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Sample Methodology for Laser Microprobe Analysis

Trace metal identification and quantitation have been widely used in criminalistics to aid in investigations and in court testimony. Types of samples analyzed range from automobile paint to primer residues. Several techniques of trace metal detection and quantitation have been proposed and are currently in common use or under active investigation [1,2]. An ideal criminalistic method might be characterized as having: (1) low overall sample degradation from the analysis, (2) wide range of elements determined, (3) high quantitation accuracy, (4) high sensitivity, and (5) little or no sample preparation for analysis.

While traditional methods of emission spectrography meet Criteria 2 and 4, laser emission spectrography (laser microprobe) appears, from the literature [3], to meet Criteria 1, 2, 4, and 5. We are presenting results of a preliminary investigation which examines this proposition. Others have investigated the mechanisms of laser sample interaction [4] and, for the purpose of this investigation, the laser's only function is to provide a sample for emission excitation.

Apparatus and Equipment

A Jarrell-Ash Mark II Laser Microprobe which has a Neodymium laser, emission at 1.06 μm , was used. Laser power can be attenuated by aperturing the beam, lowering the potential of the laser power supply, or by inserting a 50 percent neutral density filter in the unfocused laser beam. The laser is focused on the sample through a noncemented $\times 10$ microscope objective. The lower lens surface of the objective must be protected from sample spatter to prevent loss of laser power, to prevent possible pitting or cracking of the lens surface, and to retain necessary optical clarity for positioning the sample. We have found that a glass cover slip, cut and glued to the metal housing of the objective, provides an easily changed cover. Alignment of the sample and laser with the cross hair of the eyepiece is critical, especially when small samples are to be analyzed. This alignment must be checked periodically and the laser spot position can be easily changed by adjusting the mounting of the gold deflecting mirror in the microscope housing. We use a small piece of iron stock both to check spot position and to place an iron calibration spectra on the film.

National L3775 SPK graphite counter electrodes were mounted as cross-excitation electrodes. Surface contaminants, such as copper, were removed by sampling a third

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counter electrode. For convenience, the "cleaning" electrode is held in position with a hemostat and can be used to clean a large number of electrode pairs before being discarded. An electrode blank spectra is also recorded since cyanogen, carbon, and electrode contaminant spectral lines must not be confused with the sample's spectral lines.

Spectral analysis was accomplished with a Wadsworth 1.5-m spectrometer with a grating ruled at 590 grooves/mm (dispersion 5.4 Å/mm) and Kodak 103-0 film. This gives an effective wavelength range of 2200 to 5000 Å. The spectrograph entrance slit, bilateral adjustable set at 50 μm, was uniformly illuminated with a combination of a 250-mm focal length spherical quartz lens and a 100-mm focal length, 30-mm diameter cylindrical quartz lens. A 1-mm slit height was used and the camera was racked at 2-mm intervals, thus giving a maximum of 12 spectra per film. Typically, three exposures per racking of the film were made to increase sensitivity. With 103-0 film, we found up to 6 exposures could be made without troublesome background darkening. The film was developed according to manufacturer's specifications using a Jarrell-Ash 34-300 film developer and read with a Jarrell-Ash 21-300 microphotometer comparator. A Jarrell-Ash master film was used for wavelength alignment and spectral line identification.

Samples included Jarrell-Ash 367-10 wear oil standards in a silicon oil base, British Chemical Standards No. 316 8 percent aluminum-magnesium alloy, National L4100 spectroscopic graphite powder, and Jarrell-Ash 367-60 Spectro Quality (S.Q.) powders in a graphite matrix. Paint samples were obtained from the Illinois Bureau of Identification, Joliet, Ill. The rest of the materials were scavenged from the University campus. Alpha Teflon[®] spaghetti, grade TFT 200 natural color, National L4036 cup electrodes, Duco cement, and 3-M tape were used as sample holders.

Results and Discussion

Samples are classified as three types: solids, semisolids, and liquids.

Solids

Most solids require no prior preparation other than removal of obvious extraneous surface contaminants. Problems are encountered if the solid is: (1) finely divided, (2) highly reflective, (3) transparent to the laser pulse, or (4) in an indentation deeper than 1.5 mm. Problem 1 will be discussed with semisolids. Problems 2 and 3 are encountered with materials such as glass, highly polished metals, and plastics.

Absorption problems, either reflection or transmittance, are most easily detected if the cross-excitation electrodes do not discharge. When the laser vaporizes an adequate sample, there are enough ions to cause the electrodes to discharge and emit an audible crack. Sometimes an inadequate sample cannot be diagnosed until the film is developed. Here the analyst must have experience in working with the specific sample type (or with known materials that are similar in physical characteristics to the sample) to diagnose accurately that the apparent absence of certain elements is the result of sampling difficulties, rather than to conclude that the elements are absent.

Problems 2 and 3 are easily solved by placing a small amount of spectroscopic graphite powder on the sample. The graphite will absorb laser energy and transfer enough energy to vaporize an adequate sample for analysis. We have been successful in analyzing laser transparent glasses by focusing the laser on one graphite particle.

Problem 4 results from the configuration of the instrumentation. The sample must be positioned 1.5 mm below the cross-excitation electrodes for optimal performance and the

spark between the cross-excitation electrodes is focused on the spectrograph's entrance slit. Therefore, by focusing the laser on a sample which is in a 2-mm indentation or cavity, light from the spark will be effectively blocked from reaching the entrance slit. This problem is solved by removing the sample and remounting as a semisolid.

Painted surfaces or paint chips need additional comment because these are homogenous in only two axes and very restrictive in the third, whereas other solids are treated as being homogeneous in all three axes. Here the problem is to analyze one layer without sampling other layers or supporting surface. We have found that paints need much less laser energy to vaporize an adequate sample. Because there is the requirement of not exceeding the depth of the layer, we have found that aperturing down to a smaller spot size does not always solve the problem. Also, when the spot size is reduced too much, inadequate sampling occurs and a spot size of 400 μm with the 50 percent neutral density filter is still too deep. Use of other neutral density filters is currently being investigated. If the paint chip has thick enough layers, then layer analysis can be performed by mounting the chip on its side (here depth should not present a problem). No matter which procedure is followed, the analyst must examine the specimen after analysis, if possible, to determine whether or not multiple layers have been sampled.

Semisolids

We define semisolids as small samples, powders or chips, and very viscous liquids. Examples are metal filings, loose soils, putty, and greases. These materials may not only have absorption or reflection properties similar to solids, but they also have the property of being easily scattered by the laser pulse or the cross-excitation electrode discharge or both. In the latter case, most of the laser energy is dissipated in moving around rather than vaporizing the sample. Examination of a powder packed in a cup electrode reveals a crater that is many times deeper than wide, which is not observed for solids. Using standard S.Q. powders in a graphite matrix, packed in a cup electrode or pelletized, we find an unacceptably low number of elements detected at the 0.1 percent level. Scotch tape and Duco cement work equally as well in containing the sample. Table 1 gives the results for the S.Q. powders for a selected set of elements.

The sample is sprinkled on a drop of Duco cement which is placed on either a microscope slide or carbon electrode. It is important not to cover the sample with Duco cement. A dummy sample of spectrographic graphite should be used as control. Scotch tape should be used sticky side up as the tape is transparent to the laser and may entrap most of the vaporized sample. A spectrographic graphite sample should be used as control. Highly reflective powders can be analyzed by mounting with cement or tape, then sprinkling with graphite powder. Table 2 gives results for this type of analysis. Again, the analyst should examine the sample after analysis to be sure the support was not sampled. A carbon electrode, rather than a glass slide, would be preferred if there is a high probability of the support also being sampled. Duco cement on a glass slide does not appear to add any extraneous lines to the electrode blank spectra.

When putty, grease, or lipstick packed in a cup electrode is subjected to the laser pulse, the remaining material resembles a small volcano with a crater that runs its entire depth. Duco cement and Scotch tape do not work as well in containing putty or grease as powders. We have found that white cotton wiping rags provide a good surface for sample containment. The sample is placed on the cloth surface as a smear and then analyzed. A good ashless filter paper may also be suitable, but whatever the support it should be analyzed for metal content.

TABLE I—Selected elements detected in S.Q. powders^a.

%	Ag	Al	As	Au	B	Ba	Be	Ca ^b	Co	Cr	Cu	Fe	Mg ^b	Mn	Mo	Ni	Pb	Sb	Si	Sn	Ti	V	
0.1	+	+	0	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
0.01	+	+	0	-	-	-	+	+	+	+	+	+	+	+	-	-	-	0	+	+	0	+	+
0.001	0	-	-	-	-	-	+	+	-	-	+	-	+	-	-	-	-	-	-	-	-	-	-
0.0001	-	-	-	-	-	-	+	+	-	-	-	-	+	-	-	-	-	-	-	-	-	-	-

+ 2 or more spectral lines observed
 0 1 spectral line observed
 - no lines observed

^a Two exposures each, mounted on Duco Cement.

^b Line intensities greater than blank.

TABLE 2—Elements detected in British Chemical Standards No. 316 8Al–Mg alloy^a.

	Al	Zn	Mn	Cu	Si	Fe	Ni	Pb	Sn
Observed % Element	+	+	+	+	+	–	–	–	–
	8.01	0.68	0.28	0.040	0.05	0.009	0.004	Trace	Trace

+ two or more lines observed.

– no lines observed

^a Sample mounted on Duco Cement, 2 exposures.

Liquids

Liquids are by far the most difficult sample type to analyze with the laser microprobe. The problems of transparency and sample containment are acute. Using wear metal oil standards in a silicon oil matrix as sample, we found this liquid could not be analyzed when placed in a cup electrode, when a single drop was placed on a third electrode, or when it was coated on graphite powder. Even silicon was not detected. In the case of the cup electrode, the sample wax completely ejected and splattered on the surrounding surfaces—electrodes, holder, and microscope objective.

Since solids are easily analyzed, the liquid sample was solidified with liquid nitrogen and analyzed. Table 3 gives the results of this technique for wear metal standards. Unfortunately, the freezing technique has serious disadvantages: condensation of water and ice on the sample and, possibly, the creation of concentration gradients.

TABLE 3—Analysis of wear metal standards using the freezing technique^a.

ppm	Al	Cr	Cu	Fe	Mg ^b	Ni	Sn	Pb	Ag
100	+	+	+	+	+	+	–	–	^c
50	–	–	+	–	+	–	–	–	^c
20	–	–	–	–	+	–	–	–	–

+ at least two lines observed

– no lines observed

^a Three exposures, refrozen after each exposure.^b Intensity of lines greater than blank.^c Not present in solution.

Using the notion of sample confinement as yielding a successful analysis, we explored the use of a capillary tube. Teflon[®] was chosen over glass because of its inertness and low metal content. Table 4 gives the results of this technique for wear metal standards.

TABLE 4—Analysis of wear metal standards using the Teflon[®] capillary sample technique^a.

ppm	Al	Cr	Cu	Fe	Mg ^b	Ni	Sn	Pb	Ag
100	+	+	+	–	+	+	+	+	^c
50	+	+	+	–	+	–	–	–	^c
20	+	+	+	–	+	–	–	–	+

+ at least 2 lines observed

– no lines observed

^a Three exposures with fresh liquid for each exposure.^b Line intensities greater than blank.^c Not present in solution.

Teflon[®] spaghetti, sold as wire insulation, is readily available and appears to be relatively free of inorganics. B&S Gage 28 was chosen since it slips over the needle of the 10- μ l syringe. A sample can be drawn from the bulk liquid. When a sufficiently long piece of Teflon[®] is used, the sample never enters the syringe. The laser is focused on the liquid in the tip of the capillary and if the sample is transparent, a few particles of graphite are floated on the liquid surface. After sampling, it is an easy matter to force more sample to the end of the capillary for another exposure.

The laser microprobe is readily used with a wide variety of sample types and this instrumental technique requires little or no sample preparation. More extensive accuracy and sensitivity studies are currently underway. We do not care to speculate about the sensitivity and accuracy of the technique at this time, because the data given in this paper are from films read only by eye. We have found that sensitivity is increased by photometrically scanning the film and recording the photomultiplier output. Realizing that the criminalist does not usually have prior knowledge of the elemental composition of the sample, and that a pure laser emission process may yield unexpected spectral lines, no identifications were made using lines other than those previously published as the most sensitive [5] or when less than two lines were present, except where noted.

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