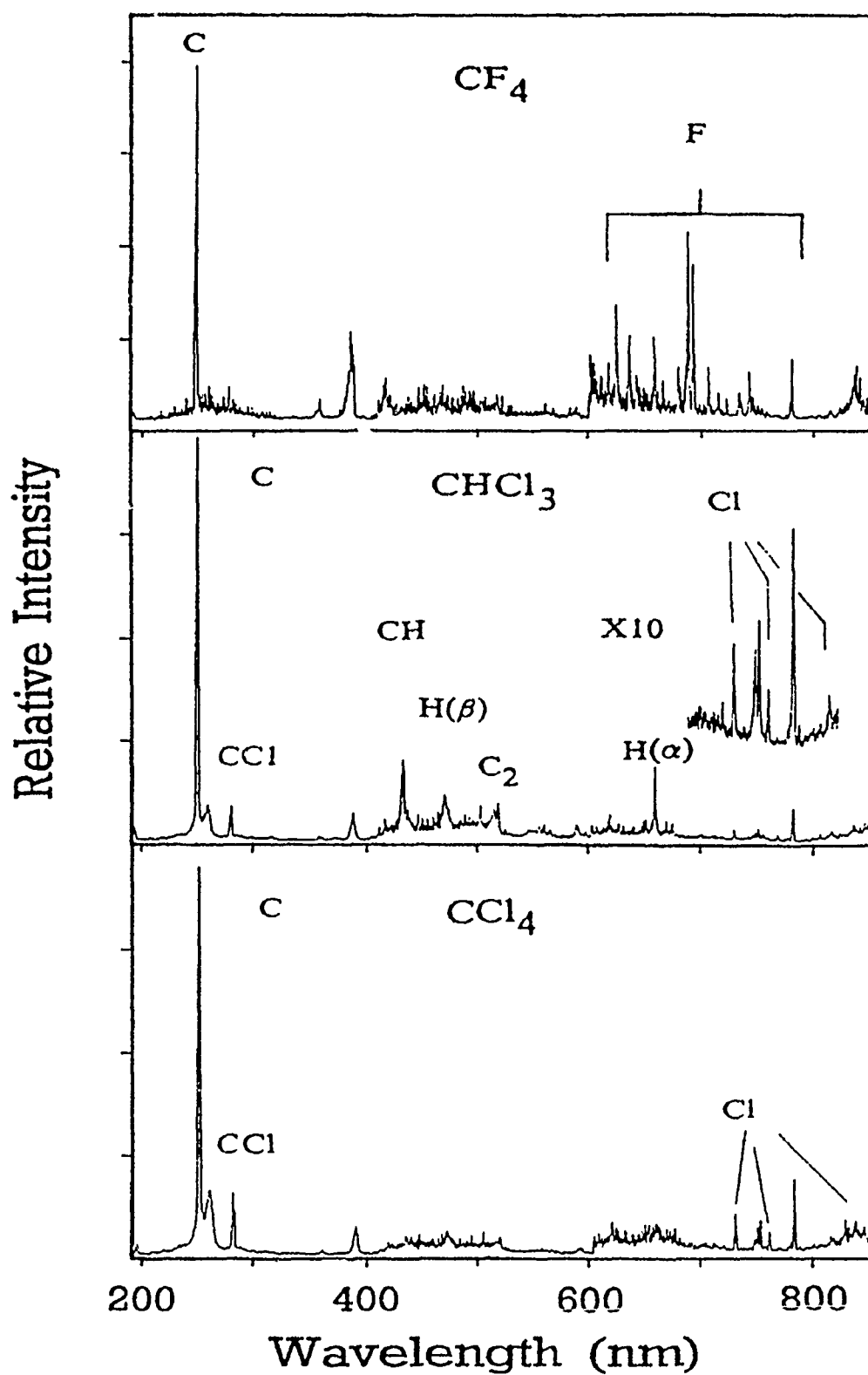


Figure 4. ArF Laser-Produced Microplasma Emission Spectra for CF_4 , CHCl_3 , and CCl_4

Table 1. Laser-Produced Microplasma Emissions from Various Carbon Containing Sample Molecules

Molecule	Overall Plasma I ^a	Species ^b	Emission nm ^c	I ^d
CH ₃ CH ₂ CH ₃	1.00	C	248.2	7.8
		CH	431.8	1.1
		H(β)	486.1	2.0
		H(α)	657.2	8.8
		O	778.2	2.6
CH ₄	0.74	C	248.3	5.8
		CH	432.0	1.2
		H(β)	486.5	3.8
		C ₂ (0,0)	516.7	0.9
		H(α)	657.2	6.7
CH ₃ OH	e	C	248.2	8.0
		CH	431.3	0.8
		H(β)	487.0	1.3
		H(α)	657.0	4.3
		O	777.8	1.5
CO	0.92	C	248.3	7.2
		O	778.2	4.3
CO ₂	0.56	C	248.3	4.4
		O	777.8	2.5
C ₆ H ₆	e	C	248.3	7.1
		CH	431.5	2.1
		C ₂ (2,0)	438.1	1.0
		C ₂ (1,0)	474.1	2.2
		C ₂ (0,0)	516.9	5.1
		C ₂ (0,1)	564.0	2.3
		C ₂ (0,2)	619.6	0.5
		H(α)	657.4	0.6
		O	778.2	1.3
C ₆ H ₅ F	e	C	248.2	10.0
		CH	431.2	4.0
		C ₂ (2,0)	437.8	2.6
		C ₂ (1,0)	474.0	5.2
		C ₂ (0,0)	516.5	9.2
		C ₂ (0,1)	563.8	4.6
		C ₂ (0,2)	619.2	1.4
		H(α)	657.0	1.1

Table 1. Laser-Produced Microplasma Emissions from Various Carbon Containing Sample Molecules				
Molecule	Overall Plasma I ^a	Species ^b	Emission nm ^c	I ^d
CHCl ₃	e	C	248.3	7.9
		CCl	278.3	0.8
		CH	431.3	1.7
		H(β)	468.5	0.9
		C ₂ (0,0)	516.7	0.8
		H(α)	657.0	1.5
		Cl	726.4	0.3
		O	755.3	0.2
			809.2	0.1
			778.0	0.7
Cl ₄	e	C	248.3	9.6
		CCl	278.3	1.6
		C ₂ (0,0)	516.8	0.5
		Cl	725.8	1.1
			755.5	0.5
			809.6	0.4
			778.2	2.0
CF ₄	0.67	C	248.3	5.2
		F	623.8	1.3
			634.9	0.8
			641.5	0.9
			686.1	2.8
			691.1	2.2
			704.8	0.9
			740.7	0.8
		O	777.7	1.0

Annotations:

- Plasma emission intensities relative to strongest carbon emission (CH₃CH₂CH₃).
- The transitions listed for C₂ are (ν' , ν'').
- Approximate wavelength readings obtained directly from monochromator.
- Intensity is given in arbitrary units and is uncorrected for instrument response.
- Liquid samples (see text).

Conversely, the spectrum of benzene is dominated by the presence of a complex series of band structures. These features are found to be the various transitions of the C_2 Swan system of bands ($A^3\Pi_g \leftarrow X^3\Pi_u$);¹⁰ (2,0) at 438.1 nm, (1,0) at 474.1 nm, (0,0) at 516.9 nm, (0,1) at 564.0 nm, and (0,2) at 619.6 nm. Additional emissions noted in the benzene microplasma spectrum are CH and H_α . Spectral results similar to those obtained for benzene and propane were also obtained from microplasmas formed in the respective flows of fluorobenzene (C_6H_5F) and methane (CH_4) (see Table 1). The emission observed at approximately 777.8 nm in these spectra is attributed to atomic oxygen and is indicative of the difficulty of totally isolating the GC effluent gases from room air. One solution to this problem under evaluation is the construction of a flow cell in which the effluent gases can be probed without interference from room air.

Figure 4 displays the emission spectra of electronically excited fragments from the microplasmas generated in the flows of Freon-14 (CF_4), chloroform ($CHCl_3$) and carbon tetrachloride (CCl_4), top, middle and bottom, respectively. Upon close inspection of Figure 4, the only common feature is found to be that attributed to the emission of atomic carbon. A closer examination of the $CHCl_3$ spectrum reveals that in addition to the CH bands and the H_α and H_β lines, a new set of lines appears in the 700-825 nm region. These lines, which are assigned to the emission of atomic chlorine,^{5,11} also appear in the microplasma spectrum of CCl_4 . Furthermore, a band visible at 278.3 nm in the emission spectra of only $CHCl_3$ and CCl_4 is attributed to the $CCl A^2\Delta \leftarrow X^2\Pi$ (0,0) transitions.¹⁰ The identity of the other band at 257.7 nm common to both $CHCl_3$ and CCl_4 is as of yet unresolved.

The longer wavelength region of CF_4 (600-800 nm) is remarkable due to the presence of an elaborate set of relatively intense lines wholly attributable to atomic fluorine emission.^{5,11} As with the previous examples, Figure 4 demonstrates the species specificity of the laser-produced microplasma emission technique. Of the three compounds shown in Figure 4, conventional FID is unresponsive to both CF_4 and CCl_4 .

IV. CONCLUSION

It has long been known that many substances are not amenable to detection by conventional GC methods. Those compounds that produce little or no response in FID (e.g., O_2 , H_2 , CO, CO_2 , halogenated compounds, etc.) must therefore have some other means for detection. Presented here are qualitative laser-produced microplasma emission results which indicate that the LM-GCD offers not only broad chemical response, but also considerable chemical specificity. These results, in addition to our previous work which demonstrated considerable sensitivity potential, suggest that the LM-GCD approach is worthy of serious consideration as a universal carbon detector.

Further improvements are currently being made to the experimental apparatus. These include the replacement of the photomultiplier with an optical multichannel analyzer (OMA) which will allow for quicker data collection and the ability to take large portions of the spectrum simultaneously. Future work will concentrate on the time resolution aspects of the microplasma emission as well as on the determination of the realistic

detection limits of which the LM-GCD is capable. In general, a number of technological advances should make it possible for practical implementation of the LM-GCD. These include the development of a compact and inexpensive UV laser* as well as improvement in the UV transmission characteristics of optical fibers.

*A contract to design and construct a compact and field-worthy UV laser under the BRL SBIR Phase I program is in progress.

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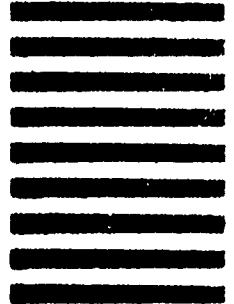


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