

## MICROSPECTROCHEMICAL ANALYSIS OF MINERALS WITH THE LASER MICROPROBE<sup>1</sup>

KENNETH G. SNETSINGER AND KLAUS KEIL, *Space Sciences Division,  
Ames Research Center, NASA, Moffett Field, California.*

### ABSTRACT

Study of reproducibility and detection limits shows that quantitative estimation of trace elements in minerals may be carried out with the laser microprobe. Spectrochemical analysis with this device involves vaporization of a small volume of sample by means of a focused laser beam, followed by excitation of the vapor with an auxiliary spark source. Spectra are recorded photographically and interpreted according to usual spectrographic procedure. Areas as small as 50 microns in diameter and half that in depth may be examined, so recourse to separation of minerals in the pure state from their matrix is not necessary.

At a concentration level of 1000 ppm, it was possible to detect 38 out of 42 elements in a test sample when approximately 20 micrograms of the sample were vaporized. Lower trace element levels were detected in a series of stainless steel standards and aluminum and copper alloys. Detection limits for a number of elements are lower than those generally obtainable with the electron microprobe, and the laser probe thus can provide a useful supplement to major element analysis with the electron probe.

Reproducibility of spectra obtained from a compositionally homogeneous steel standard averaged  $\pm 6.4$  percent, corresponding to a coefficient of variation of 11 percent. Percent transmission ratios of nickel to iron lines in a series of spectra obtained from the same standard showed a standard deviation of  $\pm 0.051$  percent (coefficient of variation, 5.1 percent), indicating that precision of analysis can be improved by using a variation of the internal standard principle.

A number of practical aspects of the method are considered.

### INTRODUCTION

The laser microprobe utilizes the intense energy of a focused laser beam to vaporize very small volumes of sample for spectrochemical analysis. The broad (0.5 cm in diameter) beam from a ruby laser is demagnified to a minute focal point by means of a conventional microscope objective (Fig. 1). Visual selection of the area of sample to be analyzed is made through the microscope and the target is given a burst of laser light. The energy delivered at the point of focus is sufficient to vaporize a minute volume of the sample and a small crater is formed at the target area. Sample vapor expands upward into a gap between two charged carbon electrodes positioned just above the sample. Potential across the electrodes is kept at approximately one kilovolt, so a spark occurs, and the atoms in the sample vapor are excited to spectral emissive levels. The resulting light is directed to the entrance slit of a spectrograph and re-

<sup>1</sup> Portions of this paper were first presented at the 80th Annual Meeting of the Geological Society of America, New Orleans, Louisiana, November 20-22, 1967.

recorded photographically; spectra are interpreted according to conventional spectrographic procedure. Efficient excitation of the sample vapor is achieved only during cross excitation by the electrodes. When these are removed and only the laser is operating, some excitation of sample material is produced owing to interaction of the laser beam with sample and sample vapor, but the spectra are weak in comparison with those obtained when auxiliary electrodes are used. The laser beam should in this configuration therefore be regarded as a sampling device, for it is simply a means of introducing minute amounts of material between the electrodes.

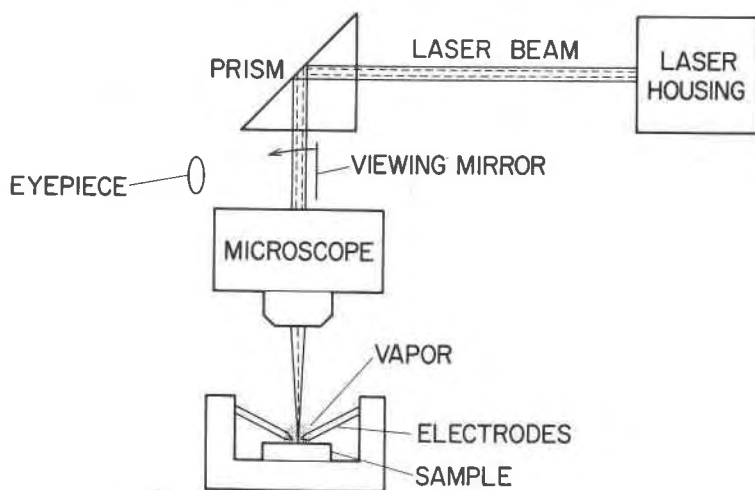


FIG. 1. Schematic diagram of the laser microprobe.

Depending upon the energy of the laser and the nature of the sample material and optical system, between 0.5 and 20 micrograms (a microgram is  $10^{-6}$  gram) of sample are vaporized from an area ranging from 50 to 200 microns in diameter. Thus, besides offering the possibility of analyzing small volumes of samples, the method is attractive because it allows *in situ* analysis of individual mineral grains in rock sections. Time-consuming mechanical purification of the mineral to be analyzed is thus unnecessary.

Two previous papers have dealt with the application of the laser microprobe to the study of minerals; Maxwell (1963) and Berndt *et al.* (1965) drew attention to the usefulness of the method for mineral analysis, but only considered qualitative determination. In the present paper, however, the possibility of quantitative analysis is investigated, and par-

ticular attention is directed to methods of determining trace constituents of minerals. In addition, a number of practical analytical considerations leading to quantitative work are discussed, and note is taken of some ways in which the laser microprobe may be used in conjunction with, and as a supplement to, the electron microprobe.

#### HISTORY OF THE METHODS

Early in the development of the laser (for example, at the Hughes Aircraft Company Research Laboratories, Malibu, California, 1960 *ca.*<sup>1</sup>) consideration was given to use of high-energy laser bursts for spot excitation of spectra. Brech and Cross (1962) were able to achieve excitation in this way when laser energy was high and crater diameters were large, but could not obtain spectra from small craters, presumably because (1) the laser energy used to form a small crater was insufficient to produce adequate excitation of the vapor, and (2) insufficient amounts of sample vapor were available for excitation. Debras-Guédon and Liodec (1963) obtained satisfactory spectra using giant-pulse lasers; craters with diameters of the order of 100 microns were produced. Similar experiments were carried out by Runge *et al.* (1954) and Ferguson *et al.* (1964).

The first workers to suggest use of charged electrodes to excite the sample vapor appear to have been F. Brech and J. Schuch of the Jarrell-Ash Company, Waltham, Massachusetts; they are credited with the invention of this analytical arrangement, called the laser microprobe, in advertising literature of that company (Anonymous, 1963). The Jarrell-Ash Company has a U. S. Patent pending to the device.

Brown, (1964) has provided a theoretical discussion of vaporization of materials by laser pulses for spectroscopic study and Klotzbaugh *et al.* (1964) treat some theoretical and practical considerations. Devlin and La Conti (1964) have investigated some properties of the laser microprobe, but they considered excitation of sample vapor by the laser beam alone and did not employ cross excitation in their experiments. Ryan *et al.* (1965) analyzed defects in glass. Rasberry *et al.* (1967) provided a thorough description of the method; they studied aspects of reproducibility, and established a correlation between laser energy, crater size, and spectral intensity. Aside from the two strictly qualitative mineralogical treatments (Maxwell, 1963; Berndt *et al.*, 1965), a half-dozen papers, not cited here, have dealt with qualitative analysis of organic materials such as bone, tooth enamel, freeze-dried tissue *etc.*, using the laser microprobe. There does not, at the time of this writing,

<sup>1</sup> Dr. W. I. Linlor, personal communication.

appear to be any published account of quantitative mineralogical analysis with the laser microprobe.

#### EQUIPMENT AND OPERATION

The laser used in this investigation is an air-cooled, Q-spoiled, Brewster-angle ruby laser with nominal output energy of 0.4 joule<sup>1</sup>. Voltage to the flashlamp is set at 600 volts above the 2200 volt threshold. The cross electrodes are capacitor charged, potential across them being continuously adjustable to a maximum of 2180 volts. Electrode gap is one mm, and the electrode tips are one mm above the sample. For qualitative work, the sample surface may be irregular, but for quantitative analysis both sample and standard should present similar geometry, a thing most easily accomplished by polishing both.

Light resulting from cross excitation of the sample vapor is concentrated and directed to the spectrograph slit by a spherical quartz condensing lens mounted on the optical bar of the spectrograph; the lens is arranged so that its focal point is between the electrodes, precisely at the location of the vapor plume. Spectra were recorded with a 1.5 Meter Wadsworth-mounted spectrograph having a reciprocal linear dispersion of 10.9 Å/mm in the first order and a wavelength range of 2300 to 7800 Å (first order). Kodak 103-0 or 103-F emulsions were used, either of which type is extremely sensitive; some photometric error is introduced, however, owing to the coarseness of these emulsions.

As voltage control to the electrodes is available, reproducibility of sampling by the laser is the main parameter affecting the precision of the method. Temperature control is important in reproducibility of laser output, so if temperature control of the laser head is not available, operating in an air-conditioned laboratory is desirable.

In the experiments described below, a filter, transmitting about 40 percent of the laser light, was placed at the exit port of the laser head. Thus, the energy deposited at the focus was reduced to about 0.2 joules and, at this lower energy level, damage to the internal lens system of the objective, described by Rasberry *et al.* (1967), was not noted, even after 500 or so laser bursts. The front lens of the objective, is, however, subject to damage by crater ejecta or particles from the electrodes and it is necessary to protect the lens by stretching transparent film (*e.g.*, "mylar") over it.

When, as in the present study, the ruby laser is operated appreciably above threshold, each laser burst consists of a series of pulses, called "spikes" because of their appearance on an oscilloscope display. Oper-

<sup>1</sup> For a general background to lasers, the reader may consult Birnbaum (1964) or Brotherton (1964).

ated under the conditions cited above, the laser used in this study produces a three-spike pulse of roughly 5 microseconds ( $5 \times 10^{-6}$  second) duration. Closer to threshold, single-spike output can be achieved.

In contrast to the usual appearance of conventionally-obtained spectra, laser microprobe excitation gives rise to spectral lines that are lensed, an effect which is especially evident when a large (*e.g.*, 10 mm) slit height is used. Lensing is a result of the small amount of material involved in the laser microprobe method: the vapor plume is not large enough to allow uniform vertical illumination of a large slit. With more normal slit heights (*e.g.*, 2 mm) lines of uniform density may be recorded if the height of the condensing lens is adjusted to sample the central portion of the vapor plume. But even with smaller slit heights, upward or downward tapering of a few lines may be noted, and when establishing a film calibration curve, these lines must be avoided for obvious reasons. In choosing analytical lines tapered ones must of course be avoided; the condensing lens should be adjusted to record the most intense portion of the line.

By changing the voltage to the flashlamp that pumps the laser, variability of laser output and, accordingly, variability of crater dimensions is obtained. Crater dimensions may, however, be more conveniently adjusted by changing the size of the focused laser beam optically or varying the intensity of the laser light with density filters. Thus, if a 10 power objective is used to focus the laser light, craters are wider in diameter and shallower than if a 20 power objective is used; and the effect of filtering is such that if a filter of only 15 percent transmission is placed between the prism and the laser head, craters 50 microns in diameter and 20 microns deep are produced in razor blades using the 20 power objective, whereas the focused, unfiltered light has sufficient energy to penetrate a stack of three razor blades, leaving a hole 200 microns in diameter in the top blade. An appreciable range of crater dimensions may thus be obtained, and in fact the theoretical lower limit of width of the beam of focused laser light is as small as the wavelength of the light involved: 6943 Å. Holes as small as one micron in diameter have been drilled in thin biological specimens with a ruby laser (Schawlow, 1965). For mineralogical trace element work, however, it is clearly advantageous to use the largest crater volume commensurate with the volume of sample whose composition is to be determined, because, assuming a hemispherical crater, sample volume decreases approximately as the cube of the radius of the crater, and a point is reached at which the amount of sample introduced between the electrodes is so small that sensitivity for trace elements is lost.

The crater diameters referred to above do not include the splash area around the crater, produced by ejection of molten material (Fig. 2).

Presence of condensed ejecta is clear evidence that not all material derived from a crater passes between the electrodes. Because this splatter rim increases the distance which must be left between successive craters when making serial analyses, the resolution of the method is decreased somewhat. The size of the deposit decreases rapidly, however, with decreasing crater size.

Crater depth must be considered as well as crater width during routine analysis, because deep craters may penetrate through a grain whose composition is of interest and spoil the trace element analysis by sampling material underneath. Interference of this sort would be suspected if an element, known to be absent from the analytical grains but present in

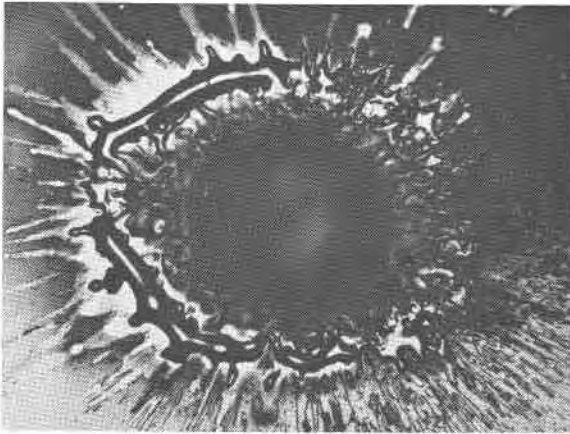


FIG. 2. Laser crater in nickel-iron alloy. The diameter is approximately 100 microns and the depth 80 microns. Photograph courtesy of T. E. Bunch.

major amounts in possible contaminating phases, were found in spectra from the analytical grains. If the major element were, however, spectrographically less sensitive than trace elements present in the contaminating grains, absence of the major element from spectra would not necessarily eliminate the possibility of contamination by trace elements. The extent of the interference should then be judged by obtaining spectra from the possible contaminating grains. Because the depth to which an analytical grain may extend is impossible to judge, it is advisable to analyze only the largest mineral grains in a polished section.

Difficulty was experienced in obtaining cross-excitation with very small craters, because the amount of sample vapor passing between the electrodes is then so minute as to be insufficient to break down the electrode gap; sparking of the vapor can in this case only be achieved by decreas-

ing the gap distance, placing the electrodes closer to the sample surface and increasing the voltage across the gap. Considerable oxidation and pitting of the surface surrounding the target area then occurs, and it is necessary to mask the surface with transparent plastic, leaving a small hole above the area to be analyzed. Masking of the surface in addition prevents contamination of the rest of the sample by vapor from the target area. Oxidation is also suppressed by flooding the sample area with an inert gas (*e.g.*, argon). Use of such a gas has incidental advantages in that (1) reproducibility is improved because day-to-day differences in spark intensity due to changes in humidity are reduced and (2) cyanogen band interference is lowered.

#### REPRODUCIBILITY

The writers have studied reproducibility of the laser microprobe by investigating (1) constancy of output of the laser light, (2) reproducibility of volumes of craters formed in a homogeneous substance and (3) reproducibility of intensity of spectral lines resulting from excitation of a homogeneous material. For the latter two experiments, National Bureau of Standards steel standard 461 was used; electron microprobe and optical study shows this standard is compositionally homogeneous at the sampling scale provided by the laser (Michaelis *et al.*, 1964).

*Reproducibility of Laser Output.* Reproducibility of output of laser light was determined in the following way. The cross electrodes and the objective were removed from the system, so that unfocused laser light was directed down onto the microscope stage. The convex surface of a low-power lens, placed directly beneath the laser beam dispersed the laser light toward the entrance slit of the spectrograph, and the condensing lens was removed in order to prevent vaporization of the slit. When it enters the spectrograph, the laser light is dispersed by the grating and recorded at the appropriate place on the film as a spectral line. The reproducibility of percent transmission of this line relative to clear film is a measure of reproducibility of output of the laser.<sup>1</sup> When the laser was fired at one minute intervals, a series of pulses showed a standard deviation of  $\pm 1.8$  percent from the average percent transmission for the series, and pulses spaced ten minutes apart gave a standard deviation of  $\pm 1.2$  percent (coefficient of variation:<sup>2</sup> 3.9 percent). The slight improvement

<sup>1</sup> This method gives no information about reproducibility of (1) peak power, (2) total energy over time or (3) pulse train shape, but it does provide a means of characterizing reproducibility. The procedure is analogous to measuring output with a slow-response ballistic thermopile.

<sup>2</sup> The coefficient of variation (also known as relative deviation) of a series of measure-

with ten minute shot spacings is an effect of temperature. Heat generated by the flashlamp that pumps the laser causes temperature gradients in the ruby rod, which, if time between pulses is short, are not dissipated by the air flow that cools the laser. On the other hand, if shots are widely spaced, the rod has time to cool to ambient (room) temperature between shots and reproducibility is improved.

*Reproducibility of Crater Volumes.* Reproducibility of crater volumes produced by the focused laser beam is, however, lower than reproducibility of light output of the laser; for example, the coefficient of variation obtained by measuring the depth of a series of 20 craters produced in the stainless steel standard was 7.0 percent.<sup>1</sup> A tentative explanation of this difference involves considering the result of interaction of laser light with the sample vapor plume. At a given average power level, the front of the train of laser light vaporizes a certain amount of sample, and the remainder of the light is partially absorbed by the vapor. At a power level slightly higher than the average, however, the front of the light train vaporizes more sample; a denser vapor plume is formed, and the rest of the light is more strongly absorbed by the vapor than with the lower-energy burst. In the experiment just described, laser energy was apparently at a critical value such that the small change in energy associated with a pulse on the high side of the average output was sufficient to produce an appreciably more dense vapor plume as compared with a pulse on the low-energy side of the average laser output, and this effect may account for lower reproducibility of crater dimensions as compared with reproducibility of the laser. It should be emphasized, however, that variation in time spacing of spikes probably also plays a role in lowering reproducibility of crater dimensions.

*Reproducibility of Spectra.* At the same time that the 20 craters were produced in the steel standard to estimate reproducibility of volumes, cross excitation of sample vapor from these craters was carried out to compare reproducibility of volumes with that of spectra recorded on

---

ments is calculated by dividing the standard deviation of the values by their arithmetic average and converting to percent. Coefficient of variation provides a more common basis for comparing reproducibility of measurements of different quantities than does standard deviation.

<sup>1</sup> The main effect of slight increase or decrease in laser energy is to produce deeper or shallower craters in a given material: diameters change only slightly. Therefore measurement of depth was used as an indication of reproducibility of volume of craters. In addition, depth is more precisely measurable than diameter, owing to rounding of crater lips (Fig. 2).



film. Percent transmissions<sup>1</sup> of a weak nickel line and a weak iron line were measured in the series of 20 spectra; the nickel line showed a standard deviation of  $\pm 5.8$  percent from the average of the measurements, while the iron line gave a  $\pm 6.9$  percent standard deviation (coefficients of variation: 10.0 and 12.5 percent, respectively). Reproducibility of spectra in this experiment is thus somewhat lower than that of crater dimensions, and it is possible that spikes spaced somewhat differently in time from shot to shot interact with slightly different density vapor plumes and prepare the sample vapor to varying degrees for cross excitation by the electrodes. Precision on film can, however, be further improved by using the internal standard or variable internal standard principle, as evidenced by the fact that the ratios of percent transmissions of the nickel to the iron line in the series of spectra mentioned above show a standard deviation of only  $\pm 0.051$  percent from the average for the ratios, corresponding to a coefficient of variation of 5.06 percent.

*Discussion.* The value cited for reproducibility of laser output is valid only for the particular laser in use in our laboratory, and other units using the ruby rod may be expected to give a slightly different result. The cited values of reproducibility of crater dimensions and spectra apply only to the specific standard studied and the laser power level used in these experiments. For comparison with the present results it should be noted that Rasberry *et al.* (1967) used N.B.S. standard 461 to determine reproducibility of spectra and line intensity ratios. Their single-spike precision is comparable to our multiple-spike reproducibility, but line percent transmission ratios<sup>2</sup> obtained with their instrument are somewhat less reproducible than those obtained with our unit.

#### DETECTION LIMITS

Detection limits for the laser microprobe were estimated in the following ways. To determine detection limits at 1000 ppm, a standard powder containing this concentration of 42 elements mixed in a matrix of spectrochemically pure graphite was briquetted in a half-inch diameter press.<sup>3</sup> Despite pressures of 40,000 pounds per square inch *in vacuo*, considerable pore space remained in the standard. But the density of the briquette

<sup>1</sup> We have used reproducibility of percent transmission of lines rather than reproducibility of intensity of lines as a measure of reproducibility of spectra in order to eliminate possible errors due to film calibration, and effect of slope of the film calibration curve on the conversion of percent transmission values to intensity. It should be noted that in most instances reproducibility of intensity and intensity ratios will be somewhat lower than that of percent transmission.

<sup>2</sup> M. Margoshes, pers. comm.

<sup>3</sup> The standard powder was obtained from the Jarrell-Ash Co., Waltham, Mass.

was calculated from its weight and volume, and measurement of volumes of craters produced by the focused laser beam allowed approximate calculation of the weights of sample introduced between the electrodes. The sample weights amounted to an average of 20 micrograms. Although this is a small amount of material, replicate spectra obtained from the briquette showed that at 1000 ppm the trace elements were homogeneously distributed at this sampling scale. Results of the experiment<sup>1</sup> are as follows:

Elements detected in 20  $\mu\text{g}$  at 1000 ppm:

Si, Al; Li, Na; Be, Mg, Ca, Sr, Ba; Ti, V, Cr, Mn, Fe, Co, Ni; Cu, Ag, Cd, Hg; Sn, Pb, Bi, Sb, Te; Zr, Cb, Mo, W; Ce, Th, U; B, P; Ga, Ge, In, Tl.

Elements not detected:

Zn, As, Hf, Ta.

At concentration levels lower than 1000 ppm, however, briquetted powders could not be used because replicate spectra revealed inhomogeneous distribution of the trace elements in the graphite matrix. Accordingly, to establish detection limits below 1000 ppm, analyzed alloys containing precisely-known quantities of sixteen trace elements were used; these proved to have satisfactory trace-element homogeneity. Detection limits below 1000 ppm with 3 microgram samples are listed below.

Detection Limits (in ppm) for Certain Elements (3 Microgram Sample)<sup>2</sup>

Al: 200; Be: 12; Ti: 280; V: 830; Cr: 60; Mn: 40; Co: >700; Ni: 210; Ag: 10; Sn: 480; Pb: >200; Bi: 180; Sb: >500; Te: >400; W: >480; B: >32; P: >1100; Ga: 80; Si: 270; Fe: 240.

Overall limits of detection in this experiment are not as high as those obtainable in conventional spectroscopy, owing to the very minute amount of material involved. Detection limits may, however, be lowered considerably by obtaining spectra from several areas of sample, or from several grains of the same mineral, without changing film position, thus "building up" intensities of trace element lines. For example, the writers have detected vanadium in an alloy at a concentration level of 270 ppm by superposing spectra from four 3 microgram craters, and this extends the detection limits for vanadium far below the 830 ppm limit obtainable with one 3 microgram spectrum. Limits cited by Rasberry *et al.* (1967) for

<sup>1</sup> Kodak 103-F emulsion was used, with a slit width of 50 microns and cross electrode voltage of 1200 volts.

<sup>2</sup> Conditions as with 20  $\mu\text{g}$  above, except that Kodak 103-0 film and a 20 micron slit width was used. Copper and aluminum alloys with known amounts of trace elements were obtained from Johnson Matthey and Company, Ltd., London, England for use in these experiments, together with stainless steel standards from the Bureau of Analyzed Samples, Ltd., Middlesbrough, England.

five metals appear to be somewhat better than those cited here; they detected 10 ppm of copper and magnesium, 20 ppm of manganese and silicon, and 50 ppm of iron in a one microgram sample of zinc.

The sensitivity of the method is sufficiently high as to raise the question why it should be, considering the minute amount of material employed. It is suggested the answer may lie in the very efficient use which is made of the sample vapor. While the vapor plume is small, it is precisely aligned with the optical axis of the spectrograph. The spectrograph is relatively fast, and spectra are recorded on very sensitive emulsions. The detection limits are such as to make the laser microprobe a useful supplement to the electron microprobe: intense, continuous background (Bremsstrahlung), generated by decelerating electrons, often prevents accurate determination of elements present in concentrations below about 1000 ppm with the electron probe.

#### CONCLUSIONS

It appears that reproducibility of the laser microprobe technique is sufficiently high and detection limits sufficiently low so that the method is suitable for quantitative trace element analysis of minerals. Complete quantitative analysis of major and trace elements present in a single unknown mineral grain could perhaps be done with the laser microprobe if the proper standards were at hand, but in the present laboratory an electron microprobe is available for major element mineral analysis. The following procedure is, however, currently being investigated as a means of using the laser microprobe in conjunction with the electron probe to estimate abundance of trace elements in minerals. Analysis of the mineral whose trace element content is of interest is obtained with the electron probe, and one or more elements present in low amount (one half to one percent, say) are chosen as internal standards for the trace elements. Standards (alloys or well-analyzed minerals) containing known concentrations of the internal standard and trace elements are analyzed with the laser probe and intensity ratios of internal standard lines relative to analysis lines are measured; the ratios are used to establish a working curve in which the concentration ratio of the trace element to internal standard is plotted *vs.* the intensity ratio of trace element line to internal standard line. The working curve is then used to estimate trace elements in the mineral. Analogy with the well-known variable internal standard procedure of conventional spectrography is apparent, and the precision of this method would reduce errors introduced by lack of reproducibility of laser output.

We have had some success with the above approach using well-analyzed minerals as trace element standards (accuracy averaged  $\pm 23$  per-

cent), but the problem of nonhomogeneity is acute because of variations in trace element content produced by zoning and grain-to-grain compositional differences. Alloys appear to offer the best means of standardization<sup>1</sup>, but even alloys whose average trace element content is precisely known may contain local concentrations of these elements. In such instances a number of spectra should be obtained from the alloy and the average intensity of trace element lines related to the composition. Rasberry *et al.* (1965, 1967), Runge *et al.* (1964, 1966) and Devlin and La Conti (1965) have all been successful in establishing working curves for analysis of various alloys with the laser microprobe.

Quantitative analysis of trace elements in meteoritic minerals is currently in progress in our laboratory and these results will be reported later.

*Note added in proof:* The Jarrell-Ash Company now has a neodymium laser microprobe in production. The newer unit reportedly affords greater reproducibility. In addition, this company is developing a one-channel direct-reading spectrograph for the laser probe. Use of a photomultiplier tube instead of film apparently increases sensitivity sufficiently so that the probe may be run without cross excitation, using smaller craters.

#### ACKNOWLEDGMENTS

We are grateful to Dr. W. L. Linlor, Ames Research Center, NASA, for discussions on aspects of laser operation, and to M. Margoshes and S. D. Rasberry, National Bureau of Standards, Washington, D. C., for critical manuscript review. One of us (K. G. Snetsinger) is supported by a National Academy of Sciences—National Research Council Postdoctoral Resident Research Associateship.

#### REFERENCES

- ANONYMOUS (1963) Jarrell-Ash Laser Microprobe. Jarrell-Ash Co., Bulletin 45-600, Newtonville, Massachusetts.
- BERNDT, M., H. KRAUSE, L. MOENKE-BLANKENBURG AND H. MOENKE (1965) Micro-Emissionsspektral-Analyse mit Festkörper-Laser. *Jenaer Jahrb.*, 45-57.
- BIRNBAUM, G. (1964) *Optical Masers*. Advances in Electronics and Electron Physics, Supplement 2. The Academic Press, New York, 306 pp.
- BRECH, F. AND L. CROSS (1962) Optical microemission stimulated by a ruby maser (abs.). *Appl. Spectrosc.* 16, 59.
- BROTHERTON, M. (1964) *Masers and Lasers*. McGraw-Hill Book Co., New York, 207 pp.
- BROWNE, P. F. (1964) Vaporization of materials by Q-spoiled laser pulses for spectroscopic analysis. *U. S. Clearinghouse Fed. Sci. Tech. Inform.* AD673536.
- DEBRAS-GUÉDON, JEANNINE AND NICOLE LIODEC (1963) De l'utilisation du faisceau issu d'un amplificateur à ondes lumineuses par émission induite de rayonnement (laser a rubis) comme source énergétique pour l'excitation des spectres d'émission des éléments. *C. R. Acad. Sci.*, Paris, 257, 3336-3339.

<sup>1</sup> Alloys may be used as standards for minerals (even silicates) if the concentrations of internal standard and analysis elements are comparable in the standard alloy and in the mineral.

- DEVLIN, JAMES J. AND A. B. LA CONTI (1964) An investigation of properties of the laser microprobe. *U. S., Clearinghouse Fed. Sci. Tech. Inform.* AD632416.
- FERGUSON, H. I. S., J. E. MENTAL AND R. W. NICHOLLS (1964) Laser excitation of powdered solids. *Nature* 204, 1295.
- KLOTZBAUGH, G. A., A. L. WOLFE, J. E. PATERSON, AND T. A. OSIAL (1965) Investigation of the use of a laser as a spectrographic source. *U. S., Clearinghouse Fed. Sci. Tech. Inform.* AD622102.
- MAXWELL, J. A. (1963) The laser as a tool in mineral identification. *Can. Mineral.* 7, 727-737.
- MICHAELIS, R. E., H. YAKOWITZ AND G. A. MOORE (1964) Metallographic characterization of an N.B.S. spectrometric low-alloy steel standard. *Nat. Bur. Stand. (U.S.) Misc. Publ.* 260-3.
- RASBERRY, S. D., B. F. SCRIBNER AND M. MARGOSHES (1965) Laser probe excitation. *Nat. Bur. Stand. (U.S.) Tech. Note* 272, Sec. 2E, p. 21-27.
- (1967) Laser probe excitation in spectrochemical analysis. I: Characteristics of the source; II: Investigation of quantitative aspects. *Appl. Optics* 6, 81-93.
- RUNGE, E. F., S. BONFIGLIO AND F. R. BRYAN (1966) Spectrochemical analysis of molten metal using a pulsed laser source. *Spectrochimica Acta* 22, 1678-1680.
- , R. W. MINCK AND F. R. BRYAN (1964) Spectrochemical analysis using a pulsed laser source. *Spectrochimica Acta* 20, 733-736.
- RYAN, J. R., C. B. CLARK AND E. RUH (1965) Laser microprobe analysis of glass defects (abs.). *Amer. Cer. Soc. 67th Ann. Meet., Philadelphia, Penn., May 1965.*
- SCHAWLOW, A. L. (1965) Lasers. *Science* 149, 13-22.

*Manuscript received, March 23, 1967; accepted for publication, May 12, 1967.*