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IN-1341

September 1968

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THE ANALYTICAL CHEMISTRY BRANCH LASER MICROPROBE
FACILITY FOR THE ELEMENTAL ANALYSIS OF SMALL
FEATURES OF A SAMPLE

J. M. Baldwin

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Laser Microprobe Facility Used in the Elemental Analysis of Small Feature of a Sample

SCHEMATIC DIAGRAM OF THE LASER PROBE

The problem:

To develop a laser probe facility for analyzing small areas of heterogeneous samples so that the capabilities of such a facility can be determined. The areas of major concern in laser probe analysis are: 1) the number of elements that can be analyzed; 2) the types of samples amenable to analysis; 3) spatial resolution; and 4) sensitivity.

The solution:

A laser microprobe facility has proved effective in the elemental analysis of small areas of heterogeneous samples. The instrument uses the focused beam of a pulsed laser to evaporate a small volume of material

from a relatively massive sample. The vapor so produced is excited to emission of optical radiation characteristic of the elemental composition of the selected area of sample. This radiation is analyzed by conventional emission spectroscopic method to produce qualitative and/or quantitative information about the composition of chosen region of the sample.

Any element that can be analyzed by conventional dc arc emission-spectroscopy can be analyzed by the laser probe technique. This includes 60 to 70 elements.

The laser probe can analyze a huge range of sample types. Good electrical conductivity and surface flatness are not prerequisites. The analysis can be performed

(continued overleaf)

in air or other atmosphere; a vacuum is not required. Any shape or size of sample that can be placed on the microscope stage can be examined. Little or no sample preparation is necessary.

The spatial resolution attainable with the laser probe is a function of laser power, thermal properties of the sample and quality of the microscope objective. Resolution of one to three microns has been attained. The sensitivity is a function of laser power.

How it's done:

The laser probe components are illustrated in the figure. The active medium of the laser is a neodymium-doped glass. The laser is Q-switched by a rotating dielectric reflector. The output of the laser is a single pulse of about 10μ sec duration, or a train of several such pulses, depending upon the operating conditions. The beam is focused by a standard microscope objective on the surface of a sample. A binocular viewing system is made confocal with the laser so that microscopic selection of the area to be analyzed is possible. A pivoted mirror allows one to switch rapidly from the viewing position to the sampling position. The sample stage is movable in three dimensions.

Impact of the focused laser beam on a sample produces heating, melting and vaporization of the selected portion of sample. As little as a few tenths of a microgram of sample can be evaporated per laser pulse.

If desired, a high potential of up to two kilovolts from a power source can be applied to a set of graphite electrodes to supply additional excitation to the sample. The partially ionized vapor short circuits the electrodes, causing the power supply to discharge.

This cross-excitation provides greater sensitivity than is available from the laser output alone.

The laser probe has been applied to: a) examination of a weld on an Inconel tube to determine the weld material; b) examination of corrosion deposits on SPERT fuel rod cladding; c) examination of irradiated (2.1×10^{22} nvt) stainless steel for metallurgical effects; and d) analysis of successive layers of deposits on metals.

Notes:

1. Complete details are available in Idaho Nuclear Corporation Report CI-1121, dated September 1966, "The Analytical Chemistry Branch Laser Microprobe Facility for the Elemental Analysis of Small Features of a Sample" by J. M. Baldwin.

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IN-1341

Issued: September 1968

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U. S. Atomic Energy Commission Research and Development Report
Issued Under Contract AT(10-1)-1230
Idaho Operations Office

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ABSTRACT

The Analytical Chemistry Branch Facility for laser probe analysis is described. Operational features, present capabilities and development work now in progress are discussed.

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I. INTRODUCTION

This report describes the capabilities of a newly acquired facility for elemental analysis of small areas of heterogeneous samples. . . The laser microprobe. This instrument uses the focused beam of a pulsed laser to evaporate a small volume of material from a relatively massive sample. The vapor so produced is excited to emission of optical radiation characteristic of the elemental composition of the selected area of the sample. This radiation is analyzed by conventional emission spectroscopic methods to produce qualitative and/or quantitative information about the composition of the chosen region of the sample.

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II. OPERATION OF THE LASER MICROPROBE

The components of the laser probe are illustrated in Figure 1. The active medium of the laser (a) is a neodymium-doped glass. The laser is Q-switched by a rotating dielectric reflector (b). The output of the laser is a single pulse of about 10 microsecond duration, or a train of several such pulses, depending on the conditions of operation. The beam is focused by a standard microscope objective (c) on the surface of a sample (d). A binocular viewing system (e) is made confocal with the laser so that microscopic selection of the area to be analyzed is possible. A pivoted mirror (f) allows one to switch rapidly from the viewing position to the sampling position. The sample stage is moveable in three dimensions.

Impact of the focused laser beam on a sample produces heating, melting and vaporization of the selected portion of the sample. As little as a few tenths of a microgram of sample can be evaporated per laser pulse. A series of typical laser-produced craters are shown in Figure 2. These craters were produced in a sample of brass. The smallest one shown has a diameter of about 20 microns.

If desired, a high potential of up to two kilovolts from a power source (g) can be applied to a set of graphite electrodes (h) to supply additional excitation to the sample. The partially ionized vapor short-circuits the electrodes, causing the power supply to discharge. The use of this cross-excitation provides greater sensitivity than is available from the laser output alone.

III. PRESENT CAPABILITIES

The areas of major concern, with respect to the capabilities of laser probe analysis, are four: Number of elements that can be analyzed, types of samples amenable to analysis, spatial resolution, and sensitivity.

In general, any element that can be analyzed by conventional D.C. arc emission spectroscopy can be analyzed by the laser probe technique. This includes sixty to seventy elements, mainly metals, but also including some nonmetals such as phosphorous and carbon. At present, not all of these elements have been studied with the laser probe in the Analytical Chemistry Branch; but it is a reasonable expectation that most of these could be analyzed if the need should arise. An exhaustive compilation of applications of the laser probe that have appeared in the literature is included in IN-1219, "A Bibliography of Laser Publications of Interest to Emission Spectroscopists".

With respect to the range of sample types that can be analyzed, the laser probe is in a particularly advantageous position. Good electrical conductivity is not a requisite for analysis. Surface flatness is not a critical factor. The analysis may be performed in air or any other atmosphere. A vacuum is not required. Materials which have been successfully analyzed by various users of the laser probe include: glass, ceramics, minerals, bone, dental calculi, animal tissues (both in vivo and in vitro and wet or dry), metallurgical specimens, structural features such as welds and fractures. Again, the reader is referred to in IN-1219 for a thorough bibliography.

The shapes and sizes of sample suitable for analysis extend to all those that can be conveniently placed on the microscope stage. In general, little or no sample preparation is necessary. For those samples thus far submitted to the Spectroscopy Section of the Analytical Chemistry Branch for laser probe analysis, the maximum amount of preparation required has been sectioning of the sample to reveal the feature of interest at the surface.

The spatial resolution attainable with the laser probe is a function of laser power, thermal properties of the sample and quality of the microscope objective. With the laser probe on hand, a hole on the order of 10 microns in diameter can generally be produced in a sample. It has

been suggested (1) that with improved optics, resolution of one micron is attainable. Resolution of one to three microns has recently been attained (2). There is no reason to believe that the presently available equipment could not be improved to this extent, should the need arise.

Sensitivity is a function of laser power. In setting up an analysis it is necessary to determine a suitable compromise between spatial resolution and sensitivity. Usually, the spatial resolution is selected to be just adequate for the task at hand. This then automatically provides the maximum attainable sensitivity for that particular analysis. For the materials for which this laser probe facility has been utilized, major constituents have usually been detectable with a single laser firing. Detection of minor constituents usually has required summation of the light from four to six laser firings. If the sample feature of interest is large enough to allow summation over 10-12 firings, trace constituents can often be detected. This summation may be achieved either by selecting identical features on the surface of the sample or by successively evaporating material from the same spot if the sample feature is of sufficient depth.

Samples to which this laser probe has been applied include: (a) Examination of a weld on an Inconel tube to determine type of weld material. (b) Examination of corrosion deposits on SPERT fuel rod cladding. (c) Examination of irradiated (2.1×10^{22} nvt) stainless steel for metallurgical effects (3). (d) Analysis of successive layers of deposits on metals. As each layer is analyzed, the layer immediately beneath is exposed for subsequent analysis.

IV. DEVELOPMENTAL STUDIES

Work is being carried on with the intent of extending the present capabilities of the laser probe technique. The results of these studies are reported in Analytical Chemistry Branch Monthly Progress Reports for 1968. Specifically, these studies are directed at increasing spatial resolution by improving laser optics, increasing sensitivity by increasing the efficiency of excitation of spectra and by improvements in the

spectrograph entrance optics, and at increasing the capability for quantitative analysis by improving control of excitation and by acquiring a variety of suitable standards.

One particularly promising new technique is the collection of the vaporized material on a mylar or polystyrene film. This deposit is then transferred to a graphite electrode and analyzed by conventional D.C. arc emission spectrographic techniques. The greater controllability of excitation conditions in the D.C. arc and, in particular, use of the cathode layer effect provide an increase by a factor of 2 or 3 over the sensitivity figures quoted in the previous section.

The analysis of small features of hot samples is an item of practical interest. The laser probe possesses a basic advantage over other emission spectrographic methods for hot samples by virtue of the fact that only a small amount (less than 1 μg) of the sample is evaporated per laser shot. This is much less than the amount vaporized by D.C. arc techniques. The danger of contamination can thereby be drastically reduced. The analysis of the highly irradiated steel sample has indicated the practicability of using the laser in such applications. In the case of the irradiated steel, personnel shielding was accomplished by stacking lead bricks around the laser probe. The resulting arrangement was cumbersome but workable and clearly illustrated the feasibility of constructing a permanent shielded laser probe facility for the routine examination of hot samples.

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V. SUMMARY

The laser probe operated by the Analytical Chemistry Branch is currently available for the solution of problems requiring the elemental analysis of small areas of a sample. Attainable resolution is presently on the order of ten microns. Quantitative analysis can be performed contingent upon the availability of suitable standards. Experienced spersonnel are available for consultation with regard to specific applications. Studies directed at extending the analytical capabilities of the laser probe are in progress. Additional studies of this nature will be considered upon advisement by potential users of this facility.

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- (1) N. Peppers, Appl. Opt., 4, 555 (1965).
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- (3) Analytical Branch Monthly Progress Report, May 1968.

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Fig. 1 Schematic Diagram of the Laser Probe.

Fig. 2 Craters Produced in a Brass Sample by the Laser Probe.