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TITLE OVERVIEW OF APPLICATIONS OF LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS)

AUTHOR(S): David A. Cremers CLS-4

MASTER

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Overview of Applications of Laser-Induced Breakdown Spectroscopy (LIBS)

David A. Cremers

Chemical and Laser Sciences Division
Los Alamos National Laboratory
Los Alamos, New Mexico 87545

Abstract

Laser-induced breakdown spectroscopy (LIBS) is a method of performing elemental analyses of solids, liquids, and gases using the microplasma produced by a focused laser pulse. Because the microplasma is formed by optical radiation, LIBS has some important advantages compared to conventional laboratory based analytical methods. Three applications are discussed which use the LIBS method.

Introduction

Laser-induced breakdown spectroscopy (LIBS)[1] is one method of performing elemental analyses of materials. It is similar in principle to other techniques of atomic emission spectroscopy (AES). There are three basic steps in AES analysis: (1) atomization of the sample, (2) excitation of the resulting atoms, (3) detection of emissions from the atoms. Most methods of AES use a hot source that vaporizes and excites the material to be analyzed in one step. The light from the source is then spectrally and in some cases (pulsed sources) temporally resolved to determine the identity and amounts of different elements present in the material. Conventional sources for AES, which include the electrode spark and arc, the inductively-coupled plasma, and the microwave-induced helium plasma, require that the sample be transported to the source for analysis.

In the LIBS method, the source is the microplasma or spark formed by focusing powerful laser pulses in or on the material to be analyzed. The temperature and electron density of the laser plasma are very high initially[1], on the order of 20,000 K and 10^{18} cm^{-3}, respectively, so material in the spark volume is vaporized to its constituent atoms. Because of the small size of the laser plasma (typically 20 mm^3) and its low energy content (< 500 mJ), only small amounts of sample are required for analysis. Typically, micro- or nanogram quantities are sufficient. Depending on the elements present, the atoms excited by the plasma may be neutral or ionized. Emitting species are identified by spectrally and temporally resolving the spark light. Note that because the laser plasma is formed by focused optical radiation, it can be generated at a distance from the laser source, in contrast to conventional AES sources which require an adjacent physical device to produce the plasma (e.g. electrode, waveguide). Only optical access to the sample is needed for LIBS analysis.

The temperature and electron density of the laser plasma are comparable to or significantly greater than those characteristic of conventional AES sources. This provides better excitation of atoms (e.g. Cl, F) having strongly emitting levels difficult to excite by cooler sources and results in the excitation of more ionic lines. For some elements, ionic lines offer better analytical results than neutral lines. The high electron density, however, broadens spectral lines via the Stark effect so that LIBS cannot, in general, be used for isotope analysis.

The apparatus for performing a LIBS experiment is shown in Fig. 1. A pulsed laser must be used to generate the laser plasma because of the high electric fields required to initiate dielectric breakdown of materials. Unfocused laser pulse power densities of several MW/cm^2 are typical. A convenient source of such pulses is the Q-switched Nd:YAG laser having a pulsewidth of 9-15 ns, a wavelength of 1064 nm, and a pulse energy of 100 mJ or more. The repetition rate of these lasers ranges up to 50 Hz. A short focal length lens is normally used to form the spark on the sample which may be contained in a chamber or may be a gas or aerosol in ambient air. Visually, the laser spark appears as a bright flash of white light. The light from the plasma is imaged by a lens onto the entrance slit of a spectrograph or monochromator to provide spectral resolution. To monitor a wide spectral range simultaneously, an image-intensified photodiode array detector can be used to record the light dispersed by the spectrograph, as shown in Fig. 1. The image-intensifier, a high-speed electro-optic shutter, is timed to the laser pulse so specific events after plasma formation can be monitored. Using the photodiode array, the spectrum from a single laser plasma can be recorded.

Because the laser plasma is a pulsed atomization and excitation source, the spectrum evolves as the plasma decays. Analysis of many different samples shows that the evolving spectrum can be divided into three distinct periods. Immediately after plasma formation and out to a few microseconds, the spectrum is dominated by a spectrally broad background continuum light due to bremsstrahlung radiation from the plasma. This is the origin of the white light from the plasma observed visually. During this period, emission lines due to ionized atoms may also be observed. As the plasma cools and the electron density decreases because of recombination between ions and electrons, the continuum radiation and ion emissions decrease in intensity. At times between 2-10 µsec, emissions from neutral atoms are observed and at times beyond about 10 µsec emissions from simple molecules become apparent. The molecules are formed from recombining atoms in the plasma. There are some notable exceptions to this general scheme. For example, emissions from once-ionized beryllium and uranium atoms, Be(II) and U(II), respectively, are observed out to many tens of microseconds after plasma formation and emissions from CN molecules are present within a few hundred nanoseconds after the plasma is formed. The temporal evolution of the spectrum from a spark formed on steel is shown in Fig. 2. In the figure, t_d is the delay time between spark formation and start of recording of the spectrum and t_b is the interval over which the spectrum is recorded. The numbers at the right indicate the factors by which each spectrum was expanded vertically with respect to the top spectrum.

The LIBS method has been used extensively for laboratory-based analyses[2] whereas development of the method for use in industrial monitoring situations has not been reported. This paper describes three recent applications of the LIBS method at Los Alamos National Laboratory. These are (1) determination of uranium in solution for process monitoring and control, (2) identification and analysis of metals at a distance, and (3) development of a prototype beryllium monitoring instrument.

Determination of uranium in solution

The ability to measure rapidly the uranium content of flowing liquid streams is important for process monitoring and control in nuclear-fuel reprocessing plants. Presently, these measurements can be made using absorption spectroscopy and nuclear-based counting methods (gamma-ray, x-ray, etc.). Matrix effects, however, limit the utility of these methods in some situations. For example, changes in the acid molarity of the solutions can complicate calibration of the absorption techniques whereas background counts from other radioactive elements can mask counts from uranium. LIBS, being an optical emission technique, offers one possibility to overcome these difficulties. In addition, the LIBS method can provide in situ analysis because the spark can be formed directly in the solution through a window on the pipe carrying the liquid.

Early LIBS analysis of solutions involved forming the laser plasma in the bulk liquid some distance below the surface.[3] In the case of uranium detection, however, the lowest detection limit was achieved by focusing the laser pulses at near normal incidence on the liquid to produce a surface spark.[4] This can be attributed to the higher temperature of the plasma formed in the gas above the liquid compared to the plasma generated in the bulk sample. The spectrum from a solution of 10 gm/liter uranium in 4 molar nitric acid is shown in Fig. 3. A survey of the 350-480 nm spectral region showed the 409 nm U(II) line to be the strongest feature not exhibiting a spectral interference. Most of the lines shown in Fig. 3 are from U(II). The best U(II) signal was obtained by monitoring the spark light during the 8-200 μsec period after spark formation. The lines from U(I) were found to be very weak at all times.

The analytical capabilities (dynamic range, detection limit, accuracy and precision) were evaluated using sealed vials containing uranium in solution covering the range 0.1 to 300 gm/liter, the region of most interest. Figure 4 shows a calibration curve of net uranium signal plotted against concentration. Although the curve is not linear, it exhibits good sensitivity (slope) over the entire range. The loss of sensitivity at the higher concentrations may be due to self-absorption of the U(II) emission by the outer cooler region of the laser plasma. The detection limit for uranium determination was 0.1 gm/liter assuming a signal-to-noise ratio of two.

The accuracy and precision were measured by performing ten replicate measurements of an "unknown" solution, predicting the uranium concentration from the calibration curve and calculating the precision as the relative standard deviation (RSD) of the ten measurements. Because the liquid surface splashed violently on each laser spark, the shot-to-shot reproducibility of the uranium signal was poor. By averaging over many shots, however, it was possible to obtain precisions on the order of a few percent. Specifically, by averaging 1600 spectra, corresponding to an acquisition time of 2.7 minutes at a pulse rate of 10 Hz, a precision of 1.8% RSD was obtained. Precisions of less than 1% RSD were achieved by ratioing the uranium signal to the signal recorded by monitoring a spectrally narrow region of the continuum light generated on each shot.

Experiments have shown that essentially the same analytical results noted above for static samples can be achieved with flowing samples provided a flow cell is devised that maintains the liquid level constant during analysis.

Metal identification and analysis

The majority of LIBS measurements reported in the literature have used lenses with focal lengths of 10 cm or less to produce the plasma. There are several applications in which the ability to carry out qualitative and semi-quantitative LIBS measurements at greater distances is required. Examples are scrap metal sorting, geological prospecting, and remote analysis of samples. The goal of the work reported here was to establish the analytical capabilities of LIBS using lenses with focal lengths of 0.5-2 meters.[5]

The experimental set-up is similar to that shown in Fig. 1 except that the spark light was collected by a bare fiber optic bundle 3 mm in diameter. The bundle was positioned next to the focusing lens and the spark light was not focused on the end of the bundle. The advantage of the fiber optic bundle over a lens to collect the spark light is the large light collection angle offered by the bundle, which for a quartz bundle is about 35 degrees. This relaxes the constraint that the spark be formed at precisely the same spot on the sample to collect the maximum amount of light. With lens focusing, on the other hand, movements of the spark of only a few millimeters can completely move the spark image off the entrance slit of the spectrograph. The light transmitted by the bundle was directed into the spectrograph by positioning it against the entrance slit. The spectrally resolved light was detected using a photodiode array.

The aim of the first experiments was to demonstrate that the major elemental components of a metal could be identified using only the spectrum produced by a single laser spark. To do this, a 40 nm wide spectral region was chosen over which eight elements (Mo, Ni, Cu, Ti, Al, Pb, In, and Fe) each have at least one moderate or strong emission line that does not interfere with other lines. A composite spectrum, constructed by adding together the LIBS spectra from a series of metals each containing a high concentration of one of the elements, is shown in

Fig. 5. The shaded regions indicate the line(s) used to identify the element in the material. The total counts in each of these regions-of-interest (ROI) was computed for each spectrum. The spectrum of Fe is not shown in Fig. 5 because its high density of lines would complicate the figure.

Using a 0.5 meter focal length lens, a single spark was generated on each sample and the spectrum recorded. There are many methods to compare the relative line intensities and so decide which elements are being monitored. The method used here involved computing the ratio of the counts in each ROI shown in Fig. 5 to the counts in the ROI for Fe. Several experiments have shown that if clean samples were used, in all cases the major elemental constituents of the sample could be identified using only a single spark.

The rapid identification of metals was demonstrated by setting up an experiment in which a He-Ne laser beam passing through the volume occupied by the laser spark was detected and used to trigger the Nd:YAG laser when the beam was extinguished. In this way, a sample passing through the focal volume was interrogated automatically by a single laser spark. Because it was not easy to introduce samples into the focal volume at a high rate of speed by dropping them through the focus, different metal samples were attached to a large disc. Each sample was positioned next to a small hole in the disc aligned to pass the He-Ne beam. The disc was rotated so that 19 samples/sec were introduced into the spark volume. The spectra recorded under these conditions are shown in Fig. 6. The major elemental component of each sample is listed at the left of each spectrum. The results show that high quality spectra can be obtained at a high rate of speed using only a single spark.

Samples having surface contaminants such as paint or oil can prevent the spark from sampling the metal underneath. Experiments have shown, however, that most paints can be ablated off the metal using only a few sparks and that oils and greases can be penetrated using only one or two sparks. The main problem with contaminants is the introduction of interfering spectral lines. For example, many paints contain high levels of titanium which may mask the titanium signature from the metal.

In many cases, it may be desirable to perform semi-quantitative analyses of samples at the large distances used in the identification experiments described above. This capability would be useful to sort metals in a supply yard according to composition. Experiments along these lines were carried out using a 55 cm focal lens to form the sparks on the samples, which were steel standards of known composition. To obtain acceptable analysis accuracy and precision it was necessary to use many sparks and average the spectra. A summary of the results obtained using 10 and 100 sparks for each measurement is presented in Table 1 for the elements Si, V, Cu, Mn, and Cr.

Table 1. Semi-Quantitative Analysis Summary

no. sparks	% accuracy	%RSD
10	20	15
100	4	11

For each element, a calibration curve was constructed spanning the concentration range of about 0.11-0.94% (typical concentrations for many elements in steel). Then an "unknown" sample was analyzed by averaging the spectra from 10 and 100 sparks. Each analysis was repeated ten times. The elemental composition of each sample was predicted using the calibration curve and the accuracy was computed by comparing the actual and predicted compositions. The precision was computed as the relative standard deviation of the ten analyses. The average values of the accuracy and precision obtained for all the elements are listed in Table 1. The results indicate that semi-quantitative analyses are possible using lenses of long focal length.

Prototype beryllium monitoring instrument

Airborne particles of beryllium and its alloys represent an inhalation health hazard to workers exposed to these materials. The current maximum exposure level to these airborne contaminants is 2 $\mu g/m^3$ over an 8-hour work day, 40 hours/week. The concentration can reach 25 $\mu g/m^3$ if the exposure is limited to one-half-hour/day. The method commonly used to analyze for beryllium involves collection of the beryllium on filters by passing a known volume of air through the filter. At the end of the collection period, the filter is removed and transported to a laboratory for analysis which involves (1) chemical dissolution of the filter to produce a solution which is (2) analyzed using atomic absorption spectrometry. Step (1) is time-consuming and can require several hours to complete. To increase worker safety, a more rapid method of analyzing the filters is required.

At Los Alamos National Laboratory, the LIBS method has been used to rapidly determine beryllium collected on filters.[6] The method of interrogating a filter with a series of laser sparks is shown in Fig. 7. The laser pulses are focused on the filter by a cylindrical lens to form a long spark about 3 mm in length. The filter is rotated during analysis so a large fraction of the surface is sampled. The spark light is imaged on the spectrograph entrance slit by a lens. Emissions from the Be(II) lines at 313.042 and 313.107 nm are detected using a photomultiplier tube.

The detection limit for beryllium deposited uniformly over a 32 mm diameter filter surface is about 10 ng. At this limit, if the ambient beryllium concentration is 2 $\mu g/m^3$, then a measurable beryllium mass can be collected on the filter after only 8 sec if air is passed through the filter at 40 liters/minute. Therefore, this method provides near real-time analysis of airborne beryllium levels.

Based on the success of this work, a prototype beryllium monitor was constructed for use in routine monitoring of beryllium in a plant environment. A schematic diagram of the device is shown in Fig. 8. It consists of four basic units: (A) control section; (B) analysis station; (C) pump/fan housing; and (D) laser power supply. The monitor can be moved easily to different areas to provide immediate analysis. For operation the monitor requires a source of power (115 VAC, 15 A) and an exhaust system capable of handling beryllium particles. Table 2 lists some of the major components of the instrument.

Table 2. Components of the beryllium monitor

component	comments
laser	Laser Photonics YQL-102, Nd:YAG, 12 ns pulsewidth, 150 mJ/pulse, 1064 nm wavelength, 10 Hz
spectrograph	Jarrell-Ash Monospec 18, 156 mm fl, 3600 l/mm grating, 150 µm slits
photomultiplier tubes	Hamamatsu R1414, 13 mm diam., S-5 response
computer	EPSON HX-20
electronics	built in-house at Los Alamos

The method of analyzing filters used by the device is shown in Fig. 7. The filter is loaded into the instrument through a door at the top of the analysis station. When the door is closed, the filter is positioned vertically as shown in the figure. To obtain a representative measure of the beryllium on the filter, the filter is rotated under the sparks (formed at a repetition rate of 10 Hz) at 2 rpm and following each complete rotation, the filter is translated downward by 3 mm. In this way, four concentric annuli are formed on the filter surface and about 90% of the beryllium on the filter is sampled in two minutes (1200 sparks). The beryllium signal obtained on each spark is processed by a gated integrator so only the beryllium signal in the 2-10 µsec interval is integrated. The resulting voltage is digitized and stored in computer memory. Following each analysis, the beryllium signals are summed by the computer and a value for the beryllium mass on the filter is determined from a calibration curve (beryllium signal versus beryllium mass) stored in memory.

The analytical capabilities of the instrument were evaluated using beryllium particles of respirable size (0.5-5 µm diam.). The useful dynamic range extends from 10 to 1000 ng on a filter, the region of interest for beryllium analysis. At masses above 1000 ng the detection system becomes saturated because of the strong beryllium signals. The dynamic range can be extended to greater masses by adding a second photomultiplier tube to monitor only the stronger signals. The accuracy and precision of the instrument, about 10%, is limited by several factors: (1) nonuniform particle distribution on the filter; (2) loss of some particles from the filter during analysis; (3) incomplete vaporization of large beryllium particles. Because of the low detection limit provided by the instrument, however, the 10% accuracy is more than sufficient to satisfy beryllium monitoring requirements.

Acknowledgements

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Meet the author: David Cremers obtained his doctorate from Washington State University in 1980. He is presently a staff member at Los Alamos National Laboratory and is involved in applying the LIBS method and other optical diagnostic techniques to different monitoring problems. He is also using optical spectroscopy to probe the interaction between laser radiation and a metal during laser welding. The goal of this work is to improve the laser welding process and develop diagnostics to monitor weld quality in real-time.

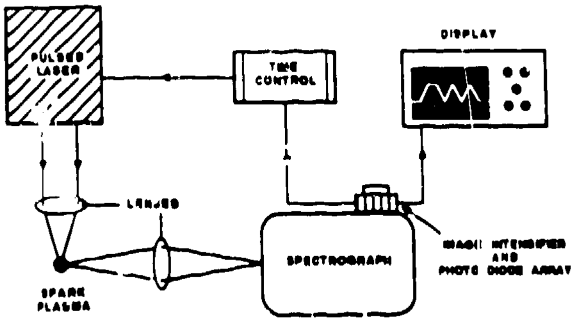

Fig. 1. Typical apparatus for performing LIBS experiments

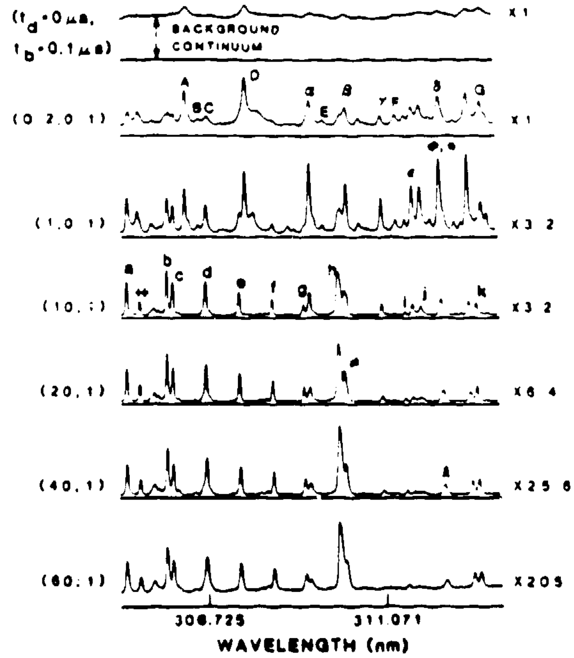

Fig. 2. Temporal evolution of the spectrum from a spark formed on steel. Fe(I) [a-ℓ], Fe(II) [A-G], V(II) [α-ε], Cr(II) [✸], Mo(I) [✱], Ni(I) [≠], Ni(I) [ǂ].

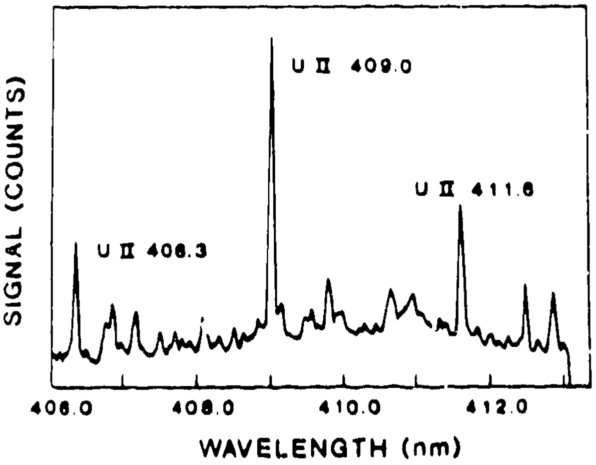

Fig. 3. Spectrum obtained by forming the laser spark on the surface of a 10 gm/liter uranium solution. Most lines are due to U(II) emissions.

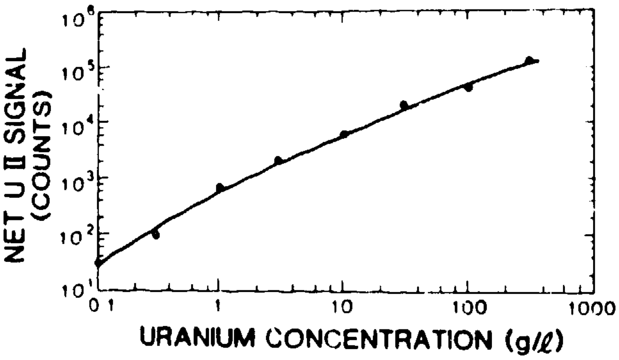

Fig. 4. Calibration curve obtained by analyzing uranium-bearing solutions with the laser spark.

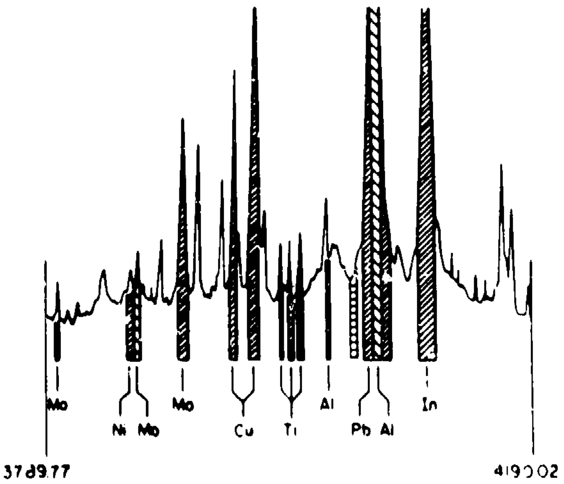

Fig. 5. Composite spectrum of seven elements. The shaded areas indicate the lines used to identify the elements.

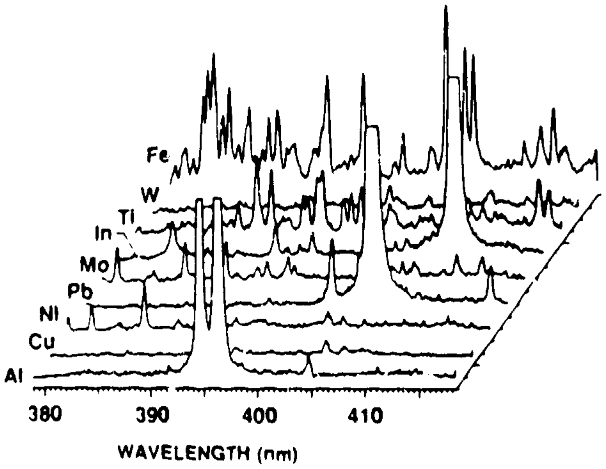

Fig. 6 Spectra obtained by analyzing nine metal samples at a rate of 19 Hz. Each spectrum was recorded using a single spark.

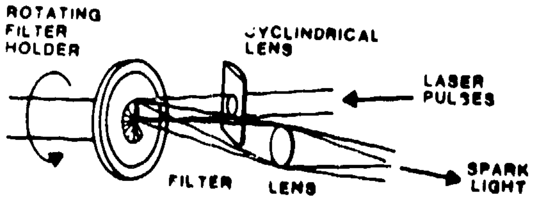

Fig. 7 Method of determining beryllium on filters using the laser spark.

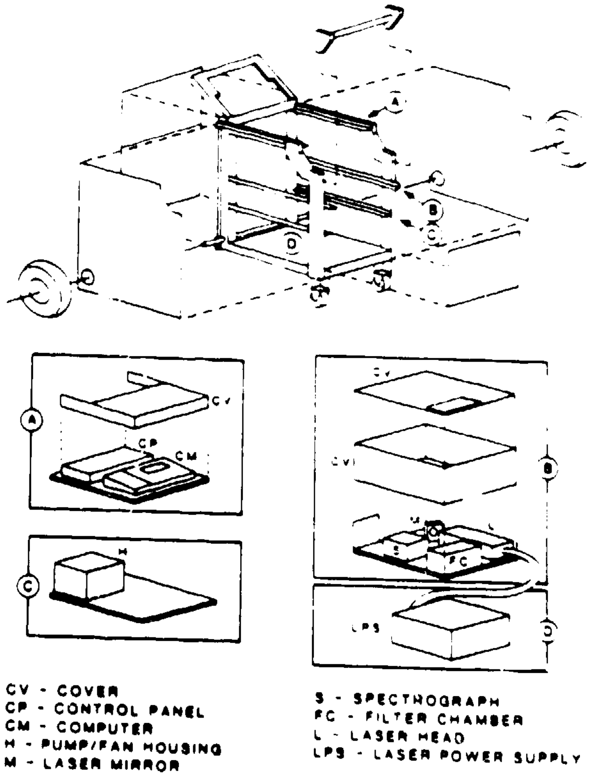

Fig. 8. Schematic diagram of the prototype beryllium monitoring instrument.