

LASERS IN SOLID STATE MASS SPECTROMETRY

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Abstract - A laser micro-analyser was used to directly produce ions from aluminium, iron and brass targets in the ion source of double focusing mass spectrometer. Relative sensitivity coefficients using aluminium and iron standards were determined. With a laser power density of about 5×10^{10} W/cm² (0.05 J), values similar to those in spark source mass spectrometry were obtained. It is concluded that the use of laser ionization enables a precision as good as ± 0.1 to be obtained but it cannot justifiably be stated that all impurities in any matrix have identical relative sensitivities.

INTRODUCTION

Modern solid state technology requires an ever increasing characterization of the materials to be used. The very first requirement is the knowledge of the chemical composition of the material. In view of this, chemical analytical methods have a steadily increasing role in technological development. In recent years developments are mainly characterized by the determination of the chemical composition in μm range with a low detection limit and high level of confidence. Such requirements cannot usually be met by "classical" analytical chemistry, which means that physical methods have to be used. One such method is spark source mass spectrometry (SSMS) which, with its really multi-element character and low detection limits, has been used successfully in the chemical analysis of solid materials for about two decades.

With high voltage radio-frequency (RF) discharge, all elements in any matrix can be ionized. The energy consumed in the spark break-down is sufficiently high at evaporation and the subsequent ionization, as a result no (or only minor) selectivity occurs between the various elements. The relative sensitivity coefficients (RSC) used to characterize this selectivity are within a factor of three for the whole periodic table. Throughout this paper the following definition of RSC will be used: RSC equals $(x/y)_m$ divided by $(x/y)_{tr}$, where $(x/y)_m$ is the ratio of the concentrations of elements ^mx and y as determined from singly charged ions and $(x/y)_{tr}$ is that of the true concentrations. These RSC's can, in principle, be determined using standards and by their use, quantitative data can be expected. The problem is, however, that RSC's cannot be determined with acceptable confidence (~ 0.1). There are many data published, but the agreement between them is rather poor. The reason seems to be due to the irreproducible character of the energy transfer in the sparking process.

In secondary ion mass spectrometry (SIMS) the energy transferred, by the primary ion beam, is well controlled, therefore the RSC's are reproducible; but the energy flux is low, therefore the chemical character of the elements strongly influences the secondary ion intensities and hence the RSC's (some orders of magnitude!).

If lasers are used, the energy transferred is more easily controlled than in the case of RF-spark and at the same time the power density is comparable with the RF break-down. It is therefore expected that, if laser ionization is used, the favourable features of SSMS and SIMS can be retained; i.e. no selectivity according to the chemical character of the elements, and a better reproducibility of RSC's.

In this paper we will try to examine how this premise is realized and we will endeavour to show some of the attractive features of laser mass spectrometry

(LMS). A comprehensive review of literature will not be given; instead, the reader is referred to a number of recent excellent review papers (1-3). We are principally concerned here with the chemical analytical aspects of metallic samples.

EXPERIMENTAL TECHNIQUE

Laser-solid interaction

Sampling represents the most crucial point in solid mass spectrometric analysis. One has to know the correlation between the elemental composition of the ions leaving the solid phase and that of the sample the ions are taken from. The interaction of laser radiation with the solid will be considered from this point of view.

Because laser radiation is coherent, monochromatic and exhibits small divergence, therefore it can be focused to a small spot with a high power density. All light, not reflected, is absorbed in a thin layer of some tens of nanometers depending on the absorption coefficient of the material (4). The mechanism of vaporization and ionization is not entirely understood and we will not go into detail. The possible ways of laser-solid interactions are summarized

(2,5). The absorbed energy is relaxed in the solid phase by its being heated, evaporated and ionized. For most metals the power density required for evaporation is of the order of 10^6 - 10^8 W/cm². Having reached this value (or more), a thin layer goes over to the vapour phase dispersing into the vacuum as well as carving a crater for itself in the solid. Thus the crater is deeper than the penetration depth of the light. The process is illustrated in Fig.1.

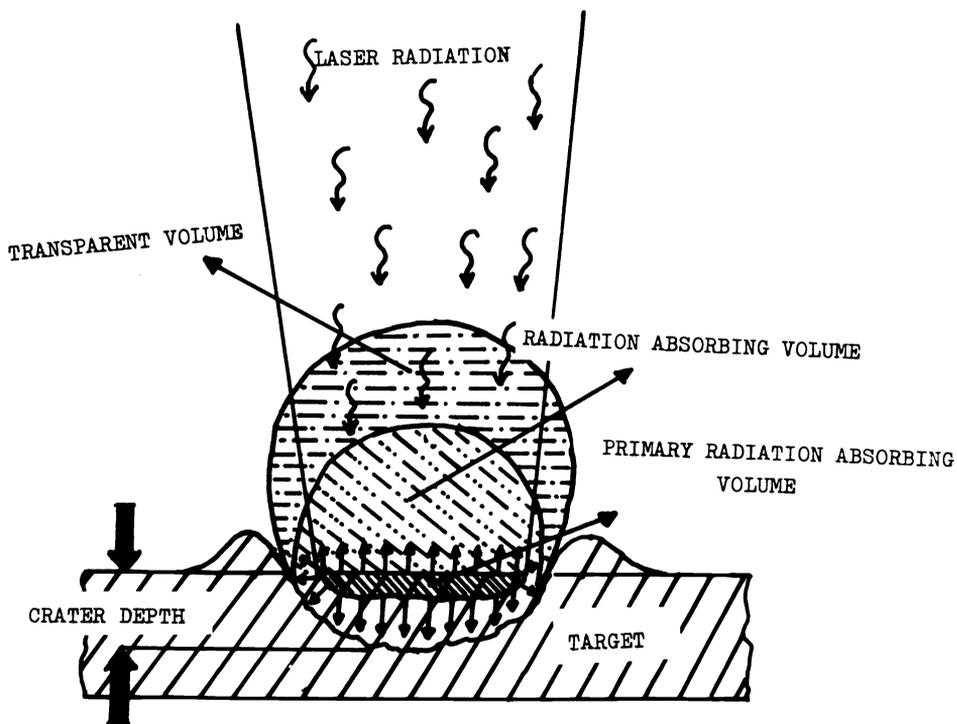


Fig. 1. Schematic illustration of laser-solid interaction

The duration of a normal laser pulse is of the order of some hundreds of μ sec and consists of many individual spikes, each of about 1 μ sec. At the onset of vaporization the subsequent laser spikes meet the already expanding plasma phase, which may quench the laser light, whereupon the vaporization stops. As the plasma density decreases by expanding - becomes transparent - the oncoming laser spikes again reach the solid phase and the whole process begins again. This phenomenon is clearly reflected by the results of Dietze et al (6) who found a significant and characteristic time dependence of the ion emission from the laser plasma.

The situation is somewhat different using Q-switched lasers. The duration of the laser pulse is of 1-4 nsec and consists of one giant pulse. During this short time of light-solid interaction, the material is heated very quickly;

pressures of the order of 1000 bars are created, generating a shock-wave into the solid phase, resulting in a crater volume greater than the absorption zone of the light. If this happens, however, the expanding cloud no longer sees the laser light and it expands freely (7). During evaporation, if the power density exceeds $\sim 10^9$ W/cm², it is not expected that any selectivity will occur between the chemical elements; so for analytical purposes the use of Q-switched lasers is proposed (8).

For both normal and for Q-switched lasers, on interaction with the solid material, a high temperature is reached; it is assumed to be between 3000 K and 20 000 K depending on the power density and material irradiated; such values are sufficiently high for thermal and/or collision ionization to occur (4,5, 9,10-12).

The ionization mechanism must be different for different kinds of materials, conducting, semiconducting and insulating (dielectrics) as is discussed and summarized by Knox in his review paper (5). Above the threshold power density $q > 10^8$ W/cm², the energy absorbed by the small layer of material is greater than its heat of vaporization and an ionized vapour cloud appears above the target. The ionization efficiency, $\alpha = N^+/N_0$ (where N^+ is the number of ions, and N_0 the total number of atoms evaporated) may be very high, sometimes approaching 1 (8).

For practical mass spectroscopy, ions formed directly in the laser-solid interaction process (LIMS) are primarily of interest. Methods using additional ionization of the evaporated neutrals, laser evaporation mass spectrometry (LEMS), are not discussed here. The acronym LMS (laser mass spectrometry) will be used for either or both of them.

Cratering-depth resolution

One of the main advantages of the laser is its ability to sample small areas. With the aid of an additional conventional light microscope for observation, the sampling area can be localized with a precision of 3-5 μ m. Some of the lasers designed for analytical purposes have a light microscope or a pilot laser (He-Ne) as a standard. The light microscope needs the same objective; so by focusing the surface by light microscope the laser radiation will also be focused on the surface. The spot size to be irradiated by the laser can be varied from a few μ m up to some hundreds of μ m. The crater shape is hemispherical and the dimensions increase with power density, starting from a threshold of $\sim 10^7$ W/cm² to 10^9 /cm². Above this value the crater dimensions do not change much. The crater volume is dependent on the chemical element. Zahn and Dietze (9,13) observed conically shaped craters ranging between 30 and 325 μ m in diameter, 15 and 800 μ m in depth and between 0.3 and 130×10^{-7} cm³ in volume, for 13 different metal elements using normal pulses of a ruby laser. The smaller dimensions were observed for the elements of higher melting points. The number of atoms evaporated was of the order of 10^{16} - 10^{17} per pulse. On increasing the beam diameter the power density on the sample surface is reduced as is the vaporization-crater depth. Devyatykh et al. (14) using a Nd-YAG laser of power density of 2×10^9 W/cm² investigated 17 metals and, by defocusing the laser beam spot to 10^{-2} cm², they obtained a depth resolution between 0.17 and 3.22 μ m. Using light absorbers to reduce the power density to 8.7×10^8 W/cm², they claim to have obtained a depth resolution as good as 0.05 μ m for metals of high melting points: iron, copper, nickel, molybdenum etc. . This is probably the best result published in the literature so far.

Bingham and Salter (15) reached 0.9 μ m depth resolution on metals; Eloy (16) studied autodiffusion of oxygen in uranium dioxide; Brochard and Eloy (17) measured the levels of metallic constituents present in autopahts for forensic purposes; titanium, barium, chromium, calcium, aluminium and iron have been determined. Eloy and Brochard (16,17) achieved a depth resolution of about 1 μ m. Devyatykh et al. (14) demonstrated the carbon distribution along the thickness of the chromium layer and obtained a depth resolution of better than 0.5 μ m. The capability of the laser in layer analyses is of great importance and is reasonably easy to realize by defocusing the laser beam and/or by using light filters. (We have, however, to state right here that the requirements of semiconductor technology cannot be completely fulfilled with depth resolution attainable by laser analyses.)

There is another point to be mentioned here. By defocusing the laser beam, the imperfections in the homogeneity of the beam across its cross-section become apparent and as a result of this, the erosion will no longer be homogeneous across the spot diameter and the resolution will be distorted. In view of

this, the literature data sometimes seem to be somewhat optimistic.

The parameters characterizing LIMS compared with SSMS are summarized in Table 1.

TABLE 1. Comparison of some characteristics of LIMS and SSMS

	LIMS	SSMS
Atoms removed per pulse	10^{14} - 10^{16}	10^{14}
Ions detected per pulse	10^7	10^7
Relative sensitivity per pulse	0.1 %	0.1 %
Crater depth per pulse (Q-switched)	0.5-50 μm	1-5 μm
Pulse repetition rate (sec^{-1})	0.1-100	300 (broad range)
Pulse length (Q-switched) (sec^{-1})	1-50x 10^{-9}	10^{-6}
Power density (W/cm^2), Energy (J)	10^9 - 10^{11}	$\sim 2 \cdot 10^{-3}$ J

Apparatus

The ions of a laser plasma have an energy spectrum depending on the power density used. Below a power density $q < 10^8$ W/cm^2 no ions are formed. On increasing the energy, singly charged ions are first formed with small energy spread. Working at or just above the threshold energy both single focusing, static or dynamic, mass spectrometers of adequate mass resolution can be used (1,7,10,14,16-19). To obtain sufficient mass resolution the ions have to be accelerated up to some kV before entering the magnetic field. If the energy spread is higher than 50 eV, either energy filter (20-22) or double focusing (DF) machines have to be used (6,9,14,23,24). If a TOF mass spectrometer with an energy filter is used, the energy spectrum of the ions can also be investigated in a rather simple way. The most simple situation is with the DF machines, because the only change needed is for the sparking place to be replaced by laser-solid interaction point. The different laser beam-target surface-ion optical axes are illustrated in Fig.2.

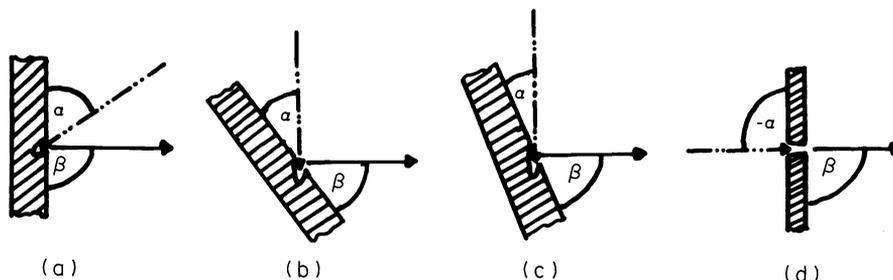


Fig.2. Preferential geometric configurations of laser beam-sample- and ion optical axes. (---) laser beam, (—) optical axes. (variations a-d)

A large α angle and $\beta = 90^\circ$ (variation a) is recommended but this is not a very strict requirement.

Static mass spectrometers with photoemulsion detect the whole spectrum simultaneously; with electrical detection only one ion (or a few) can be detected. Time of flight machines (TOF's) have an electrical detection system of high speed and amplification and are thus also able to detect the whole spectrum.

The lasers used are solid lasers; mainly ruby, Nd-glass or Nd-YAG, with wavelengths of 0.694, 1.06 and 1.06 μm , respectively. The crater diameter decreases on frequency doubling or quadrupling. The maximum rate of repetition with ruby is some shots per minute; with Nd-YAG is about 100 Hz. The latter is recommended especially with frequency doubling. In all cases the target must be adjustable in three directions. With Nd-YAG, a rastering

mechanism, to keep the target in the focal plane, thus allowing a large area to be probed, makes the speed of the analyses quicker and comparable to that of SSMS.

Particular attention needs to be paid to the laser micro mass analyser (LAMMA, produced by Haereus Balzers, FRG), mainly aimed at investigating biological materials, i.e. the elements sodium, potassium, magnesium, calcium, chlorine etc. So far as the author is aware, this is the only machine of its kind in serial production. It has an excellent spatial resolution ($0.5 \mu\text{m}$) and a detection limit of 10^{-17} - 10^{-20} g corresponding to 0.1-10 ppm. The analysed volume, in the form of a thin organic specimen, is not greater than 10^{-11} - 10^{-13} cm^3 . It can be used both in positive and in negative ion detecting mode. The lasers used are nitrogen ($0.337 \mu\text{m}$), ruby, frequency doubled ($0.347 \mu\text{m}$) and neodymium, frequency quadrupled ($0.265 \mu\text{m}$). The laser energy is absorbed in transmittance, (Variation d in Fig.2). The mass spectrometer used is a TOF apparatus of high transmittance ($\sim 80\%$) and with a sensitive electrical ion detection system. It is being used with great success in biomedical research (1,26).

Figure 3 shows, schematically, the LMA-10 laser (Carl Zeiss, Jena, GDR) and the mass spectrometer (MS-702/R) system installed in our laboratory.

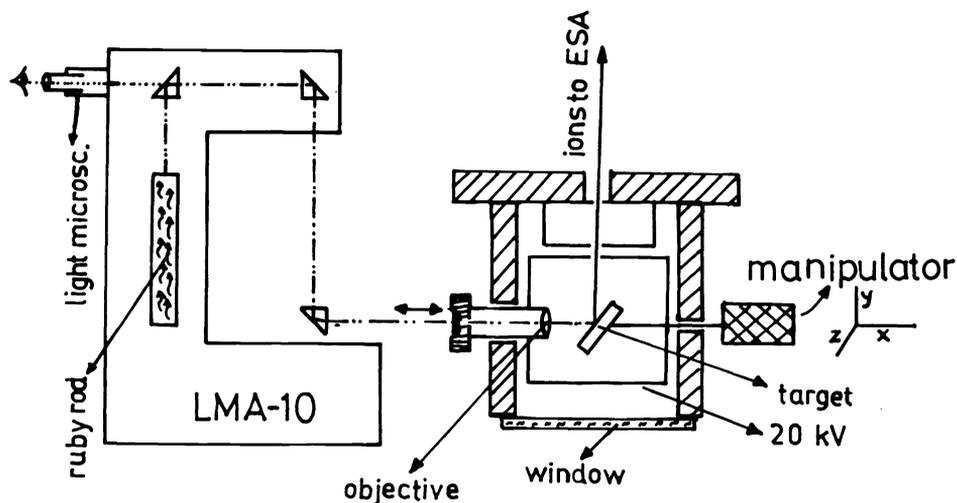


Fig.3. Schematic arrangement of the laser-mass spectrometer in our laboratory

The LMA-10 laser micro-analyser uses a ruby laser. The laser beam-target-ion optical axis arrangement chosen was that of variation b shown in Fig.2 ($\alpha \sim \beta \sim 45^\circ$). In the course of our work we used the Q-switch No.4 and the aperture No.1. The energy of the giant pulse obtained in this way was of about 0.05 J. The crater diameters were of about 30-60 μm depending on the material investigated. The pulse duration measured at half maximum was about twenty nsec, not changing much with the energy fluctuation of the individual pulses. One pulse was released every 20 sec. For practical analytical work (RSC determinations) we shot on the same area (crater) until the charge obtained did not decrease below 50 % of that of the first two or three shots. The number of pulses shot into the same crater was strongly dependent on the material analysed. With brass, for example, after 30 shots, the charge measured on the monitor integrator of the mass spectrometer was unchanged. In the case of aluminium, after 3-4 shots a new area had to be taken. Graded exposures were taken as with SSMS and the blackening on the photoplate were measured with the semi-automatic microdensitometer (Modified G-II, Carl Zeiss, Jena, GDR) developed in our laboratory. The concentrations were calculated from absorbance-log exposure curves as with those used in SSMS:

$$C_i = \frac{f_i Q_o C_o}{f_o Q_i (\text{RSC})_i}$$

where f is the isotope factor, Q the exposure at absorbance of 0.7 and C the concentration; i refers to the element and o to the matrix or the standard.

A practical point that should be mentioned here, is that the ionization

chamber, the target and the objective are at a high negative potential and they must be very carefully screened so as to prevent the ions of the plasma reaching the housing of the ion source. If this were to happen, the escaping ion would cause the accelerating voltage to drop and as a result of this, the peaks on the photoplate would broaden or even split. This phenomenon has also been mentioned by Bingham and Salter (15).

Reproducibility

From the analytical point of view it is very important how reproducible data with laser ionization can be obtained. With twelve separate shots, each in a different place, with Q-switched ruby laser pulses of power density of $\sim 5 \cdot 10^{10}$ W/cm², relative standard deviation, $\sigma = +0.06$ was obtained for absorbances of ⁵⁴Fe and ⁵⁶Fe isotopes in steel and of ⁶³Cu, ⁶⁵Cu, ⁶⁴Zn, ⁶⁶Zn, ⁶⁷Zn and ⁶⁸Zn isotopes in brass. The isotopic composition of molybdenum was determined with $\sigma = +2-3$ % (rel.). We measured the energy spread of 60 subsequent laser pulses and obtained $\sigma = +0.2-0.3$. The charge measured simultaneously on the monitor integrator showed, however, a value of $\sigma = +0.1$. No correlation was observed between the laser pulse energy and the amount of ions produced, at least not at about 10^{10} W/cm² power density that was used.

From these figures two conclusions can be drawn. First, the laser energy used was above that of the plasma formation threshold because the fluctuation of the laser energy had only a minor effect on the amount of ions produced. This is supported also by the appearance of the multicharged ions. Second, the reproducibility of absorbances is significantly better than obtained by SSMS - with which σ -values better than ± 0.3 is rather difficult to achieve.

Accuracy, RSC's

The accuracy (systematic error) is strongly related to the ionization mechanism. This aspect was to be discussed under laser-solid interaction, but because of its basic importance, we decided to deal with it in a separate section. We are of the opinion that the question of RSC' is very important and may justify alone the effort made in the application of LMS as a conventional analytical method. One of our main goals is to try to answer this question. As we have seen above, the reproducibility allows one to determine the relative sensitivity coefficients with a precision of about ± 0.1 . If it were the case in practice, the same error (or close to it) would be expected for the concentration measurements as well.

Fenner and Daly (27), Eloy (16) and Bykovskii et al. (8,24,25,28) all hold - though not all to the same extent - that the RSC's are 1 (or close to it) for all elements, if the power density does not greatly exceed the threshold value of the plasma formation. This can be understood from the point of view of the qualitative picture of the ionization mechanisms that may occur. At relatively low temperatures (power density 10^6-10^8 W/cm²), no plasma is formed; thermal ionization takes place that is selective. At the threshold power density of the plasma formation ($\sim 10^9$ W/cm²) collision ionization appears (as a result of collision assisted inverse bremsstrahlung) that is not selective. With even higher power densities (10^9-10^{11} W/cm²) multiphoton ionization also takes place; this is again selective because it depends strongly upon the ionization potentials of the elements.

Bingham and Salter (15) found a spread in RSC's similar to that with SSMS, especially if a CO₂-laser is used. Eloy and Stefani (29) did not give the RSC's but the agreement between the true and the measured concentrations was excellent. Results were published by Bykovskii et al. (25) for a geological standard and good agreement was found for 33 elements out of 43. The best agreement was for elements like sodium, magnesium and calcium and not very good for iron, chromium and nickel. These results are contrary to experience with SSMS where the alkalis are difficult and the transition metals are easier to measure quantitatively. This observation is an indication of the ionization mechanism of laser ionization, being other than with RF-spark. He found also that the ion intensities of pure materials registered with photoemulsion, I , depend upon the mass of the ion, m , viz. $I \sim m^{1/2}$.

At the same time, however, Zahn and Dietze (6) found a strong dependence of the amount of ions formed from different metals at identical experimental conditions, (See Table 2.). They were not able to find any correlation between the amounts of ions (ionization probability (α)) and the ionization energy of the atom.

Devyatikh et al. (22) found a periodic dependence of the relative ionization

1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
P	0.8								
Pb		1.83		~1.0		1.1			
S	0.6	0.57					0.5-0.6		
Sb				~1.0					
Si	1.2							1.9 \pm 0.2	
Sn	1.0	1.26							
Ta	0.28	0.42							
Ti	0.8	1.98		1.0				1.1 \pm 0.1	
V	0.67	1.10	0.94						1.7 \pm 0.1
W	0.34	1.15	0.77	0.94					
Zr	0.2	0.52							
Zn								3.0 \pm 0.3	

The results obtained with geological standards are not presented here.

From the data of this table it can be seen that the data are scattered, less than with SSMS, but the agreement between them is not sufficiently good to enable any conclusions to be drawn. It is entirely understandable because the conditions may not be identical in different cases and also the requirement of sample homogeneity may be different from that for SSMS.

Our data also show deviation from 1 for different elements. In some cases the RSC's remind one of those obtained by SSMS, where the elements of high boiling points tend to have low and elements of low boiling points have high RSC's. The power density used by us allows a very hot plasma to develop; this is also supported by the appearance of rather intense multi-charged ions. According to theory, for elements with ionization potential ϕ , higher than that of iron, the RSC's should be lower than 1. This rule cannot be observed either. It seems as if, besides the ϕ -s, the enthalpy of vaporization or sublimation should also be taken into account as proposed in ref. (22), at least if the power density is significantly above the threshold energy. For definite conclusions to be drawn on RSC's, more data are needed. The good reproducibility of laser ionization gives the hope that the RSC's can be determined much more reliably than by SSMS. Our intention is to deal with this task in a future paper.

APPLICATIONS

LMS can successfully be used in the chemical analyses of metals, alloys, semi-conducting materials and also for organics. It is also used in layer analysis, stoichiometry and for the determination of gas contents of solids. The broad field of application of LMS is excellently reviewed by Conzemius and Capellen (3); from their work, the widespread possibilities of laser ionization become apparent.

CONCLUSIONS (LMS VERSUS SSMS)

Experience gained in our laboratory supported by literature data in the field of laser ionization enable the following conclusions to be reached:

- ionization efficiency is comparable with SSMS,
- the detection limit (both absolute and relative) is comparable to SSMS,
- the microanalytical capability of LMS is better in that the volume to be analysed can be precisely pinpointed with the aid of a light microscope or a He-Ne laser,
- the electrical property of the material to be analysed has no influence on the ionizing procedure (conducting, semiconducting or insulating materials can be analysed without any special preparation),
- thin layer possibilities of LMS are better than those of SSMS,
- the reproducibility of LMS is of the order of ± 0.1 compared with SSMS (about ± 0.3 at best), which gives the possibility of obtaining more

reliable RSC data,

- with laser power density in the vicinity of the threshold of plasma formation there is the likelihood of obtaining RSC's of 1 (or close to one) for all impurities, thereby making quantitative analysis easier,
- analysis with ruby laser is much slower, than with Nd-YAG (100 Hz), being about the same as with SSMS,
- because of the energy spread of the ions in LMS, double focusing machines (or single focusing ones with an energy analyser, preferentially TOF's) with a resolution of about 1000 are advised.

To summarize, it is suggested that if the possibility is given to use laser technology, a change of SSMS for LMS - especially for LIMS - would offer considerable advantages.

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