LASER INDUCED PLASMA SPECTROSCOPY (LIPS) AS AN EFFICIENT METHOD FOR ELEMENTAL ANALYSIS OF ENVIRONMENTAL SAMPLES

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ABSTRACT

Laser Induced Plasma Spectroscopy (LIPS) has proved to be a powerful laser-based analytical technique due to its simplicity and versatility. Practically any kind of sample can be analysed with no or minor preparation. Here a LIPS apparatus is presented, consisting of a Nd:YAG laser beam focused on the sample surface, a XY translator as the sample holder, a UV fibre cable used to collect the plasma emission and to transfer it to a spectrometer equipped with a gated optical multi-channel analyser (OMA III system). This system allows both spatially and temporally resolved spectra to be recorded. A large number of elements encountered in environmental samples have been identified in the 250 – 700 nm region: the samples were either in the form of a mixture of their oxides or encapsulated in glass matrices. The quality of the spectra in dependence on the various experimental parameters has been studied with the purpose to use these samples as references for elemental qualitative and quantitative determination of natural samples.

INTRODUCTION

When a powerful pulsed laser is focused on a surface, a tiny amount of the material is vaporised and through further photon absorption it is heated up until it ionises. This laser-induced plasma is a micro-source of light that can be analysed by a spectrometer. The obtained spectra consist of lines corresponding to the elements evaporated from the sample surface. This is the principle of the laser-induced plasma spectroscopy (LIPS) and has proved to be a powerful surface analytical technique, capable of performing trace element measurements in any kind of solid material (1-3) as well as in liquids (4,5). The technique can be characterized as a non-destructive one and features high sensitivity, minimal sample preparation, and rapid on-line multi-elemental analytical capability. By combining LIPS with optical fibres to transfer the laser beam to the sample and the emitted light back to the spectrometer, LIPS can be characterized today as a remote analytical technique that recently finds a lot of applications in hostile environments, e.g. where radioactivity (6) or toxic samples (7) might be harmful to the working personnel.

LIPS has been used quite extensively for qualitative determinations with great success. An important question for quantitative measurements is to what extend the element composition in the plasma as it emerges from line intensity measurements corresponds to the actual surface composition. Plasma emission is dependent on laser parameters and geometry (8) that have to be optimised in each individual case, but also on surface condition and thermal properties of the sample. The latest ones are known as "matrix effects" and affect the line intensity of an element embedded in a particular matrix.

Calibration curves are needed for the quantitative determination of an element. They emerge from a number of reference samples with known elemental composition. Usually a suitable element is selected to dominate (internal standard) and relative line intensities in respect to the internal standard are measured and plotted against the concentration ratios of the sample. The unknown samples are often available as powders (e.g. coal fly ash, minerals, sediment from sea, river or lake etc) and a small amount is mixed with a 5- to 10-fold larger amount of an appropriate selected material to form a sample with similar properties as the reference ones. This procedure is quite convenient for laboratory measurements since the "matrix effects" can be strongly reduced and calibration curves obtained previously can be used.

In this paper we report on the preparation and investigation of two different kinds of materials with the purpose to use them as reference samples for laboratory elemental analysis. First a "ceramic" matrix was prepared which showed a high degree of inhomogeneity, grain structure, and sedimentation. These effects were reduced in the second "glass" matrix. Various experimental parameters were changed and their effects on the obtained spectra were studied.

For completeness we notice that a new procedure has been developed for calibration-free quantitative analysis in LIPS experiments (9) recently. In this method, matrix effects can be overcome and field measurements on solid and liquid samples have become possible now without exact knowledge of their composition and properties.

METHODS

LIPS for multi-elemental chemical analysis

There is a number of complicated processes that take place in every LIPS experiment, depending on a large number of parameters such as: laser wavelength, pulse duration and intensity, spot size, thermal conductivity, and optical properties of the sample surface, and art and pressure of the ambient gas. For a better understanding, the whole process can be divided into three time domains as illustrated in Figure 1. In the first domain, the laser heats and evaporates a small amount of the sample. The first seed electrons are created, either due to multi-photon ionisation or thermal emission of the surface. These electrons absorb further photons from the same laser pulse and transfer their energy to the atoms in the plume by collisions. Further ions are thus produced, while a shock wave is observed due to the fast heating of the gas reaching temperatures of several thousand degrees. Depending on the conditions, multiple charged ions are also present in the plume. The laser wavelength plays an important role in this time regime, since the photon absorption of the electrons has a $?^2$ dependence.
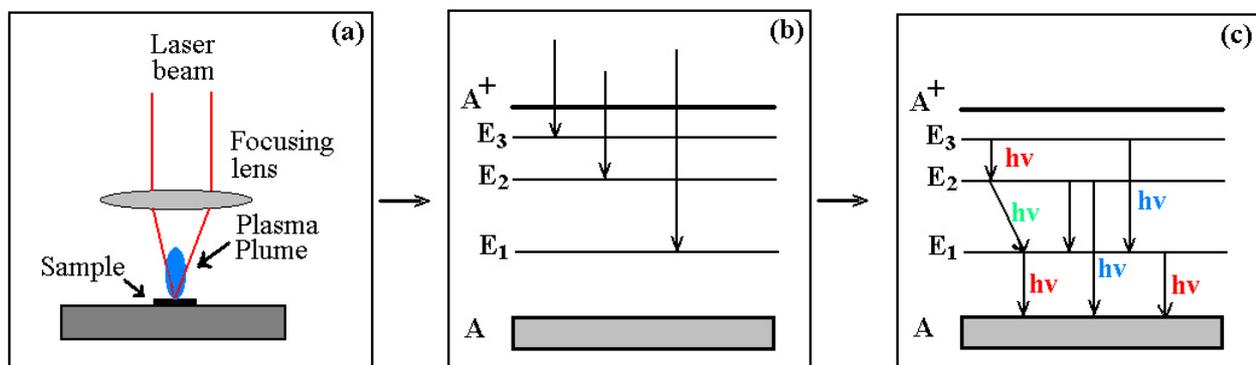

Figure 1: Timing of a LIPS process: (a) plasma ignition, (b) broadband emission due to *Bremsstrahlung* and free-bound transitions, (c) line emission due to bound-bound transitions.

Time domain (b) is characterized by a broadband emission originating from the *Bremsstrahlung* of the free electrons and electron-ion recombination and it has a duration of a few hundred nanoseconds. Weak lines show up on the strong continuum and they are mostly identified as ionic lines of the plume constituents. Finally time domain (c) is characterized by an emission spectrum, where narrow atomic lines dominate corresponding to the elements present in the plume and line strength is proportional to the atomic concentration. This time regime lasts for several microseconds and it is exactly the regime that is relevant for elemental analysis.

To complete the above description of plasma evolution, we consider Figure 2. The plasma emission of a Cu sample was dispersed by the spectrometer, set on the Cu 522 nm emission line and the photomultiplier signal was recorded with a fast oscilloscope. We observe two overlapping peaks, a narrow one with a ca. 50 nsec fast increase (maximum at 0.3 µsec) and a slow broad one with a delayed peak (maximum at 0.45 µsec) and extending to 1.2 µsec. The narrow peak relates to the unstructured emission, corresponding to regime (b) above. The broad peak is a characteristic Cu emission line: this signal disappears as soon as the spectrometer is set slightly left or right of the emission line, while the narrow peak remains unaffected by the position of the spectrometer setting.
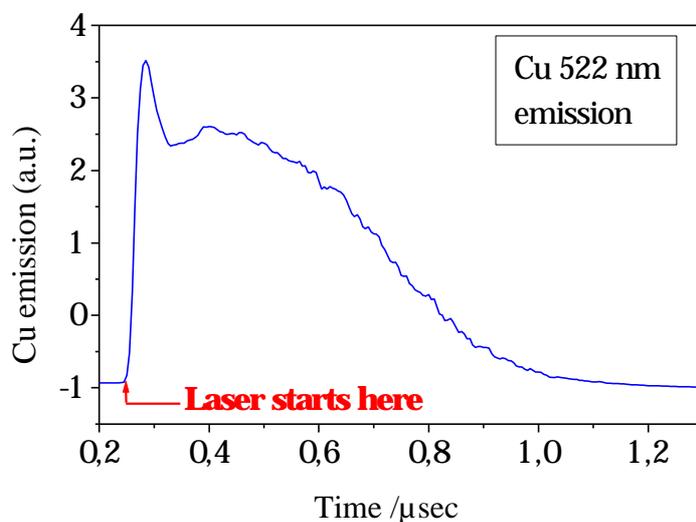
Figure 2: Time dependence of the plasma emission of a Cu sample: The narrow peak appears irrespective of the spectrometer position, the broad structure corresponds to Cu line emission at 522 nm.
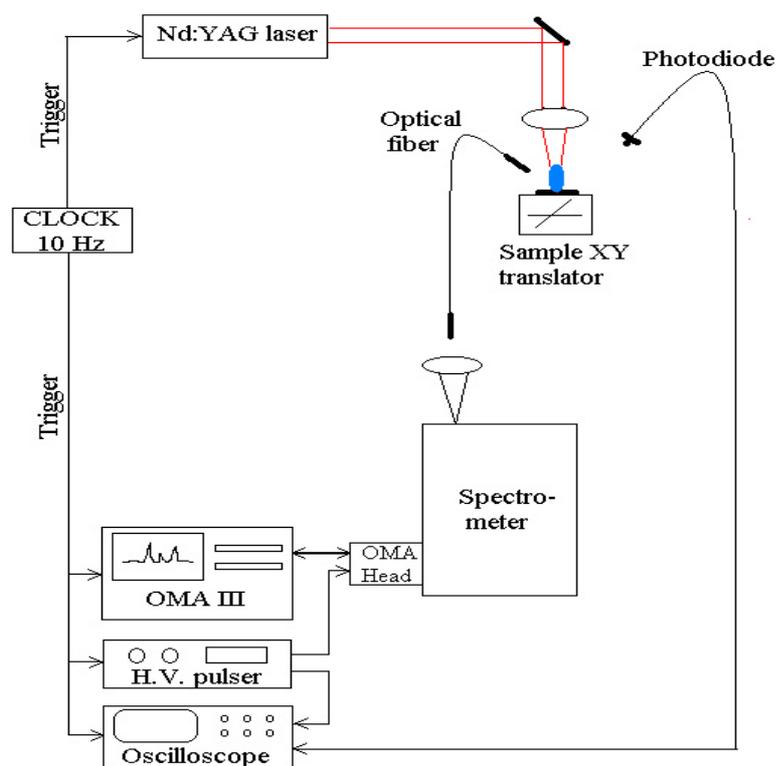
From the temporal structure of the signal of Figure 2, it is clear that elemental analysis by the LIPS method has to be performed time-resolved, that is, the delay and the width of the time window in respect to the laser pulse have to be optimised to maximize the Cu signal and avoid the early part of the signal, corresponding to the strong unstructured continuum. Experiments have shown that for different elements present in the plume, the maximum of their emission occurs at a slightly different position. Therefore, a compromise for the time window position has to be made, in order that the multi-elemental analytical capability of the LIPS technique is maintained.

Experimental set-up

A schematic diagram of the LIPS apparatus is presented in Figure 3. It consists of a pulsed Nd:YAG laser to evaporate the target and excite the vapour plume. Both the fundamental IR (1.06 µm) and the 3[d] harmonic UV (355 nm) wavelength have been used. The laser was triggered with 10 Hz by an external generator and the pulse energy varied in the 10–50 mJ range. An f=100 mm plano-convex quartz lens was used to irradiate the target with the laser. For the current pulse energy used, it turned out that the optimum lens–target distance was not the focal distance but slightly different: so the focus was placed 10-15 mm behind the target surface. Placing the focus before the target surface, air breakdown was observed that led to an absorption of the laser pulse and the emission signal suffered from strong variations from shot to shot. A 2 m long quartz optical fiber (CVI Laser Corp., Ø =0.4 mm, N.A. 0.22), placed as close as possible to the plume, was used to transfer and focus the emitted light on the entrance slit of a FL 0.6 m Jobin-Yvon HRP spectrometer (1200 gr/mm, en-

trance slit 80-200 µm). The dispersed light was captured and the spectrum (extended for 20 nm) was displayed on the screen of a EG&G OMA III system (1024 linear diode array). A HV pulser was used to set the time window for the observation of the plasma emission. A delay between 2 and 10 µsec and a gate width of 1 µsec was used during these measurements. A photodiode was used to detect the arrival of the laser pulse and gate delay and width were positioned on the oscilloscope in respect to it. All three units were synchronized with the laser by the same external generator.

The samples were positioned vertically to the incident laser beam on a pC-controlled XY translator and moved during measurements: the laser position was usually changed every 5 pulses with a step size of 0.75 mm and an area of about 10x10 mm was scanned. For every new sample, first the "single scan" mode of the OMA system was used to optimise the position of the optical fiber. Secondly, the "accumulation" mode was selected and usually 150 single LIPS spectra were summed and stored in the disk or alternatively sent to the printer. The stored files were transferred by a RS232 connection to the Lab pC and the spectra were plotted (Microcal^{TM} Origin 5.0 software). Spectrum calibration and peak assignment were performed using as a reference either emission spectra of Ne and Ar hollow cathode lamps or LIPS spectra of pure elements (Fe, Cu, Ti, Cr, Ni etc.). Wavelength values for the calibration procedure were taken from the literature (10): This method revealed a wavelength accuracy of 0.5 Å.

Figure 3: Experimental apparatus

RESULTS AND DISCUSSION

General considerations

The laser-induced plasma is a light-emitting micro-source and it is expected that the lines and their intensities observed are indicative of the elemental composition of the sample. To establish a quantitative relationship between the emission spectrum and plasma properties, two parameters are introduced: the plasma temperature T_e and the electron density n_e. Due to the rapid plasma expansion, both parameters are strong functions of time and position and they have sense only within the time-window selected to record the spectrum. The electron density is of the order 10^{17}-10^{18} cm^{-3} and can be deduced (11) from the homogeneous (Lorenzian) broadening of the atomic lines. If local thermodynamic equilibrium (LTE) is assumed, T_e can be measured and it characterizes the plasma ionisation condition. Due to the large number of electrons, their high energy, and their long-range Coulomb interactions, the collision energy transfer mechanism dominates and a Boltzmann distri-
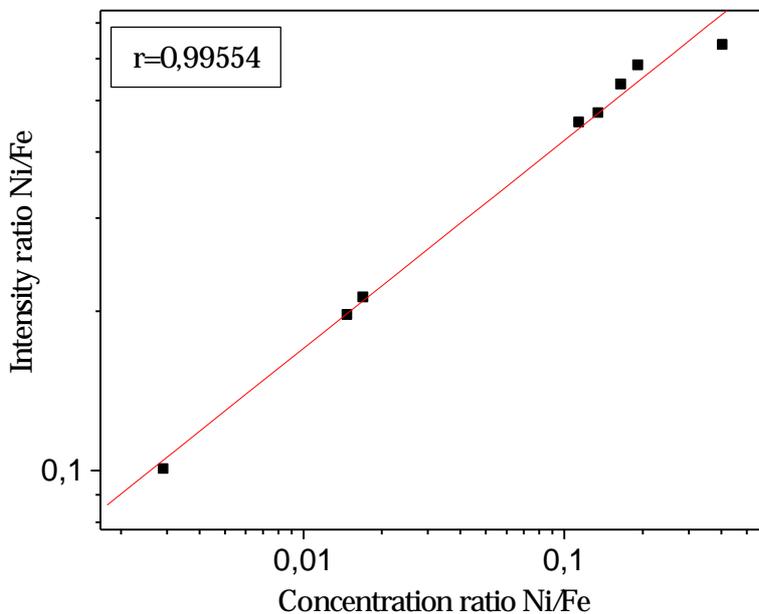
bution among the atomic levels is established. Under LTE, a linear relationship between the intensity $I_i^{(a)}$ of a line and the corresponding atomic concentration $N^{(a)}$ in the plume (12) is found:

$$I_i^{(a)} = G \frac{hc}{\lambda_i} \frac{g_i A_i N^{(a)}}{Z^{(a)}} \cdot \exp\left(-\frac{W_i}{kT_e}\right) \tag{1}$$

where g_i is the statistical weight and W_i the upper state energy, A_i the Einstein coefficient for the upper state spontaneous emission, λ the wavelength, $Z^{(a)}$ the partition function, k the Boltzmann constant, and G a geometry factor relating to the experimental conditions. Starting from (1) and applying the Boltzmann plot for the element a, T_e is calculated from the slope of the Boltzmann line.

To reveal $N^{(a)}$ from the measured intensity $I_i^{(a)}$, a number of spectroscopic data of element are needed (g_i, A_i, $Z^{(a)}$), the geometry factor G and the temperature T_e. To eliminate G being very difficult to measure, the so-called internal calibration is performed: in a number of reference samples, the line intensity ratio $I^{(a)}/I^{(r)}$ of element a to reference element r is measured. From Eq. (1) follows that this ratio is proportional to the ratio $N^{(a)}/N^{(r)}$ (known in the reference samples) and a plot versus $N^{(a)}/N^{(r)}$ in general delivers a straight line (calibration curve). Applying this method to quantitative measurements, it is supposed that the reference samples have all similar composition. In this way, the effect of the so-called matrix effects on the accuracy of the method is strongly reduced. On the other hand, a limit is set to the applicability of the method, because a similar composition for the unknown sample is also required. This can be anticipated for lab measurements, where reference and unknown samples can be embedded in the same matrix but is a severe restriction for field experiments.

This calibration method has been applied successfully in our laboratory to a series of commercial stainless steel samples with a few percent of alloying elements with good homogeneity and similar thermal properties (13). Relative intensities Cr/Fe and Ni/Fe have been plotted versus known concentration ratio values and straight lines have been obtained with correlation coefficients better than 0.99, for Ni/Fe see Figure 4. Samples taken from other manufacturers fitted well in the above calibration curves.

Figure 4: Calibration curve for Ni in stainless steel reference samples

To face the problem of matrix effects in environmental samples, we have prepared and investigated two different types of matrices and the results are presented below:

Sample: Oxides

Oxides of the most common elements encountered were selected and mixed to prepare a ceramic matrix. The powders were commercially available with purities of the order of 99%. Water was added to the powder mixture, and discs with Ø =20 mm and 5 mm thickness were formed and left to dry overnight. SiO_2 was selected as the main component (Si: 25-40%), since it is often found in natural samples and Si therefore served as internal standard here. It is expected that SiO_2 determines the main properties of the matrix. The composition was selected to be: less than 6.5% for Mg, Al, P, and Pb, less than 1.5% for Ca and Co, and less than 0.06% for Fe and K.

Before proceeding to quantitative results, a correct assignment of the recorded lines was necessary, since there were no previous reference data available. The range of 250-700 nm was investigated and the strongest lines were assigned to the elements according to the procedure described in section 3. Emission lines to be used for the quantitative measurements were selected according to the following criteria: (1) the line should be sharp and free of interference with other lines, (2) it should be on a clear background, (3) it should be free of self-absorption, (4) it should be near (that is within the 20 nm of a "single scan") a Si line to be used as the internal standard. Accordingly, two wavelength regions appeared to be appropriate for quantitative measurements:

- the 275-305 nm region, where emission lines of Si I and Mg I and II were detected,
- the 380-400 nm region with emission lines of Si I, Al I, Co I, Mg I and II.

The second region was chosen, see Figure 5, to demonstrate some interesting features of this investigation. The two spectra correspond to two different delays of the OMA time window. In the early stage of plasma evolution, ionic lines are strong, while the atomic lines dominate later on. This may help in line identification in cases of ambiguity. Emission lines are broad and strong overlapping occurs in the early stage of the plasma due to the Stark effect. Moreover, the Stark effect may affect the linewidth of the various elements in a different way and this can influence the quantitative results. These effects are reduced in a later stage of plasma expansion.
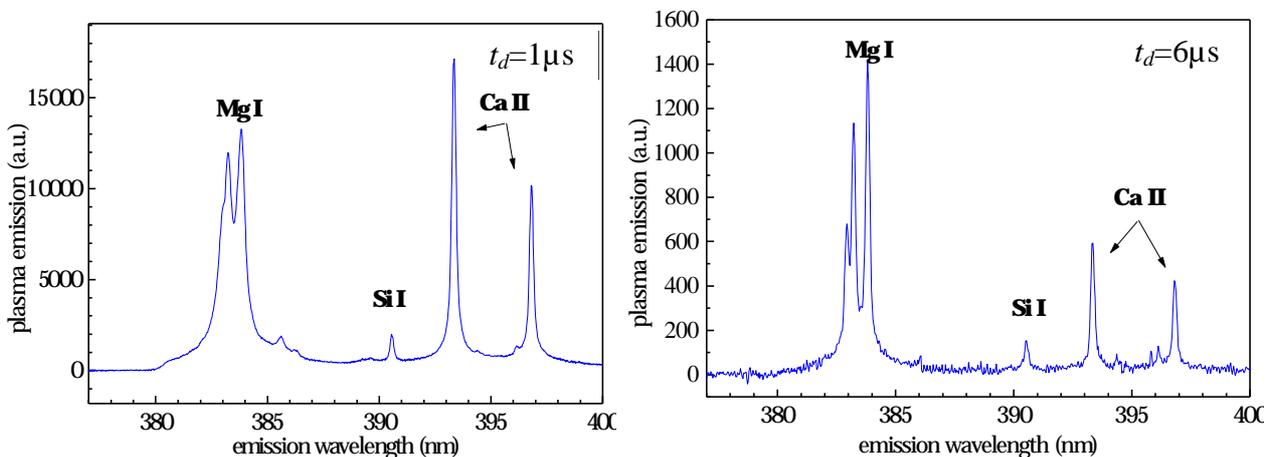
Figure 5: Plasma emission around the 395 nm. (a): 1 μsec gate delay, (b): 6 μsec gate delay.

To proceed to quantitative measurements applying the internal calibration method, we have built the relative intensities of the lines ratios Mg I(285.2 nm) and Mg II(279.55 nm) in respect to Si I(288.16 nm) and after fitting the ratios of the lines Mg I(383.8 nm) and Ca II (396.8 nm) in respect to Si I(390.55 nm). These ratios have been measured as a function of the delay of the time window of observation. It is known from the literature (14) and also from our previous work on stainless steel metal alloys that in the initial stage of plasma lifetime, clusters of atoms ("droplets") are ejected and it takes some microseconds until they fully evaporate in the hot plasma. The maximum

of emission for each element is reached therefore within a different time period and this makes the relative intensities time-dependent. Similar observations have been made in the present investigation. It was found that only for a time delay longer than 5 μsec the ratios seemed to stabilize and all following quantitative measurements were performed with this delay value. It is clear that this requirement was followed by a strong sacrifice of signal.

To create a calibration curve for Mg, the ratio Mg I(383.8)/ Si I(390.55) has been plotted versus C_{Mg}/C_{Si} for every sample. To avoid local inhomogeneity due to the grain structure of all samples, each point was the average of 5 measurements of 150 accumulated scans each, while the sample was moved. Although the RSD was about 10% or less, measurements differed significantly, when the surface layer (ca. 0.5 mm) was removed and the measurement repeated in the next layer. Moreover, we found a systematic change of the ratio when moving from one surface to the opposite one: This is a strong indication of sedimentation effects occurring during the preparation of samples: During the long drying process, heavy oxides diffuse towards the bottom giving rise to concentration gradients vertical to the surface. These final observations proved that this kind of sample preparation is rather inappropriate for reference samples production to be used in elemental analysis.

Glass samples (Andesite)

A new series of samples is now considered and their properties are investigated in respect to their application as reference samples for quantitative measurements. The sample called here andesite (standard name: JA-2) consisted of 0.6 g of natural andesite powder, 5.4 g lithium metaborate and 0.5 g lithium nitride. The powders are melted in a furnace, homogenized, put into a form to take the shape of a disc with Ø=30 mm and 5 mm thickness and let cool slowly to avoid crack building. This procedure was undertaken in a commercial furnace in the National Institute of Marine Research near Athens. It is expected that both grain structure and inhomogeneity are strongly reduced and make the glass samples superior to the ceramic ones for the purpose of the present investigation.

Andesite itself is a volcanic rock (named after the Andes) and consists mainly of Si (56.4%) and Al (15.4%) and less Fe (6%), Ca (6,3%), Mg (7.6%), Na (3%), and a large number of other elements with concentrations from 1% down to a few ppm. Si is present with the highest concentration in all samples and therefore can be used as internal standard. The elements given explicitly here had been previously identified in the ceramic samples and were easy to identify here as well. Due to the large number of elements (about 60) included in andesite, many lines remained unassigned and their identification is still in progress.

After a long irradiation with the IR laser light, we observed cracks on the sample: This was due to the strong local heating of the surface in combination with the low thermal conductivity of the glass matrix. We switched therefore to the third harmonic (355 nm) of the Nd:YAG laser and repeated the measurements. Many of the spectra remained unchanged, but in some cases the different wavelength had a dramatic effect on them, see Figure 6.

In this part of the spectrum we made two observations: (1) the lines are narrower when excited with the UV than with the IR wavelength. This may be explained by a lower temperature T_e achieved by the plasma, in consistence with the $?^2$ dependence of the laser photon absorption by the free plasma electrons: Less ions are produced and the electric fields are correspondingly lower. (2) The number of lines is reduced when UV light is used. In particular, those lines are missing that originate from ionic species. This could speak for a thermal process again which is more pronounced for the IR wavelength than for the UV. But in the 550-580 nm emission range, additional structures have been observed, when the sample was irradiated with the UV light. This implies that some multi-photon excitation/ionisation mechanism, in particular in the initial stage of the plasma formation, may play

a role. The UV photons have an energy of 3.5 eV and three of them can directly ionise a large number of atoms encountered in environmental samples.
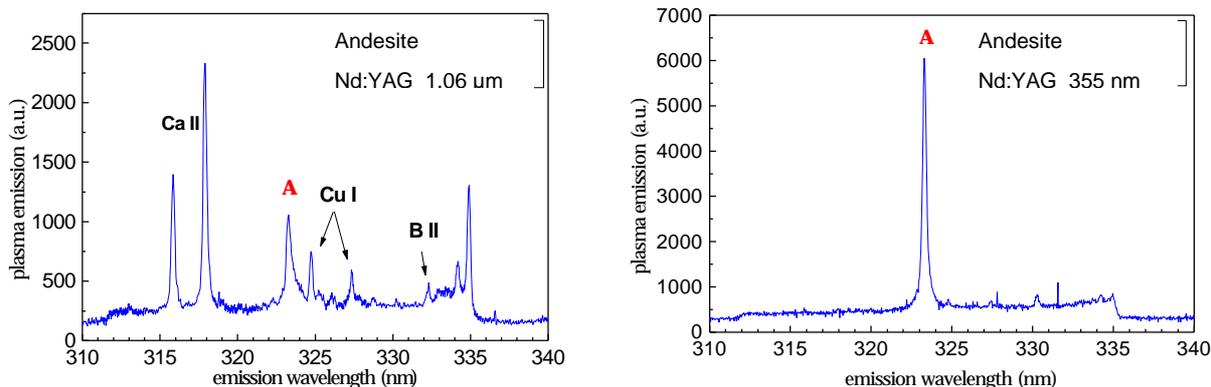
Figure 6: Dependence of the plasma emission on the laser wavelength

In view of the multi-elemental analysis that is considered here, this wavelength dependence of the plasma emission spectrum is vital, even though the details of such mechanisms may still remain unknown. This holds in particular when a large number of atoms are included in the sample and possible overlapping and line emission can be controlled by a proper laser wavelength selection. The laser wavelength should be therefore an important parameter in any database useful for multi-elemental analysis. Our group is now working towards this direction.

CONCLUSION

The principles of the LIPS method have been presented and the conditions under which the method applies for multi-elemental analytical work for environmental samples have been explained. For the preceding qualitative investigation, a number of experimental parameters have to be carefully selected, such as the delay and width of the time window of observation, and the laser wavelength for plasma ignition. For the quantitative measurements, we adopted the internal calibration method and we investigated reference samples embedded in two different matrices. The ceramic matrix appeared to be inappropriate because of its grain structure and sedimentation during the preparation process. The glass matrix is expected to be free of such effects due to its different kind of production.

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