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The Use of the Laser Microprobe in Forensic Science

From time immemorial, technicians in the basic sciences have searched for methods of analysis that require a minimum of sample and sample preparation and that involve the least amount of destruction of the sample while obtaining the maximum information from it. The laser microprobe goes a long way toward meeting these elusive standards of performance in microspectroscopy.

Prior to the introduction of the laser microprobe as an additional tool in the forensic laboratory, spectrochemical analysis was generally carried out using 1.5 or 3.4-m emission spectrographs. The New York City Crime Laboratory employs a 3.4-m Jarrell-Ash Ebert Mount Spectrograph with 15,000 grooves per inch of grating, with a grating angle of 5.42—1st order.

This instrument separates radiant energy into an ordered arrangement according to wavelength and produces a spectrum. The intensities of the spectrum lines are proportional to the concentration of the elements present, and may be used for quantitative analysis. This information is usually recorded on 35-mm film strips or on glass photographic plates and the resulting spectrum is then viewed. Due to the spectral sensitivity, the excitation source usually selected for qualitative analysis is d-c arc with a 10-mg sample. The usual parameters employed at our laboratory for qualitative analysis are: a slit width of 10 μ m, a height of 3 mm, and burning for 15 s to 3 min (depending on the burning rate for complete decomposition of the sample). Using No. 3 Kodak spectrographic film and large electrodes, National L3951 with cup L3906, the total vaporization and determination of low levels of trace elements (impurities) in a given sample can be obtained. Samples include powders, soil, paint scrapings, metal drillings, and filings of all types, with or without graphite added. This instrumentation is used as a good qualitative and quantitative forensic tool. However, it is destructive analysis. Furthermore, the method fails to maintain the separation of individual layers in a complex sample of evidence; the normal burn often creates a prohibitive cyanogen band in the upper wavelengths of most runs; and the amount, complexity, and location of a sample actually present in a case, limit this technique.

Laser Microprobe

The instrument, a Jarrell-Ash Mark 111 45-604 laser microprobe, is actually a microscope attachment for the 1.5 and 3.4-m spectrographs. It is a high intensity, focused laser,

Presented at the 25th Annual Meeting of the American Academy of Forensic Sciences, Las Vegas, Nev., 23 Feb. 1973. Received for publication 8 Feb. 1973; revised manuscript received 28 Dec. 1973; accepted for publication 7 Jan. 1973.

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with an optical sighting system. Using a laser beam to excite and then to vaporize material from the solid state, the laser microprobe² allows any appropriate sample to be analyzed relatively quickly in a nondestructive manner. This is considered nondestructive instrumentation because a minute area (in the nanogram range) is vaporized, in comparison to the massive sample of evidence remaining.

Samples of evidence that could not be readily tested with the normal spectrograph can be easily exposed to the laser without the usual sample preparation. Considering these parameters—relatively nondestructive analysis, ease, and rapidity of testing regardless of sample size—the laser microprobe is a current, valuable forensic tool.

Laser Instrumentation

The Mark 111 laser microprobe attachment is a microscope containing two objectives ($\times 4$ and $\times 10$), mechanical microscope stage mechanisms. When the piece of evidence is optically aligned, a laser pulse is generated³ from the power unit and passes through the optical head to the electrode assembly area. The sample is then vaporized by a focused, high power, short duration laser burst. Immediate excitation of the evidence vapor is accomplished by electrical discharge between charged, carbon electrodes, National L4036, positioned above the sample. The resulting "arc" (Zonal Applications of Photons or zap) ionizes the material and produces a spectrum of the sample constituent. The elemental information in the instantaneously ionized "laser cloud" is optically transferred to the usual optical system of the spectrograph by a spherical condensing lens, preset to focus at the analytical gap in the arc stand. The spectrum continues through the normal optics of the spectrograph to the film, and the resulting spectrum is read in the normal manner. Figure 1 is a diagram of the laser microprobe.

Determination of Optimum Parameters

In an effort to maximize and to standardize operational procedures, power and aperture settings were varied while maintaining the same slit width of 100 μm , objective of $\times 4$, and development time of 4 min, using National Bureau of Standards standard for iron 1166 throughout. It was found that 100 μm produced a very broad 3100 Å (triplet) line, which was objectionable. The higher energy levels increased the diameter and depth of craters in each zap. Best results were obtained using the maximum aperture (50 μm) with the highest voltage. Such settings should have been expected, considering the microsecond duration of each zap and the extended length of the light box in the 3.4-m spectrograph. The only exception to these parameters was when hair, powdered samples, and single layer paint chips were tested. On these occasions power was initially reduced by one half, due to the fragile nature of the specimens and their ability to splatter. Power settings in these cases were changed independently as determined by the spectra obtained.

It was found that the d-c arc spectrum generally has many more points of information and better line intensities than the laser. Since there are these differences between these two modes of operation, and considering that there are presently no comparison reference tables available,⁴ Table 1 is presented as a preliminary step to fill this void.

² Present instrumentation is credited to F. Breck and J. Schuch of Jarrell-Ash, 1963.

³ The energy level of each firing (zap) is predetermined by a four-position laser and three-position excitation mode knobs on the control console.

⁴ Usual intensity references for d-c arc versus Spark arc indicated in Refs 1-3.

TABLE 1—Location and intensity of d-c arc spectra versus laser spectra of selected pure elements.

Element	Line	D-C Arc	Laser	
	Wavelength	Intensities	Zaps	Intensities
Al (4S) (alloy)	2367.1 (150R I)	heavy—broad and diffuse	1	absent
			5	light
	2372.1 (181)	heavy—broad and diffuse	1	absent
			5	absent
	2373.4 (200R I)	heavy—broad and diffuse	1	absent
			5	broad and diffuse
	2378.4 (40I)	heavy	1	absent
			5	very faint
	2568.0	very heavy—broad diffuse	1	very faint
			5	very faint—broad and diffuse
	2575.1	heavy—broad and diffuse	1	very faint
			5	light and diffuse
	2652.5 (150R I)	heavy—broad and diffuse	1	absent
			5	light and broad
	2660.4 (150R I)	heavy—broad and diffuse	1	absent
			5	light—broad and diffuse
	2669.2	light—distinct line	1	absent
			5	very light
	2816.2	distinct line	1	light and diffuse
			5	heavy—broad and diffuse
	3050.1	heavy and distinct	1	light and distinct
			5	light and diffuse
	3054.7	heavy and diffuse	1	light and diffuse
			5	light
	3057.2	heavy	1	medium
			5	light
3064.3	heavy and distinct	1	light and distinct	
		5	light and distinct	
3066.2	heavy and distinct	1	light and distinct	
		5	light and distinct	
3082.1	very broad and heavy	1	reversal	
		5	reversal	
3092.7 (1000R)	very broad and heavy	1	reversal	
3092.8 (50R)	heavy	5	reversal	
3586.9	block cyanogen band	1	broad and diffuse	
		5	broad and diffuse	
3944.1 (2000R)	black cyanogen	1	reversal	
		5	reversal	
3961.5 (3000R)	black cyanogen	1	reversal	
		5	reversal	
Mn (1.2%)	2305 (40)	faint line	1	absent
			5	absent
	2472.9 (125)	heavy	1	absent
			5	absent
	2490.6 (125)	heavy	1	absent
			5	absent
	2563.6 (25)	medium heavy	1	absent
			5	light and medium
	2572.8 (200)	medium	1	absent
			5	absent
	2576.1 (300R)	heavy and diffuse	1	light
		5	medium and heavy	
2584.3 (150)	heavy	1	absent	
		5	very faint	
2592.9 (150)	medium heavy	1	absent	
		5	absent	

(Continued)

TABLE 1—Continued.

Element	Line	D-C Arc	Laser	
	Wavelength	Intensities	Zaps	Intensities
Mn (1.2%) (Cont.)	2593.7 (200)	heavy	1	light
			5	medium
	2595.8 (200)	heavy	1	absent
			5	very faint
	2605.7 (100R)	very heavy	1	very light
			5	heavy
	2618.1 (50)	medium	1	absent
			5	absent
	2618.9 (40)	medium	1	absent
			5	light and medium
	2619.5 (125)	light	1	absent
			5	absent
	2622.9 (200)	light and medium	1	absent
			5	absent
	2638.2 (25)	medium	1	absent
			5	light
	2666.8	light	1	absent
			5	light
	2672.1	light	1	light
			5	absent
	2692.7 (150)	light and broad	1	absent
			5	very faint
	2695.4 (100)	light	1	absent
			5	very faint
	2701.7 (150)	medium	1	absent
			5	light
	2704.0 (100)	light	1	absent
			5	very light
	2705.7 (25)	medium	1	absent
			5	light
	2707.5 (10)	light	1	absent
			5	light
	2726.1 (300)	light	1	absent
			5	light
	2794.8 (1000R)	Mg interference	1	absent
			5	absent
2798.3 (800R)	very heavy	1	medium	
		5	heavy	
2801.1 (600R)	very heavy and broad	1	absent	
		5	light and broad	
2933.1	heavy	1	light	
		5	light	
2939.3 (50)	heavy	1	light	
		5	light	
2949.2 (100)	heavy	1	medium and light	
		5	heavy	
3054.4 (75)	very heavy	1	light	
		5	heavy	
3066.0 (75)	heavy	1	light	
		5	medium and heavy	
3070.3 (100)	medium and heavy	1	absent	
		5	absent	
3212.9 (100)	heavy	1	absent	
		5	very light	
3228.1 (100)	heavy	1	absent	
		5	medium	
3236.8 (75)	heavy	1	very faint	
		5	medium	
3243.8 (100)	heavy	1	absent	
		5	light	

(Continued)

TABLE 1—Continued.

Element	Line	D-C Arc	Laser	
	Wavelength	Intensities	Zaps	Intensities
Mn (1.2%) (Cont.)	3247.5 (125)	very heavy	1	very light
			5	medium and heavy
	3248.5 (100)	heavy	1	absent
			5	light
	3442.0 (75)	medium	1	medium
			5	heavy
	3460.3 (60)	medium	1	light
			5	heavy
	3474.0 (20)	medium	1	light
			5	heavy
	3482.9 (50)	medium	1	light
			5	heavy
	3488.7 (50)	medium	1	light
			5	heavy
	3493.0 (1000)	light	1	absent
			5	absent
	3495.8 (25)	medium	1	very light
			5	medium
	3497.5 (15)	light	1	absent
			5	light
	3547.8 (40)	black cyanogen	1	very light
			5	medium and heavy
	3569.5 (25)	black cyanogen	1	light and broad
			5	medium and broad
	3577.9 (50)	black cyanogen	1	absent
			5	light and medium
	4018.1 (80)	black cyanogen	1	very faint
			5	medium
	4030.8 (500)	black cyanogen	1	medium and light
			5	heavy
4035.7 (50)	black cyanogen	1	faint	
		5	light	
4048.8 (60)	black cyanogen	1	very faint	
		5	medium	
4055.5 (80)	black cyanogen	1	very light	
		5	heavy	
4063.5 (100)	black cyanogen	1	faint	
		5	medium	
4079.2 (50)	black cyanogen	1	very faint	
		5	medium	
4082.9 (80)	black cyanogen	1	absent	
		5	medium	
4083.6 (90)	black cyanogen	1	absent	
		5	medium	
Mg (1.0%)	2632.9 (10)	medium	1	absent
			5	light
	2660.8 (40)	very broad—dark and diffuse	1	absent
			5	medium—broad and diffuse
	2672.5 (20)	medium	1	absent
			5	light
	2676.7 (30)	heavy	1	absent
			5	light
	2795.5 (150)	very dark	1	heavy
		5	dark and broad	
2802.7 (150)	dark and broad	1	dark	
		5	dark and broad	
2852.1 (300)	very dark—broad and diffuse	1	very light	
		5	light	

(Continued)

TABLE 1—Continued.

Element	Line	D-C Arc		Laser		
	Wavelength	Intensities	Zaps	Intensities		
Mg (1.0%) (Cont.)	2928.8 (25)	dark	1	very light		
	2936.5 (20)	dark	5	dark		
Zn (5.6%) 75S Alloy)	3283.3 (500)	very heavy and broad	1	very light		
	3302.6 (800)	very dark and broad	5	medium		
	3345.0 (800)		very dark and broad	1	very light	
				5	medium—broad and diffuse	

For practical purposes it was found that a 1-s burn in the d-c arc mode is roughly equivalent to five zaps. Therefore, when one zap is appropriate, due to the delicate nature or minute size of the evidence, a much lighter laser spectrum is seen. The examination of such evidence is now possible due to the use of a new, faster 103-0 film. Superior d-c burns (sharper information, shorter exposures, 1-3 s versus 1-3 min, and far less cyanogen bands) were also accomplished using this 103-0 film, in contrast to the more standard

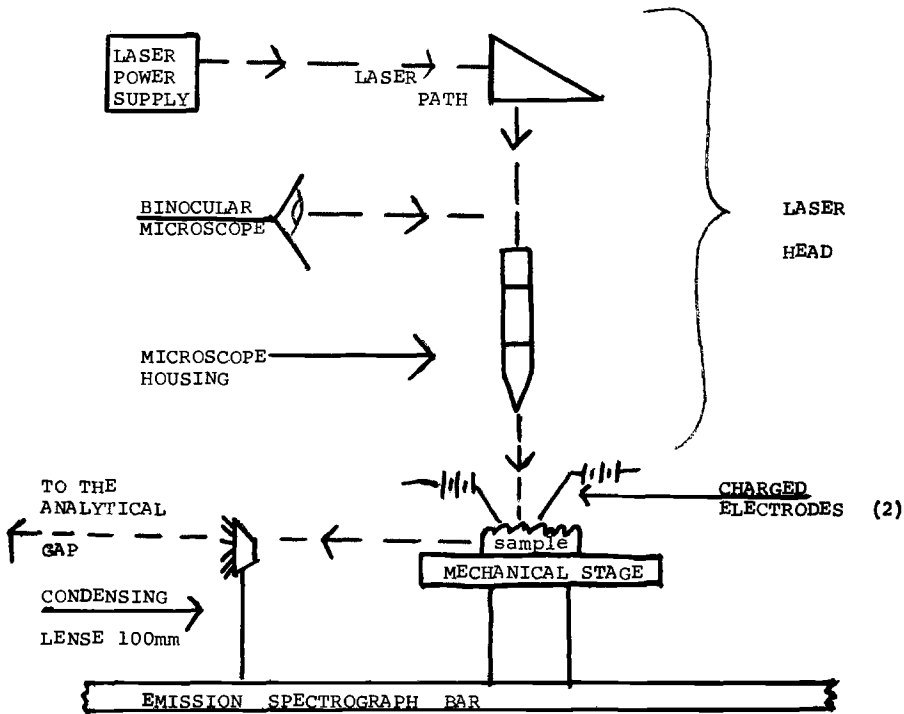


FIG. 1—Diagram of laser microprobe.

No. 3 film. The presence or absence of persistent lines of known elements in known versus unknown samples can easily be compared. The film has great sensitivity at the lower wavelengths, indicates many more iron lines, and is more sensitive for carbon.

General Evidence Examinations

The laser attachment for the emission spectrograph permits positioning with pinpoint accuracy. It is excellent for *in situ* analysis of articles of evidence that require single layer (top or bottom) examinations. Microsamples need not be removed from the evidence, and bulky evidence that would have required mechanical and time-consuming removal procedures, can now be examined with ease. Single layer specimens found on innumerable articles can be examined, namely: paint on wristwatches, shoes, and water pipes; gunshot residues (lead) on clothing; fragments of glass; particles contained in soil samples; surface examinations of precious metals, coins, shields, and similar articles of value; and minute areas of interest, such as solder joints. Even hair specimens contained on articles of evidence can be studied. In these examinations it was found that at maximum power settings at least five zaps were generally required to obtain satisfactory spectra. Rasberry [4,5] suggested that a mirror be placed behind the source to intensify this light and obtain satisfactory spectrum.

Problem Areas

For many years our profession has been attempting to develop specific methodology whereby paint samples from an auto accident, or gunshot residues on a suspect's hand, could be examined to determine conclusively whether the paint did in fact come from a specific auto, or whether the suspect did in fact recently fire a handgun. Such conclusive findings could have a major impact on particular investigations if these questions could be answered.

Paint Examination

In paint cases a multilayered chip of paint, rather than a smear, can be examined microscopically. The number of colored layers, the relative thickness of each layer, the sequence of colored layers, and any common surface imperfections (optical or UV) are noted. A destructive spectrographic analysis for total elemental content is then usually conducted. This procedure, *in toto*, establishes that two similar paint samples have similar composition, but cannot firmly establish that two samples had a common origin. To date, only a "piece match" of an irregularly shaped object compared to the known, in all the above aspects, can be considered conclusive. The laser microprobe was thought to be a worthwhile tool to apply to this problem.

It was found that cross-sectional multilayered examinations of paint chips less than 50 μm could not be accomplished with satisfactory spectra without contamination from adjacent layers. One cannot "burn through" in a vertical direction, from layer to layer, in a multilayered sample of interest without strong cross-contamination or obliterated vision or both. The former could not be accomplished due to the amount of energy required to transverse the long light box of the 3.4-m spectrograph. The latter is due to the heavy "carbonization" [4-6] of the sample from the charged electrodes.

Gunshot Residues

One of the early tests for gunshot residues on a suspect's hands was the dermal nitrate or paraffin test. For more than twenty years the New York City Crime Laboratory, among others, has rejected this test due to the ease with which many people are exposed to nitrates. Contamination may occur from fertilizers, smoking, urine, etc. In 1958 the Harrison test [7] was developed, based on the presence of lead, barium, and antimony in primer residues. The color reactions are supposed to indicate the presence or absence of these elements. The test was found to be very subjective. False positives and false negatives were obtained. Specific color reactions overlapped between lead and antimony and the color reactions could be duplicated with other disassociated chemicals. (For example, silver chloride, cerium sulfate, and cupric and cuprous ions produce a yellow color with tri-phenyl methylarsonium iodide. Strontium, silver nitrates, and stannous chloride produce colors with sodium rhodizonate.) The only fairly consistent factor was the occasional presence of lead on a known shooter's hand and a negative finding for lead on the nonshooting hand. Needless to say, such a test should not be used to deprive a person of his liberty.

In the mid-1960's neutron activation analysis was thought to be the answer to this perplexing situation. To date, our laboratory has found this technique most unsatisfactory. Of late, nine gunshot test cases have been submitted to other authorities with inconclusive results in all instances.

The laser microprobe was put to this test in a further effort to solve this complicated problem. Known 1 percent solutions of barium, antimony, and lead were exposed to the laser with positive results. However, on further tests the same questionable results (false positives and false negatives from actual test-firings) were obtained. It would seem that these last two techniques (Harrison or neutron activation analysis) might have more merit on their own as investigative leads, if the actual collection methods could somehow be improved.⁵ It is thought that this latter area needs much attention prior to discarding these techniques as being too insensitive.

Auxiliary Equipment

Excellent attachments, Polaroid cameras, and group observation viewing screens are available to record photographically and to see any of the above articles of interest, just prior to or immediately after firing. The overall mechanics are quick and simple.

Notice of Caution

No one should look at the instrument when firing nor observe a direct reflection of the laser. Window shades or other covering should be provided between the operator and any viewing by an accidental observer. The manufacturer has placed a mechanical safety lock that does prevent accidental firing of the laser while the operator is viewing the evidence or is otherwise occupied. Promotional literature stresses the use of "safety glasses," which in actual practice are not sufficient. All individuals should look away from the instrument whether wearing the "safety glasses" or not. Care should be taken so that the instrument is not energized (zapped) in a darkened room, as the human eye is dilated in such a surrounding and thereby even more exposed to injury, due to the increased sharpness of the laser and the retinal area then exposed.

⁵ Collection methods as per Hoffman [8] or adhesive tape were used to mechanically remove these residues.

Qualitative versus Quantitative Analysis

The laser microprobe has been an instrument of ever-increasing interest since the early 1960's. Ever since, individuals have varied opinions regarding the quantitative properties of this tool. When using this device as an on-line forensic tool it was found to be only semiquantitative, since no given forensic sample is weighed and then burned to completion, nor is there at present a method to determine accurately how much sample was vaporized in any given zap. Intermittent electrode discharge, and the need for multiple firings on the surface area of a sample to obtain satisfactory spectrum, are also serious limiting factors of this technique. No effort was made by these authors to measure any variation in intensity (total energy at a given power setting) of each zap over any given period of time. This also could be a limiting factor for any quantitation. At best, the laser microprobe can only be considered comparative for forensic purposes.

Areas Requiring Improvement

The overall mechanics of operation are quick and simple, but there seems to be a need for a few refinements or modifications, as follows.

1. Higher potential for the laser and across the two charged carbon electrodes, to render a stronger and brighter spectrum, is required when using the larger instruments. Many times no excitation was obtained due to insufficient sample vapor at the electrode gap. A longer condensing lens, at least twice the present 100 mm, should be considered, in order to provide the increased light intensity needed.

2. Better placement of the fine focus knob to allow easier operator access and operation is needed.

3. The present apparatus is not truly parfocal due to physical obstruction and placement of the charged electrodes. Each time the objectives need to be switched, the electrodes must be removed. If the electrodes could be redesigned, the two objectives could be more easily employed.

4. A disposable polystyrene cover for each objective should be installed. The suggested jerry-built cover system to protect the objectives (Mylar or microscope coverglass slide) is clumsy, inadequate, frustrating, and time-consuming to use.

5. Present optics, hopefully, could be improved. A comparison with the same nongloss surface of a given article of evidence (gunshot residue on cloth, multilayered flat paint) under a standard compound microscope of the same magnification, leaves much to be desired.

6. It is thought that some type of enclosure surrounding the charged electrodes would have merit. This would allow the introduction of inert gases to suppress the heavy "carbonization" one encounters when one attempts to burn through a multilayered specimen or zap an area of evidence a second time in the identical spot. This would be the same methodology used to suppress the cyanogen bands with the standard spectrograph.

Conclusions

The laser microprobe was found to be a useful addition to the tools presently available to the forensic scientist. The present state of the art clearly indicates that this instrumentation cannot be considered a panacea, despite the wide variety of application demonstrated in this study. This technique does enable investigators to examine minute or remote pieces of evidence, which in the past would have been totally disregarded or at best extremely difficult to analyze. This is an immense improvement over present instrumentation.

Acknowledgment

We gratefully acknowledge the distribution of this study by the Law Enforcement Assistance Administration through the New York State Office of Criminal Justice and the Criminal Justice Co-ordinating Counsel of the City of New York, under Grant C 58477. The study was conducted at the New York City Crime Laboratory.

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