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FEATURE ARTICLE

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Laser ablation – reflections on a very complex technique for solid sampling

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Abstract This paper is an attempt to point out the complex correlations between the experimental conditions in solid sampling by lasers. In particular, the influence of the laser properties, the surrounding gas, and the matrix on the analytical results of laser ablation techniques, such as laser induced breakdown spectrometry or laser ablation–ICP–MS, will be discussed.

Introduction

In the last 30 years laser ablation of solids has been studied extensively in different fields of the natural sciences, e.g. physics, chemistry, and engineering. An enormous body of work has been published spanning from the theory of radiation–matter interaction in pure physics to the application of lasers in areas, such as high-power plasmas for X-ray generation, pulsed laser deposition (PLD) for thin film coating, cutting and welding of workpieces with lasers, and tissue and bone surgery in laser medicine. Excellent books and review papers are available describing aspects of such laser applications [1–10]. It is not astonishing that, because of the diversity of fields and journals, many papers have been published in different areas reporting on facts and findings which have already been studied and published before in journals of other scientific communities. Analytical chemists using lasers for solid sampling are no exception. They mainly read the journals of *their* scientific community and are also in danger of working in parallel with colleagues in other fields. It must, however, be admitted that it is even difficult to follow the literature in analytical chemistry and applied spectroscopy journals, because the number of analytical papers dealing with this topic has increased substantially in recent years.

The process of ablation of solids is very complex. It depends on many parameters which are more or less dependent on each other. Simplifications or "rules of thumb" may lead to serious systematic errors in sample analysis. This paper does not claim to discuss all aspects and processes in deep detail nor to give perfect solutions for accurate analysis. It should rather be regarded as an attempt to describe the complex correlations between the experimental conditions in a relatively short paper.

Discussions of the different aspects and processes are supported by experimental results and figures published by our group at the Institute of Spectrochemistry and Applied Spectroscopy during the last 11 years. Some of the results could also be taken from other research groups. However, these results were obtained using different experimental conditions which makes comparison and discussion more complicated. Therefore, the author restricts himself to data and figures from own publications to demonstrate the very complex processes involved in laser sampling.

Basic experimental arrangements

Experimental arrangements for element analysis by laser ablation can be divided into two categories:

1. methods based on the direct measurement of the plasma produced in the ablation process, and
2. techniques which require the transport of the dry aerosol formed after the expansion and recombination of the plasma.

Typical arrangements belonging to these categories are shown schematically in Figs. 1 and 2, respectively.

The most simple, most widely applied direct technique is based on the measurement of the emission spectra of the laser-produced plasma as shown in Fig. 1a. In the literature several names can be found for this technique. The most popular names are laser-induced breakdown spectrometry (LIBS) and laser-induced plasma spectrometry (LIPS), but one can also find optical emission spectrometry (OES) of laser-induced plasmas and others. Below, we will use the acronym LIBS. LIBS requires time-resolved detection, because there are dramatic changes of the emission spectra with time, which will be demonstrated below. Furthermore, the imaging observation mode should be chosen with care. It is possible to observe the

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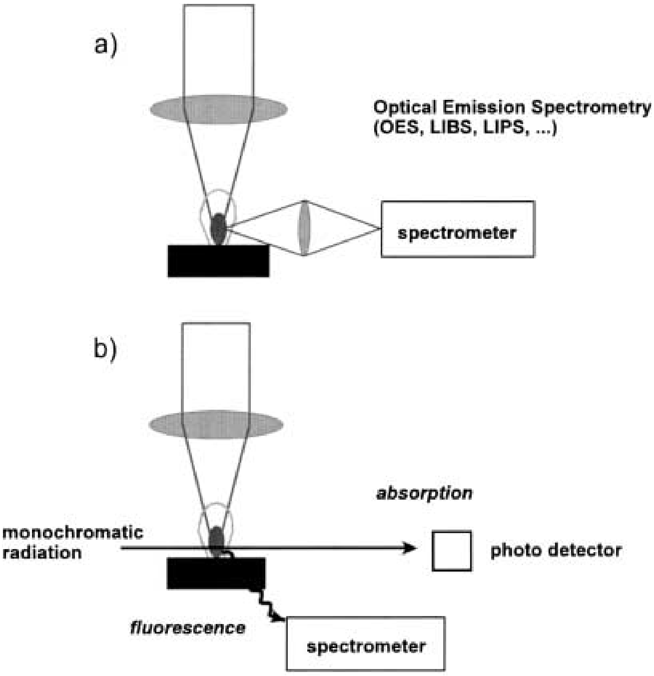


Fig. 1 Basic experimental arrangements for (**a**) optical emission spectrometry, and (**b**) absorption or fluorescence detection

plasma side-on, as shown in Fig. 1a, or from a different angle, for example, end-on. The plasma can be imaged on to the slit of the spectrometer which gives spatial information or imaging methods can be applied which give no spatial information.

Other "direct" methods shown in Fig. 1b apply absorption or fluorescence using monochromatic radiation, for example, from a tunable laser. These methods are unimportant for routine analysis, because they are generally restricted to sequential measurements of single elements. The very sensitive fluorescence technique can, however, be used for characterization of the spatial and temporal evolution of the plasma.

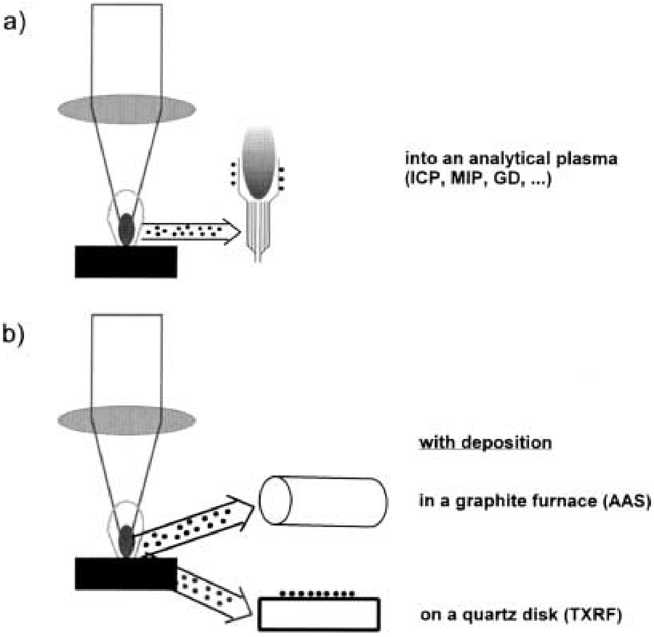


Fig. 2 Basic experimental arrangements for methods based on the transport of laser-produced aerosols. (**a**) Aerosol transport into an analytical plasma; (**b**) aerosol transport and deposition in a graphite tube furnace or on a quartz disk

The most popular method of the second category, in which the laser-produced aerosol is transported before being analyzed, is the coupling of a laser ablation cell with an inductively coupled plasma (ICP). Other plasmas, for example microwave-induced plasmas (MIP) or glow discharge plasmas (GD), can also be used, although the latter combinations are not commercially available. Most producers of ICP–MS instruments offer the option of solid sampling by lasers. ICP–MS customers can also purchase a pulsed laser, a sample cell for ablation, and transport tubes to the ICP.

Other methods based on aerosol transport (Fig. 2b) are deposition in a graphite furnace for element analysis by AAS, or deposition of the particles on a quartz disk for analysis by total reflection X-ray fluorescence (TXRF). These techniques are not currently commercially available.

All techniques have in common that they can be applied if homogeneous samples of very similar composition and morphology are be analyzed, all experimental conditions are unchanged, and standard reference samples of very similar composition and structure are available. Problems can arise if these preconditions are not fulfilled or experimental parameters must be changed to find the optimum conditions for analysis.

Ablation process of solid samples with pulsed lasers

Figure 3 shows the physical main processes of laser ablation in a simplified diagram. The laser radiation is absorbed by electrons in the surface layer of the sample. The penetration depth of the radiation depends mainly on the optical properties of the sample. The very hot electrons leave the sample immediately (femtosecond time scale). The others heat the irradiated volume by collisions with atoms of the solid sample (picosecond time scale). There is melting of the sample in the laser focus and, at sufficiently high intensities, explosion-like evaporation of the liquid sample material in form of a plasma with electrons, ions, molecules, and clusters which is further heated as long as the laser pulse is lasting.

When the sample is ablated into vacuum, the expanding plasma fills a large volume within a short time. This is different form the ablation process in a gas. Here, the

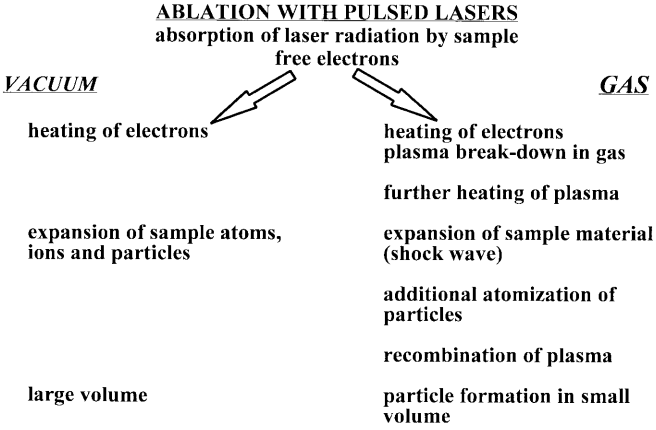


Fig. 3 The main physical processes and effects of ablation with pulsed lasers

heating of electrons outside the sample initiates a breakdown in the plasma gas, an increase in electron density as a result of ionization of the gas atoms, and further heating of the plasma. The free expansion of the sample material is, furthermore, hindered by the plasma gas. The expanding sample material forms a shock wave which can even be bounced back. The ablated material does not fill a large volume during the recombination and cooling of the plasma, as in vacuum ablation. The volume decreases as the gas pressure increases. The dependence of plasma size on gas pressure can easily be observed with the naked eye. The particle density of ablated ions, atoms, and clusters is higher than at lower gas pressure as a consequence of the reduced volume, and the reformation of particles is favored.

The process described can be studied by spectroscopy. Figure 4 shows emission spectra of a laser-generated plasma very close to the surface of a steel sample in Ar at atmospheric pressure. The spectra were measured with an intensified and time-gated diode array in the focal plane of a spectrograph. No lines from sample atoms can be observed with an integration interval of 100 ns and a start time at the laser pulse (5 ns long). Only Ar lines can be observed. Most are lines of singly ionized argon. In other regions of the spectrum even strong Ar(III) lines can be observed. The lines shown in Fig. 4 are very broad, because of Stark broadening, which indicates the high electron density in the time interval. The presence of Ar ion lines is a result of high electron temperatures. The spectrum from the same volume, however, recorded 1 µs after the ablation pulse with an integration time of 10 µs no longer shows Ar lines. Instead, emission lines from the major elements of the sample, Fe and Cr, can be observed.

However, the integration from 1 to 11 µs obscures a dramatic change in the plasma. Figure 5 shows LIBS spectra of a steel sample in Ar at reduced pressure (140 mbar) with higher temporal resolution. There are almost exclusively ion lines of sample atoms observed in a volume 1.4 mm above the sample in the time interval 0.5 to 1 µs (Fig. 5A). Some Fe ion lines are designated by stars. There is no line at the 288.2 nm position where a strong neutral Si line is expected, because this element is present in the sample. Because of the high plasma temperatures in this

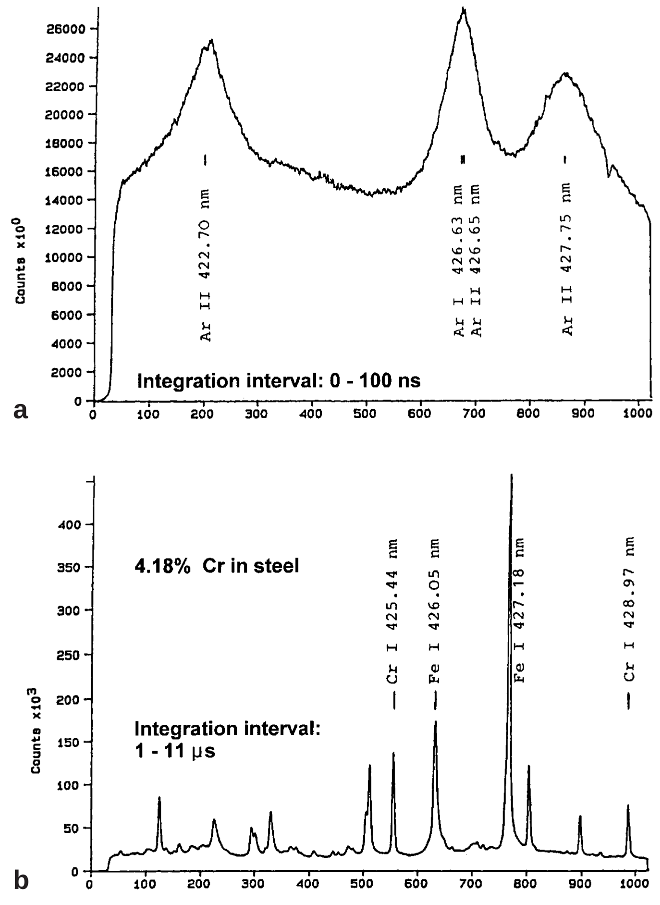


Fig. 4 Laser ablation of a steel sample in Ar at atmospheric pressure. Average emission spectra of the laser-produced plasma in the first 100 ns (**a**) and in the time interval 1–11 µs (**b**). The numbers on the abscissa are the pixel numbers of the intensified diode array used

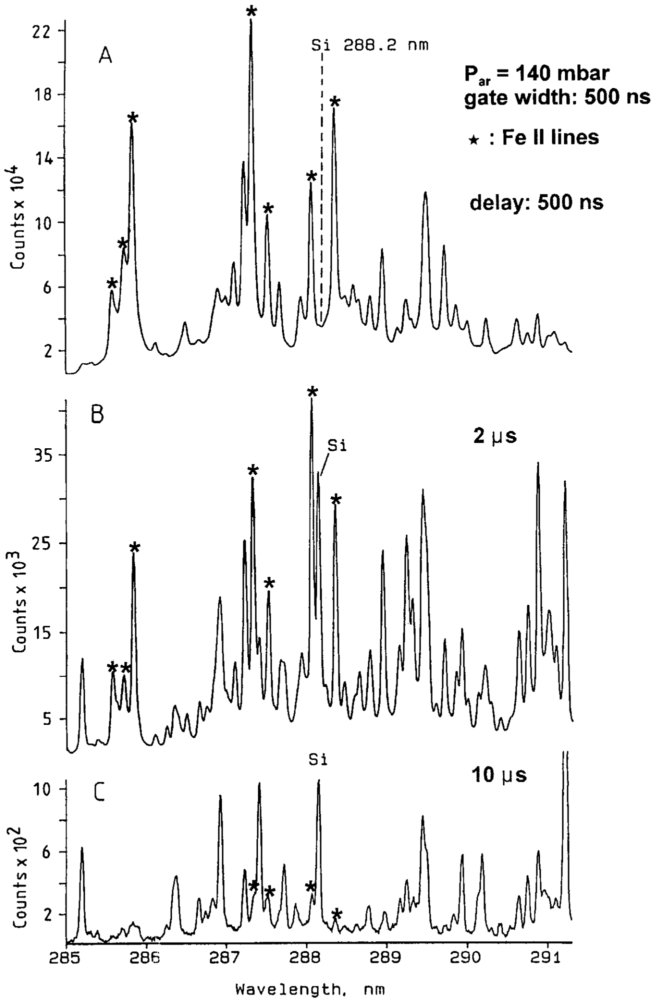


Fig. 5 Emission spectra development as a function of time from a laser-produced plasma in Ar applied to a steel sample. From Ref. [11]

time interval, Si is ionized. The Si line can be observed in the detection interval 2–2.5 µs (Fig. 5B), where the plasma has already cooled down. Also, the designated Fe ion lines are less intense, and neutral Fe lines appear. Finally, at 10–10.5 µs, the Fe ion lines have almost disappeared (Fig. 5C). The Si line and neutral Fe lines now dominate the LIBS spectrum.

It is interesting to look at the time-dependence of the relative densities of neutral and ionized atoms in the very center of the plasma. Laser-induced fluorescence (LIF) is a very good diagnostic method for this type of measurement. LIBS spectra cannot provide this information, because there is also emission from the outer, cooler regions of the plasma. Laser light collimated into a very narrow beam and transmitted through the laser-produced plasma can generate atomic and ionic fluorescence along the beam. High spatial resolution can be obtained if the fluorescence is imaged at right angles to the laser beam on to the entrance aperture of a spectrograph. Figure 6 shows the dependence on time of LIF from neutral and singly ionized Mg in a very small volume 0.8, 1.8, and 2.8 mm above the sample. The sample was copper and the gas Ar at 140 mbar. In fact, Fig. 6 gives the relative Mg(I) and Mg(II) concentrations, because the laser was tuned to the resonance lines of the Mg atom and Mg ion. There was no LIF signal from neutral Mg at 0.8 mm within the first 5 µs. On the other hand, high ion concentrations could be detected in this time interval. It is very likely that even Mg(III) is present at the very beginning. Unfortunately, Mg(III) could not be probed by LIF, because its resonance line is in the vacuum UV range. Qualitatively the same dependencies on time are obtained if the atomic and ionic concentrations are measured at larger distances from the sample surface (Fig. 6) or at different Ar pressures 1.5 mm above the sample (Fig. 7). It should be stressed that *ion to neutral ratios of elements are different in spatially different volumes of the plasma,* even later than 100 µs after the laser pulse. Even more important is the fact that *the ratios of elements can be spatially dependent.* Figure 8 shows the time dependencies of the LIF signals from neutral Mg and Si measured 0.8 mm above a copper sample. Ar at 140 mbar was used as a plasma gas. It can be seen that neutral Si atoms are present even approximately 1–2 µs after the laser pulse, when Mg is still fully ionized. The Si ion concentration, not shown in Fig. 8, peaks before the Mg(II) concentration, and the Si ion to neutral ratio is different from that for Mg. This cannot be attributed solely to the different ionization potential of Mg (61,669 cm^{-1}) and Si (65,743 cm^{-1}), because the difference is small. The main reason might be the very different atomization properties of Mg and Si. Mg vaporizes faster than Si from the laser-ablated sample material in the Ar plasma, and, therefore, experiences higher temperatures at earlier times in the

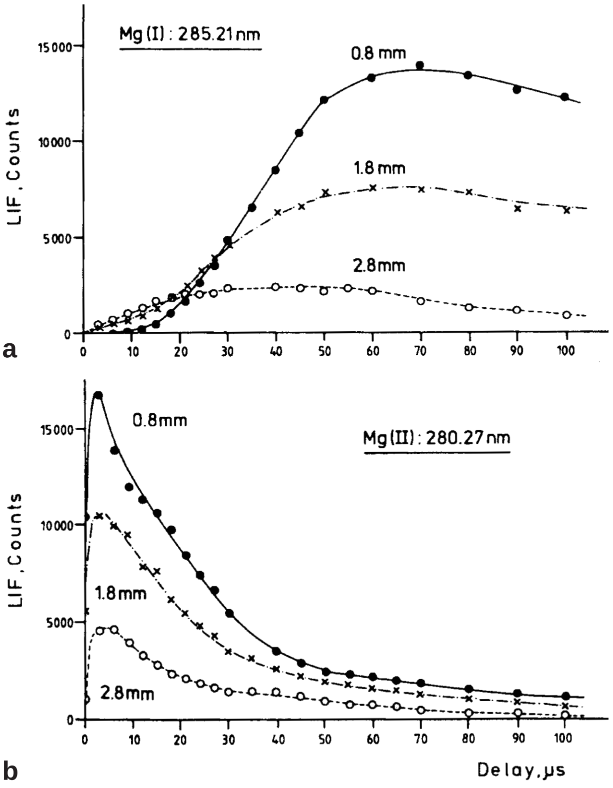


Fig. 6 Time-dependence of the fluorescence signals from neutral Mg (**a**) and singly ionized Mg (**b**) in a laser-produced Ar plasma (p = 140 hPa) measured in a small volume 0.8, 1.8, and 2.8 mm above the surface of a copper sample. From Ref. [12]

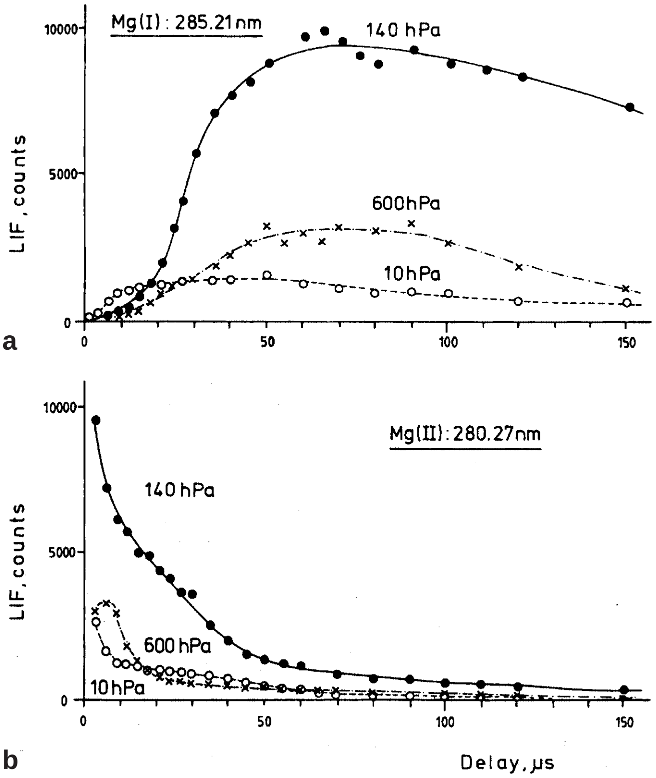


Fig. 7 Time-dependence of the fluorescence signals from neutral Mg (**a**) and singly ionized Mg (**b**) in a laser-produced Ar plasma measured in a small volume 1.5 mm above a copper sample at different Ar pressures. From Ref. [12]

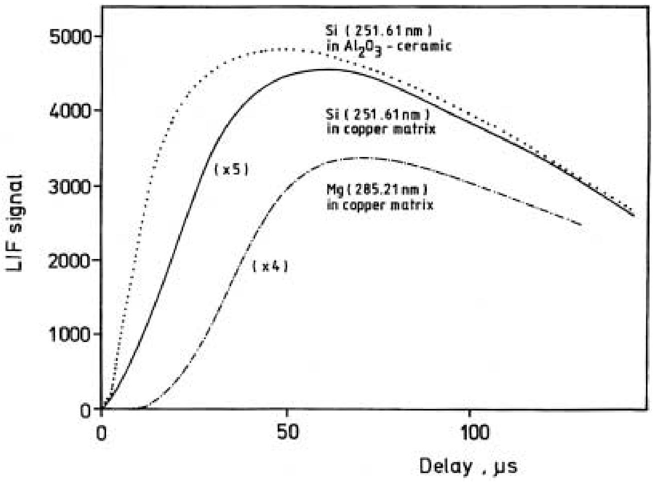


Fig. 8 Time-dependence of the fluorescence signals from Mg and Si in laser-produced Ar plasmas (p = 140 hPa) measured in a small volume 0.8 mm above the surfaces of copper and ceramic samples. From Ref. [13]

rapidly cooling plasma. This, of course, has an influence on the extent of ionization. On the other hand, compared with elements with slower evaporation, there is faster diffusion of Mg atoms to outer volumes of the plasma, leading to a kind of "spatial de-mixing". As a consequence, the element composition in aerosol particles formed after the plasma has cooled would be spatially dependent in the case of de-mixing. This can be important for methods which are based on aerosol transport, as discussed later.

Important conditions

The most important conditions for laser ablation are listed in Table 1. The result of the laser sampling depends on the properties of the laser (pulse length, wavelength, intensity, and beam profile), the plasma gas, its pressure and flow rate, and the matrix (absorption properties, structure, homogeneity, and surface orientation). Unfortunately, *the effect of a particular condition is also dependent on the other conditions*. This fact complicates the optimization of experimental conditions for laser sampling.

Laser properties

Lasers are available in continuous wave (cw) and pulsed mode. They differ in wavelength, power, and beam quality. All these parameters have a strong impact on the performance of laser sampling and should carefully be taken into account.

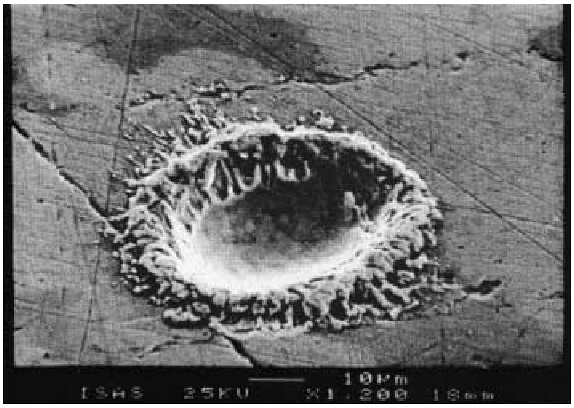
Table 1 Important conditions in solid sampling with lasers

Laser	Plasma gas	Matrix
Pulse length	Kind of gas	Laser absorption
Wavelength	Pressure	Morphology
Intensity	Flow rate	Homogeneity
Beam profile		Surface orientation

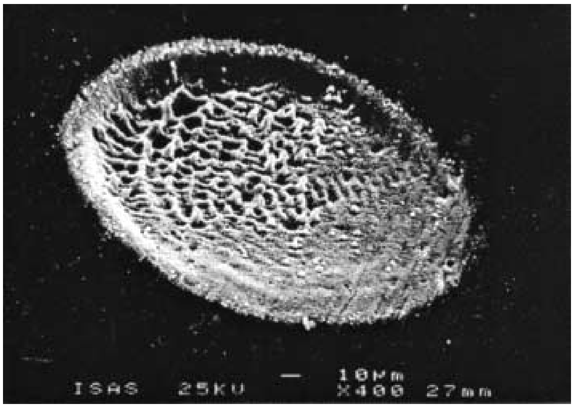
Laser pulse length

Lasers for solid sampling should always be operated in pulsed mode. The cw mode, as often used for drilling and welding in engineering, would have serious drawbacks. The application of a cw laser would require much lower intensities than the peak intensities of pulsed lasers. There would be continuous removal from the sample which is closer to ordinary evaporation than the explosion-like ablation process of pulsed lasers. The small area irradiated by the cw laser would continuously melt and the spatial composition in the liquid would change with time because of fractional evaporation and mixing in the liquid phase. Furthermore, the plasma above the sample would be continuously heated and, if the intensity is not low enough, would shield the sample from the laser beam because of absorption by high electron densities. The absorption by the plasma can be reduced by the choice of a laser with a shorter wavelength, a different kind of gas, and a lower gas pressure (see below).

The most popular lasers for ablation have nanosecond pulse lengths. Sufficiently high intensities for explosion-



ns-laser



fs-laser

Fig. 9 SEM exposures of craters produced with nanosecond and femtosecond pulses. From Ref. [14]

like ablation can be used and there is additional heating of the plasma gas. The intensities, the wavelength, the kind of gas, and its pressure, must, however, also be chosen carefully to avoid plasma shielding of the sample.

The application of lasers with shorter pulses, for example, pulses in the picosecond or even femtosecond range, reduces heat dissipation by collisions of the high-energy electrons with the atoms in the solid, and, therefore, minimizes melting of the laser crater region (see Fig. 9) and fractional evaporation from the liquid phase. On the other hand, there is also less energy deposited in the gas plasma; this usually helps to atomize the material ablated from the sample.

Laser wavelength

The absorption of the sample depends on the wavelength of the laser. Therefore, the mass ablated in single shots can vary with wavelength. One should, however, keep in mind that the absorption coefficient of the sample increases dramatically during the laser pulse, because the electron density in the conduction band of the sample rises.

The energy transfer from the laser field to the free electrons in the plasma outside the sample is also strongly dependent on wavelength. It is very well known from the dispersion theory of an electronic gas that absorption decreases at shorter wavelength. Higher intensities and also slightly longer pulse lengths can be applied with short-wavelength lasers, because plasma-shielding is reduced.

Laser intensity

The laser intensity, I_L, is an important property for the deposition of laser energy. It is responsible for the generation and heating of electrons in the conduction band of the solid and in the plasma above the surface. For example, multi-photon absorption is a dominating process for the production of electrons in the conduction band and of free electrons if the sample in an electric insulator, e.g. glass. Multi-photon production of electrons is proportional to I_L^n, where n is the number of photons involved in the process. On the other hand, the local heating of electrons in the sample as well as in the plasma can be changed by variation of the focus diameter of the laser beam.

Laser beam profile

The shot-to-shot reproducibility of the laser beam profile must be very good. Fluctuations in the transversal mode structure and hot spots in the laser beam profile can create significantly different ablation results. The beam profile should have at least Gaussian shape (TEM_{00}) which produces “bell-shaped” craters (see Fig. 9). “Flat-top” beams, which have good homogeneous intensity distributions, have advantages in laser sampling. They can be generated from Gaussian laser beams either by expansion of the beam and use of an aperture which selects the central part, or by the application of specially designed optical arrangements of lenses or mirrors. Laser craters produced by use of flat-top beams are shallower and have almost flat bottoms. With some restrictions, such beams can be used for rapid depth-profiling, for example, of technical multi-layer films.

Plasma gas

The plasma gas also provides very important conditions for laser sampling. Noble gases are the best choice, because, to a first approximation, they do not react with sample atoms, ions or clusters. The gas pressure and the gas flow also usually have strong impacts on the ablation process.

Kind of gas

Gases which dissociate into reactive atoms or radicals in a plasma, for example H_2, O_2, N_2, CO_2, or air, should be avoided because they can influence the analytical result for different elements by preferential interaction. This means that a noble gas is the best choice as plasma gas. The plasma conditions are, however, highly dependent on the kind of noble gas, as the point of plasma breakdown is different. The lighter the noble gas, the higher the laser intensities which must be applied in ablation. As a consequence, the heavier the noble gases, the higher are the plasma temperatures if the intensity is sufficiently high to achieve plasma breakdown. High plasma temperatures are connected with high electron densities which can shield the sample from the laser beam, as discussed above. On the other hand, plasmas of different temperatures have different sample material atomization properties. Finally, it should be noted that the diffusion properties for particles and the size of the plasmas depend on the noble gas selected.

Gas pressure

The plasma breakdown, the plasma temperatures, the problem of plasma shielding (electron number density), the plasma size, and the diffusion properties can be varied if the gas pressure is changed. For example, the cheapest noble gas Ar can be used even when a near IR laser (e.g., a Nd-YAG laser) with pulse lengths of several nanoseconds is used. In this case, the laser intensities applied to the sample surface can be relatively high for effective ablation if the gas pressure has been reduced. Experiments have shown that 140 mbar (hPa) Ar is the optimum pressure for ablation, plasma heating, and effective atomization if a Nd-YAG laser is used.

Gas flow rate

The gas flow rate is important for the transport of the aerosol particles from the place of ablation to the analytical plasma (see Fig. 2). Here, the loss of aerosol must be minimized. The aerosol particles must, however, also be removed from the ablation cell in all other experimental arrangements. Particles which are left from the last laser shot can generate plasma breakdown in the laser beam above the sample and change the ablation conditions dramatically.

Matrix

Laser absorption, morphology, homogeneity, and surface orientation of the matrix must be taken into account in laser sampling.

Laser absorption of the matrix

Aspects affecting laser absorption have already been discussed. In particular, the wavelength and intensity but also the pulse length have a strong influence on the ablated mass. Variations in the matrix composition change the absorption and the mass removed. Figure 10 shows the excitation temperature measured in a LIBS experiment with binary Fe/Cr samples. The excitation temperatures are lower if the chromium content in the sample increases. This is a result of the increase in mass ablation which cools the plasma because of the atomization enthalpy. It means that absorption by the matrix in the ablation process is larger with higher Cr concentrations.

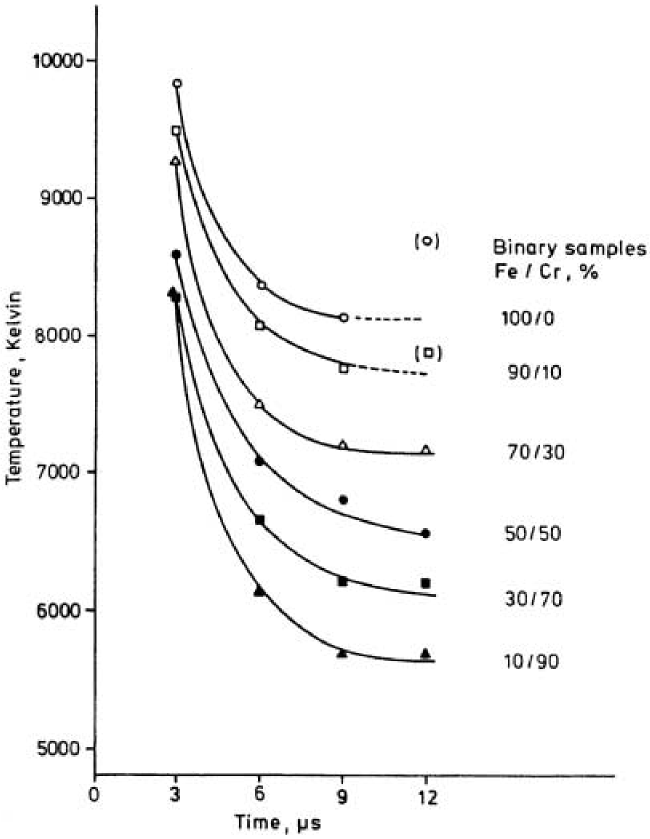


Fig. 10 Excitation temperature measured by optical emission spectrometry in a laser-produced Ar plasma (p = 140 mbar) 1.5 mm above binary Fe/Cr samples. From Ref. [15]

Morphology of the sample

It is not surprising that both absorption and plasma breakdown depend on the solid phase and the structure of the sample. As a result, there can be significant differences in mass ablation. Very often the first laser pulses modify the sample in the ablation area. These modifications, for example solidified sample mass in the crater, change the efficiency of ablation. Variations of the analytical results during the first laser shots have been reported by many groups.

Homogeneity of the sample

Laser ablation is a microchemical technique. It probes very small amounts of material from the solid surface at known positions. This is a strength of the technique. Laser ablation is, however, usually used for bulk analysis. Apart from the question whether the sample ablated is representative of the bulk, systematic errors can arise because of inhomogeneities in the sample. Inhomogeneities influence laser absorption, the mass ablated, and the plasma conditions. There can, on the other hand, also be substantial inhomogeneities in the standard reference samples which cause problems in analysis. Figure 11 shows that element concentration might be distributed homogeneously in one sample but be very inhomogeneous in another. These problems become even more severe if the laser is focused more tightly to sample smaller amounts of material.

Surface orientation

Although the laser beam hits the sample surface at right angles in most experimental arrangements, there are also

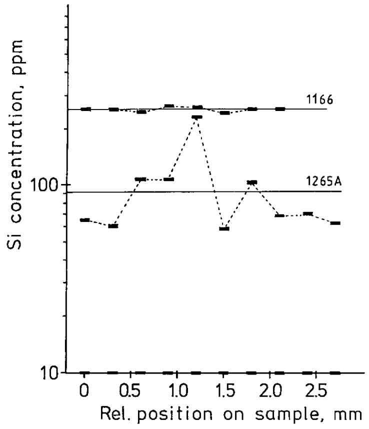


Fig. 11 Homogeneous and inhomogeneous distribution of Si in standard steel samples 1166 and 1265A from NIST measured with a spatial resolution (crater diameter) of 100 µm. From Ref. [16]

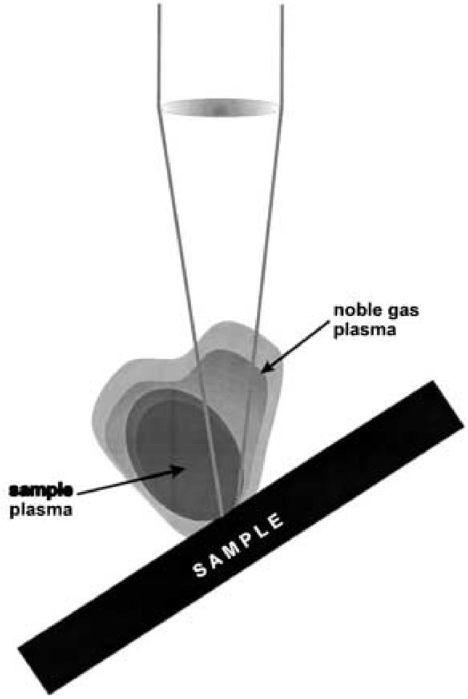


Fig. 12 Schematic presentation of the laser-induced plasma in a gas when the laser beam does not hit the sample surface at right angles

applications where the angle between focused laser and the surface is different from 90° (see Fig. 12). In this case the sample shock wave propagates at right angles to the surface while the noble gas plasma is created and heated in the laser field. The asymmetries of the total plasma can be observed by naked eye. Obviously, such gas plasmas can only partly atomize ablated material.

The charm of laser sampling is that, in principle, it does not require sample preparation. Nevertheless, many users and demonstrators of this technique machine the surfaces of the sample or even polish it. The model case illustrated in Fig. 12 and the associated problems might have to be taken into account if unfinished samples with very uneven surfaces are subject to laser ablation.

Very often many laser shots are fired on to the sample without changing position, to improve the statistics of the measurement. Here, one must keep in mind that repeated application leads to formation of craters of increasing depth. The laser intensity on the surface of the crater decreases, because the irradiated surface area grows. Furthermore, the form of the crater influences the form and characteristics of the shock wave, because the sample material always propagates at right angles to the surface.

Transport of laser-produced aerosol particles

The ideal case would be if:

1. the total mass ablated by the laser has the element composition of the sample, and

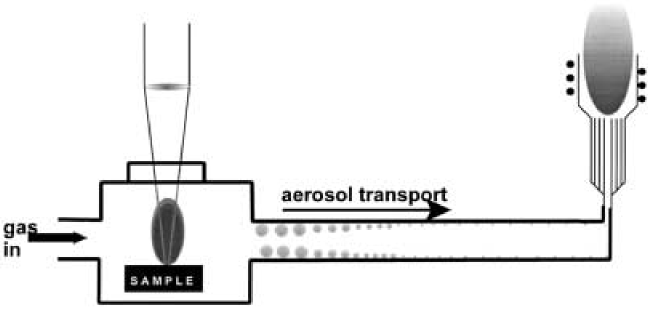


Fig. 13 Fractionating of aerosol particles in a transport tube

2. the total mass is transported to the place where it is analyzed, for example, in an ICP.

It is unrealistic to assume that both conditions are strictly fulfilled. We can come close to the realization of the first condition if we reduce or avoid thermal fractional evaporation from the crater. This can be achieved, for example, by the use of lasers with very short pulses which enable only small heat transfer to the sample (see above). There are, on the other hand, always losses when material is transported. Only the small particles will survive the transport through the tube into the plasma, the larger particles will stick to the wall of the ablation cell or to the inner wall of the first part of the tube. This is shown schematically in Fig. 13. Larger particles are lost predominately in the first section of the tube, whereas only very few and small aerosol particles can be found at the wall in the last section of the tube. The losses would be no serious problem if the element ratios in the total mass of small particles transported into the plasma would be representative of the spot on the sample probed by the laser. This is, however, questionable in the light of the discussion above, where it was pointed out that the density ratios of the elements in the laser-produced plasma can be spatially dependent. The aerosol particles formed in the different volumes should reflect the spatial inhomogeneities. We must, furthermore, consider that there are density gradients of the sample material in the laser plasma. The larger aerosol particles would mainly originate from volumes of higher density whereas the outer volumes of lower sample density would only generate small aerosols. It would be interesting to study the dependence of the analytical data from different samples on the particle distribution modified by transport through tubes. Shortening the distance between the position of laser sampling and the plasma certainly improves the situation. It should be noted that such an approach has already been realized with an MIP, as shown in Fig. 14. Here, the sample material was introduced directly into the MIP-capillary. It could be shown that as a result of complete introduction the element ratios measured by optical emission spectrometry were independent of the matrix. Metal, quartz, and ceramic samples could be calibrated with, for example, metal standard samples. A similar arrangement with a very short transport line, as in laser ablation-MIP coupling, should also be developed for the ICP.

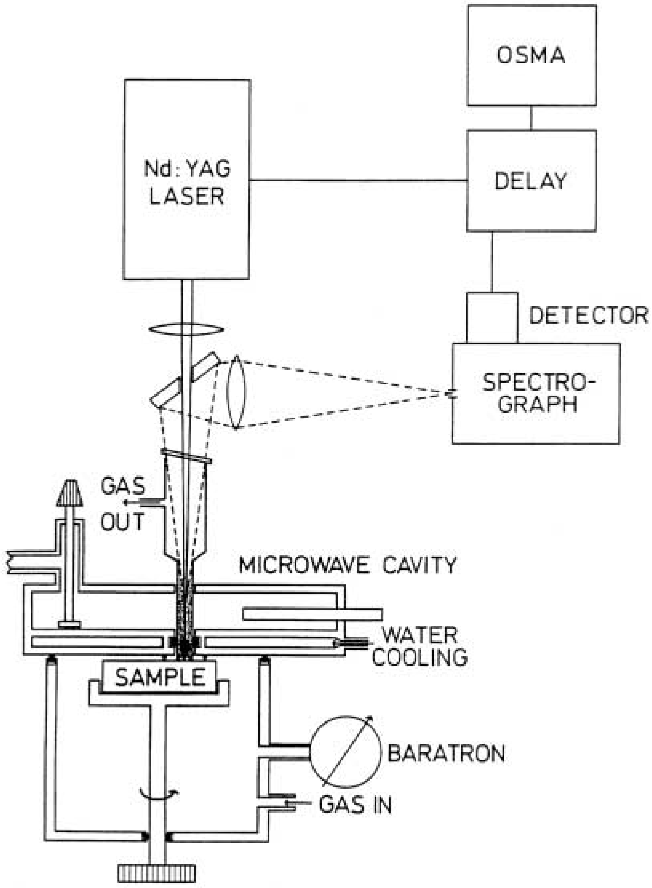


Fig. 14 Direct introduction of laser-ablated material into a MIP (OSMA: optical spectrum multi-channel analyzer). From Ref. [17]

Conclusion

The paper is a personal attempt to give a n-dimensional description of the complex technique of laser ablation for analysis of solids. The number of publications in analytical chemistry on this topic is increasing rapidly – the technique is attractive because it is fast. There are no matrices which have not been subject to laser sampling. Reports on ablation of biological soft matter, soil, artwork, or polymers can be found in the scientific literature. Scientists who wish to use the technique for the first time should, however, be aware that it is not sufficient to optimize one or two parameters. Careful consideration of this multi-dimensional optimization is necessary to avoid systematic errors in analysis.

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