XVI Laser Induced Breakdown Spectroscopy

(From: John Green (ulao10@gmail.com).)

Laser Induced Breakdown Spectroscopy (LIBS) involves directing a very high power very short duration laser pulse at a target specimen which causes a tiny amount of the target to be ablated forming a plume of material which absorbs energy from the laser pulse ionizing some of the vapor. The ionized (plasma) vapor then produces light with very distinct wavelengths which can be analyzed to determine the composition of the target as shown in Principles of Laser

LIBS is sometimes called Laser Induced Plasma Spectroscopy (LIPS), which I personally prefer, but LIBS is widely accepted. LIBS is a type of atomic emission spectroscopy and is fundamentally emission spectroscopy which you may have seen demonstrated in high school or college chemistry or physics class. In that case an unknown element is introduced into a high temperature flame then a spectroscope is used to produce a spectrum which can be analyzed to determine the unknown element. This method can be extremely sensitive especially for certain elements e.g. alkali metals. Drawbacks are to analyze some elements very high flame temperatures repeatable results the unknown has to be introduced in a controlled manner. Usually this is as an atomized solution. Another variation is inductively coupled plasma spectroscopy but here rigid vacuum and extensive sample preparation are required. to have the advantages of little or no sample preparation, little damage to the specimen, high sensitivity to nearly all elements, and stand off operation.

(From: Sam.)

Here are two DIY examples. John Green (who wrote the above introduction) first emailed me about his system using the SSY1 laser. Subsequently, Jan Beck built one also using an SSY1.

1. (From: John Green (ulao10@gmail.com).)

   I have an interest in geology but I'm neither much of a mineralogist nor much of a petrologist. So it is often elemental composition of a particular sample. There have long been tests that one can perform to determine if contains a particular element but they are the range of elements they can be used for involve equipment that is far too expensive for the amateur. After surveying numerous possibilities I identified one technology that I thought might be within the price range an yet be useful for a wide range of elements That technology is LIBS.

   The system described here hits the target with a pulse of infrared radiation (1064 nm) lasting a few nanoseconds but delivering nearly a gigawatt per square centimeter on a very small area for that brief interval. This power (maybe 10 millijoules) vaporizes a tiny volume of the material. The initial spark that is created may reach 100,000 K and radiates a lot of energy peaking around 28 nanometers which is extreme ultraviolet bordering on soft X-rays. Much of this energy is absorbed in the plume of vaporized material breaking chemical bonds and ionizing atoms. As time goes on this plasma expands at supersonic velocity and begins to cool. As it cools electrons begin to re-combine with atoms. produces the line spectra that we are looking for and begins around 1 to 5 microseconds after the laser pulse and continues for as long as hundreds of microseconds.

Upon selecting LIBS as a means to accomplish my goal I first did some research to determine the requirements in terms of laser power, spectral sensitivity, and resolution. The laser would meet the requirements and cost considered reasonable. My research also indicated that a section of a DVD disc would suffice as a diffraction grating at least for the purpose of evaluating the usefulness of such a system.

This system was designed to be simple and economical to produce mainly with simple hand tools and from commonly and cheaply available materials and parts. The semi-finished version is shown in John Green's LIBS System. There are some exceptions. Most people won't have a variac handy but a small 3 amp variac can be bought for less than $40. I happened to have a spherical concave mirror on hand so I used it. This mirror does not have to be a high quality optical component it just has to be capable of projecting an image. I found a small bench lathe to be practically indispensable in manufacturing the spectrometer components from 1-1/2″ PVC pipe. I am sure however that a resourceful individual who is good with hand tools can find ways of making these parts as extreme precision is not required. I also designed each subsystem to be adjustable because I knew that during the development process many changes would be required and that they might depend on some parameter in another subsystem so making it adjustable meant that I didn't have to rebuild it. I also bought the pulse forming network and trigger transformer from Meredith Instruments as I wanted a reliable system and military stuff is generally pretty solid. Both are pretty cheap (under $40 ea. from Meredith Instruments, Feb. 2014).

The base of the entire system is mounted on a piece of 1/2″plywood which is approximately 2 ft by 3 ft. The Laser assembly support (1″ aluminum square tube, Lowes item 216099) is mounted normal to this with 4, 4″ zinc braces (Lowes item 19165). This provides stable support for the laser while allowing it to be adjustable.

The laser itself is mounted on a 1/2″ piece of plywood approximately 13″ by 4-1/2″ cut to fit the cover (12″ plastic mud pan, (Lowes item# 58140). The two black cable clamps originally held a cat-toy laser (very Cheap) that functioned as a targeting beam, bore sighted to the main beam, however several of them each slowly lost power after a couple hundred shots by the main laser

(I think the light from the laser somehow destroys them). The main laser should be parallel to the aluminum tube so the beam doesn't wander as the laser height is adjusted. Below the laser assembly consisting of the grey tube which 3/4″ PVC electrical conduit which was turned on the lathe to provide a snug fit into the next PVC pipe to enable focusing. The next part is a short length of 1inch PVC plumbing pipe which in turn fits tightly into a 1 inch coupling. A grove was cut inside the 1 inch coupling then a section just less than half the circumference was cut out to allow lenses to be changed. The lenses themselves which snap in and out of the coupling easily are components I used a set of cheap eye loupes from Harbor Freight (item # 98722) said to be 2x, 3x, 5x, 7x, & 10x and priced at $1.99 (Feb. 2014). I have never actually measured the focal lengths of these lenses and don't really care. I am currently using the 3x lens.

The next assembly is the sample table. The table itself is made from a plastic conduit box (less than $1.00 at any hardware store). The main complication was that a cutout had to be made to clear the mirror. Otherwise it is Masonite with a length of 10-24 threaded rod held captive at the top and bottom with a coupling nut epoxied to the table such that the table can be raised and lowered by turning

The next assembly is the spectrometer including the concave mirror and camera. The mirror is used because it significantly increases the amount of light entering the spectroscope slit. While evaluating the efficacy of the mirror I found that it provided a power gain of approximately 6 compared to placing the slit 3/8″ from the spark. In this case the source of the light rays is placed between the focus of the mirror so that it forms a some greater distance. For an explanation Wikipedia Curved Mirror. Again the placement of these components is not critical and can be varied to suit conditions. The spectrometer is constructed of 1-1/2″ Plumbing PVC pipe. The slit was produced by facing a PVC cap (Lowes item # 260594) on the lathe. Since the interior surface of the cap is domed the facing operation leaves a round hole and a convenient flat surface to which razor blades may be glued. A length of pipe connects the slit to the holder forthe diffraction grating. This length is not critical but a shorter length provides while a longer pipe produces a higher resolution spectrum. I chose a full optical path length of approximately 13 inches which is just a little longer than the minimum focal distance of my camera lens. The other end of the spectrograph was constructed from a inch PVC ″Y″ fitting (Lowes part # 23377). The 43 degree angle (2-3 degrees to the camera lens axis) is fairly critical (+/-1 degrees) if you want the spectrum in the center of the camera field of view. The section of DVD is to be placed here. Tape it in place to begin with so you can adjust it as needed to obtain a straight level spectrum with respect to the horizontal image plane. The inside (spindle center) of the DVD should toward the slit side of the ″Y″. The other cut on the ″Y″ is not terribly critical because it simply interfaces with the camera lens. The base for the spectrograph assembly is cut from a piece of 1/2″ inch plywood and pivoted on one end. The camera I am using is a Nikon D3000 with Nicor 18-55 mm zoom lens and I have been shooting max zoom (55 mm) f/5.6 ASA 1600 0.5-30 seconds. Focus is very critical. The inside of all spectrometer components should be painted flat black to reduce reflections.

Now for the power supply. WARNING: LETHAL OUTSIDE THE POWER SUPPLY. You have been warned, if you are not sure that you know what you are doing don't try with the knowledge that kids and cats would be around. That's why you have to use a screwdriver to open the power supply. Also note the warning labels on the device. Also notice is constructed inside a wooden box as shown in John Green's SSY1 Power Supply. Not exactly fire safe. Find a better way.

The fundamental power is provided from 120 autotransformer (Variac) which is my only means of adjusting flash tube voltage and thus laser radiation fluence. I scrounged a transformer from an old microwave oven. These things are manufactured cheaply (but not sold cheaply) and have two secondary windings. A filament winding (which is not used but could be) and a high voltage (about 2 kV) which I used to provide high voltage to the pulse forming network. Warning, one side of the high voltage winding is usually grounded to the transformer housing. I also added a new secondary of about 40 turns (as I remember) because I anticipated the need for low voltages for other functions. The only components I had to buy for this were the pulse forming network and the trigger circuit (both from Meredith Instruments, PFN-1 $35.00 , SSY-1-XFM $25.00, Feb 2014) and the High voltage full wave rectifier (Mouser part # 844-GBPC3512W). I do not at this time have a circuit diagram however the only complication in this circuit is the low voltage circuit and regulators. Otherwise the circuit is straightforward and well documented elsewhere in Sam's Laser FAQ.

At this point I must point out what I consider to be the most important shortcoming of this system. As noted above, the initial spark produces a lot of radiation. outside the narrow window to which the camera is sensitive (visible light) however a lot of such radiation nevertheless gets through. This radiation is essentially black body radiation (like that from the Sun or an incandescent light bulb) and is worthless for our purposes and is in fact quite detrimental to goal of obtaining a line spectrum. Expensive professional LIBS systems have ways of eliminating this radiation mostly by waiting a microsecond or two before turning on the light sensing device. There are (as far as I know) no cheap options for doing this. We are working on possible solutions but so far nothing looks very promising and that is one of the main reasons for this document. By interesting others we might get more minds working on the problem. This shortcoming however does not totally invalidate the method as I shall try to demonstrate.

I have taken hundreds of spectra involving the process of developing this instrument which speaks well for the longevity of the laser components. I find I typically have to take between 10 and 30 spectrum. Individual lines of different elements vary greatly in power, for example while trying to get a spectrum of the sodium D line to assess the resolving of the present setup I had to keep reducing the number of shots of sodium chloride till I finally got a usable spectrum at 3 shots. Compare this to the sodium chloride spectrum which required 15 shots. In other cases I have had to take as many as 60 shots. The instrument became useful only after it was component parts were rigidly fixed.

Once the system became usable I began by building a spectrum library of elements I had on hand. Where possible is not always easy to find whether a particular sample is pure (or at least nearly pure) unless one buys them from reputable suppliers, and that gets expensive. The composition of coins for example is well documented. Otherwise I used what was available and as time goes on I will refine these spectra. One might be inclined to ask "Why not use spectral libraries available, for example, do but these were usually produced with very sensitive specialized equipment and are fine for locating specific lines but many elements produce a "forrest of lines" and it is simpler to make comparisons to spectra produced on the same system. With was time to try some unknowns. The first sample I tried was a mineral called sodalite. The chemical formula for Wikipedia as Na8(Al6Si6O24)Cl2 . The details of this elude me at present and I must brush up a bit (a lot) on chemistry but I think the strength of lines depends on mole fraction. Regardless one can clearly see that sodium, aluminum, and silicon are all significant components of this mineral. So what does the spectrum of sodalite look like and how does it compare to the components? See Several LIBS Spectra.

Let's do one more. I have in my collection contains grains of kyanite (Al2SiO5). I also happen to have a specimen I bought which is labeled kyanite kyanite. Compare them! Remember this tells us nothing about the chemical formulae only the elements present.

This one isn't as dramatic but I think the valuable tool even in the hands of a rank amateur like me. Much work remains to be done. For example the spectra must be calibrated in terms of wavelength or wavenumbers to be really useful and there is software available (mostly for amateur astronomy) that facilitates this operation. One program in particular useful and I have worked with it quite a bit with some success but it was written by a Frenchman and whoever translated the documentation into English does not appear to be a profoundly talented English speaker. I have several times given up exasperated but I will go back and try again.

2. See Jan Beck's LIBS Spectrometer – Project Page.