High repetition rate and low energy femtosecond laser ablation coupled to ICPMS detection: a new analytical approach for trace element determination in solid samples

C Pécheyran¹, S Cany¹, P Chabassier², E Mottay³, O F X Donard¹

¹ Laboratoire de Chimie Analytique Bio-Inorganique et Environnement, CNRS UMR 5034, Hélioparc, 64053 Pau, France
² Novalase SA, ZI de la Briqueterie, 6 impasse du bois de la Grange, 33610 Canejan, France
³ Amplitude Systèmes, 6 allée du doyen Georges Brus, 33600 Pessac – France

E-mail: christophe.pecheyran@univ-pau.fr

Abstract. A low energy and high repetition rate infrared femtosecond laser system was developed for direct trace elements analysis by laser ablation/ICPMS. This system provides improved analytical performances in terms of limits of detection, repeatability, elemental fractionation and depth profile analysis in comparison to conventional nanosecond UV laser ablation used so far in analytical chemistry. Preliminary results show that limits of detection are improved by more than one order of magnitude and the elemental fractionation reduced to negligible values. In addition, depth profile resolution better than 20 nm are easily achievable on a Cr-Ni multilayer material which opens new fields of application in surface analysis.

1. Introduction
Laser ablation coupled to Inductively Coupled Plasma Mass Spectrometry (ICPMS) is a well established technique appearing as a tool of choice for direct solid bulk and microanalysis of trace elements. However, some major problems related to matrix-dependent ablation yield, elemental fractionation and sensitivity requirements, have limited its use for routine analysis. The laser wavelength, the pulse duration, the nature of the carrier gas and the aerosol transport efficiency are some of the main parameters governing the quality of the analysis. During the last decade, tremendous efforts have been devoted to study these effects in order to provide simple, quantitative and reliable analysis. The recent applications of femtosecond laser sources in analytical chemistry have demonstrated a huge potential in terms of signal stability, sensitivity enhancement and suppression of elemental fractionation compared to nanosecond UV laser ablation [1-5]. These benefits rely chiefly on the ultra fast energy transfer from the laser to the sample that induces “cold ablation” processes with very limited collateral damages and smaller particles.

A compact and integrated femtosecond laser ablation device (ALFAMET, Novalase, France) has been specifically designed for Inductively Coupled Plasma Atomic Emission Spectrometry (ICPAES) and ICPMS coupling. This instrument is operated at low energy (<100 µJ) and high repetition rate...
(<10000 Hz) opening new fields of investigation in analytical laser ablation. We present in this paper, the main features of this instrument as well as preliminary results.

2. Instrumentation

2.1. ALFAMET Femtosecond laser: The femtosecond laser source used in this instrument is fitted with a diode-pumped KGW-Yb crystal delivering 360 femtosecond pulses at 1030 nm as described in table 1. The laser source operates at low energy (<200 µJ/pulse) and high repetition rate (1-10000 Hz) which represents a new approach in analytical laser ablation, where, to date, high energy (>1mJ/pulse) and low repetition rates (<20 Hz) were commonly used. Precise adjustment of the energy delivered to the sample is achieved by the use of a half waveplate in the range of 0.1 to 100 µJ/pulse with a precision better than 0.1%. The system provides also pulse to pulse stability better than 0.5%.

Table 1: Femtosecond laser and ICPMS parameters

| Laser parameters (ALFAMET, Novalase SA, France) |  |
|-----------------------------------------------|---|
| Laser source (S-pulse, Amplitude Systèmes, France) |  |
| Crystal                                       | KGW, Yb |
| Wavelength                                    | 1030 nm |
| Laser pulses                                  | 360 fs |
| Pulse to pulse stability                      | <0.5% |
| Pulse energy (at the sample surface)          | 0.1 – 100 µJ ± 0.1% |
| Repetition rate                               | 1Hz – 10000 Hz |
| Laser platform                                |  |
| Size (L x W x H)                              | 1.4 x 0.9 x 1.3 m |
| Mobility                                      | 16 cm diam. wheels |
| Objectives                                    | 25 – 50 – 80 mm |
| Spatial resolution (crater size)              | 5 µm – few mm |
| Sample positioning                            | Motorized XY board ± 1µm |
| Beam scanning (patent pending)                | 280 mm/s (obj. 50 mm) |
| Ablation cell                                 | 9.5 mm³ |
| Carrier gas                                   | He |

ICPMS parameters (X7 Series CCT, Thermo Electron, Winsford, UK)

| Cones                                          | Ni |
| Power                                         | 1400 W |
| Isotopes (dwell time)                         | [43} Ca, 51} V, 59} Co, 68} Zn, 71} Ga, 85} Rb, 89} Y, 90} Zr, 95} Nb, 99} Mo, 109} Ag, 115} In, 118} Sn, 120} Sn, 121} Sb, 133} Cs, 139} Ba, 139} La, 140} Ce, 141} Pr, 146} Nd, 147} Sm, 153} Eu, 157} Gd, 159} Tb, 163} Dy, 165} Ho, 166} Er, 169} Tm, 172} Lu, 178} Hf, 181} Ta, 184} W, 185} Re, 197} Au, 205} Tl, 208} Pb, 209} Bi, 232} Th, 238} U] (14 ms) |

The laser source is integrated in a compact and mobile structure mounted on wheels, which allows movement of the instrument from one room to another without the need of optic realignment. The ablation cell is mounted on a motorized XY stage used for sample positioning (±1µm) or for slow sample displacement when the laser is firing. In addition, a galvanometric scanning module is fitted to the optical line for rapid displacement of the beam at the sample surface with high repositioning precision (<1µm). The main features of this instrument are reported in table 1. The low energy laser
source used here implies the formation of small craters at the sample surface, corresponding to the laser beam spot size (<20 µm in our case). In certain cases, when high detection sensitivity is required this limited ablated area appears as a limiting factor. This was overcome by combining the ultra fast beam scanning system and the high repetition rate of the laser (patent pending). Larger craters can then be formed during a short period of time that can be considered as quasi simultaneous in relation to the ICPMS detection scale: small craters corresponding to the laser beam spot size (20 µm for example) are then repeated in such a way that they can be overlapped while the beam describes a succession of concentric circles. For instance, 200 µm diameter craters can then be formed in less than 150 ms. By repeating this multiple trajectory a given number of times, craters of up to few hundreds microns in depth can be obtained. In these conditions, high quality crater profiles are obtained showing neither border effects nor heat-affected-zone which underlines the minimal thermal processes taking place during femtosecond ablation. Moreover, even at moderate energy (> 30 µJ), the high repetition rate system combined to the fast beam scanning allows to ablate very rapidly the sample resulting in a narrow ablation peak (30 s) and a higher signal to noise ratio. This approach is called “flash ablation” further in the text.

2.2. UV 266 nm nanosecond laser ablation (8 ns): a LSX 100 (Cetac, Omaha, US) operated at 266 nm, 20 Hz and 2 mJ was used in order to compare the analytical performances of the standard nanosecond UV laser ablation/ICPMS to the performance of the low energy and high repetition rate femtosecond ablation/ICPMS. In such conditions, the craters formed were 150 µm wide when ablating glass standard.

2.3. ICPMS detection: A X7 Series CCT quadrupole ICPMS (Thermo Electron, Winsford, UK) was used. The ablated aerosol was carried by a 0.6 L/min helium flow and introduced via Teflon tubing (l = 70 cm, ID = 1/8”, OD = 1/4” Tygon SE200) into the ICP-MS in order to prevent memory effects. The main parameters are listed in table 1.

3. Experimental results
Figure 1 shows an example of the transient signal profile recorded on 59Co during the flash ablation (10 kHz) of a certified glass material (NIST 614).

![Figure 1](image.png)

Three flash ablations have been performed at different locations. The craters formed were 150 µm wide with a depth of 240 µm. The material was ablated during approximately 10 seconds, after which the ablation was extinguished due to the beam defocus as the crater depth advanced. The whole particles are introduced into the ICPMS in about 30 s. Flash ablation repeatability (n = 5) was found to
be excellent (less than 5 %) for all the isotopes considered, even for low concentrations standards (< 1 ppm). This ablation mode was also found to be quantitative and linear since calibration curves obtained from certified NIST material (NIST 612, 614, 616) showed a linear shape with determination coefficient ($r^2$) better than 0.9999.

Limits of detection (3 x SD blank) were evaluated from the NIST 600 glass series for both 266 nm UV ablation and high repetition rate and low energy femtosecond ablation, considering the blank signal recorded prior to ablation. Both laser systems were adjusted to produce 150 µm diameter craters. The limits of detection obtained for the main isotopes of interest are reported in table 2. These results clearly show that flash femtosecond ablation provides limits of detection improved by more than one order of magnitude compared to a 266 nm nanosecond ablation. The related enhancement factor ranges from 10 to 40 according to the elements of interest and results from the fact that the whole ablation process takes place in only a few seconds, leading to a high mass of sample transported to the ICPMS which, in turn leads to a higher signal to noise ratio. In our conditions, the noise is recorded on a given mass prior to ablation and results from the combination of various instrumental effects such as plasma energy fluctuation, ions extraction and focalization, as well as the introduction into the plasma of some remaining particles deposited in the ablation cell or along the connection tube.

In addition, the distribution size of the particles associated to the pulse duration of the laser has to be considered as a criterion of sensitivity enhancement. As demonstrated in recent studies [2,6] femtosecond pulses are prone to generate small particles in the nanometer range. These small particles are more efficiently digested in the plasma of the ICPMS compared to the larger particles formed during nanosecond ablation and consequently result in enhanced signal.

**Table 2:** limits of detection (ppb) obtained from the NIST 600 glass standards series, with the high repetition rate (10 kHz) and low energy (30 µJ) femtosecond laser ablation/ICPMS coupling and with the 266 nm nanosecond laser ablation/ICPMS coupling (1.8 mJ, 20 Hz). Craters of 150 µm were formed in both configurations.

| LOD (ppb) | Femtosecond Flash ablation | Nanosecond 266 nm ablation | Enhancement Factor |
|-----------|---------------------------|---------------------------|-------------------|
| $^{59}$Co | 10.5                      | 267.4                     | 25                |
| $^{65}$Cu | 46.4                      | 568.6                     | 12                |
| $^{69}$Ga | 10.0                      | 144.7                     | 15                |
| $^{88}$Sr | 1.9                       | 49.4                      | 26                |
| $^{107}$Ag | 1.3                      | 10.2                      | 8                 |
| $^{121}$Sb | 2.3                      | 26.1                      | 11                |
| $^{197}$Au | 0.7                       | 7.3                       | 10                |
| $^{205}$Tl | 0.7                       | 9.2                       | 13                |
| $^{208}$Pb | 4.2                       | 46.9                      | 11                |
| $^{232}$Th | 0.8                       | 31.5                      | 41                |
| $^{238}$U | 1.3                       | 21.2                      | 16                |

Elemental fractionation is a situation in which the composition of the mass analyzed is not representative of the bulk sample [7]. This situation occurs during the ablation process, the mass transport to the ICPMS and within the plasma of the ICPMS itself. The fractionation can be evidenced as a change in elemental ratio with time as the crater is drilled at a single location. For a given element, an elemental fractionation index (EFI) can then be defined as the second half of the time signal divided by the first half and normalized to another element (e.g Ca). The elemental fractionation index was calculated with our system for 41 elements, when ablating a certified glass material (NIST 612) for 3
minutes. The femtosecond laser was operated at 60 µJ/pulse and 300 Hz whereas the nanosecond laser was operated at 1.8 mJ and 20 Hz. Results are presented in figure 2.

Figure 2. Elemental Fractionation Index (EFI) normalized to calcium, calculated for the high repetition rate (300 Hz) and low energy (60 µJ) femtosecond laser ablation and for the 266 nm nanosecond laser ablation respectively. The ablation time was 3 minutes and a NIST 612 certified glass sample was used.

The EFI calculated for femtosecond laser ablation are close to the unit indicating that negligible fractionation effects occur. On the contrary, the EFI calculated for nanosecond UV ablation are for some elements (Pb, Au, In, Cs, …) significantly higher than the unit and are in accordance with previous observations reported in the literature. Recent studies have identified particle size dependant behaviour with regards to elemental fractionation, the smallest particles resulting in the lowest fractionation [8-9]. Far UV nanosecond lasers (157 nm, 193 nm) and infrared femtosecond lasers operated at high energy (> 1 mJ) and low repetition rate (< 20 Hz) were found to significantly reduce the elemental fractionation. In these studies, EFI close to the unit were reported for both systems.[8-10]. The results presented here show that low energy and high repetition rate femtosecond ablation behaves similarly to high energy and low repetition rate femtosecond ablation in terms of elemental fractionation.

Depth profiling is of growing interest in many industrial fields such as the semiconductor industry or steelworks, where precise elemental signatures have to be characterized as a function of the depth of a given sample. Depth profile resolution was then investigated with our system by using a well characterized multilayer Cr/Ni certified material (NIST 2135c). Layers thickness was 57 nm and 56 nm respectively for Cr and Ni for a total number of nine certified layers. A low fluence (0.5 J/cm²), close to the ablation threshold, was delivered to the sample in order to remove the thinnest amount of material per laser shot. Figure 3 shows an example of depth profiling with low energy femtosecond laser ablation.

What emerges from these results is that four successive laser shots in the Cr layer are required to reach the Ni layer indicating a depth resolution better than 19 nm. These results are in good agreement with previous observations from Margetic et al., [11] where depth resolution within 15 nm and 19 nm were reported for a Cr-Ni multilayer material. Similar results were also reported for a TiN-TiAlN multilayer material with depth resolution within 13 nm and 17 nm [12]. However, beyond the two first layers, the Cr/Ni layers signature becomes unclear which, is mainly due to the Gaussian shape of the laser beam. A flat top beam profile would be of great interest in order to solve the merging of thin metal layers.
4. Conclusion

We have demonstrated that high repetition rate and low energy IR femtosecond laser ablation coupled to ICPMS is a new powerful tool for direct determination of trace elements in solid samples. The flash ablation method, which relies on the combination of the high repetition rate with a fast beam scanning, improves drastically the analytical sensitivity while keeping excellent repeatability and linearity. This system provides also high resolution depth profiling analysis that could be successfully applied to semiconductors industry or steelworks. It is also worthwhile to note that this new technology is cost effective compared to conventional Ti-Sapphire femtosecond laser system and should promote the democratization of femtosecond laser ablation in the world of analytical chemistry.

Acknowledgements:
Thermo Electron is acknowledged for the loan of ICPMS.

References
[1] Russo R E, Mao X L, Liu C and Gonzalez J 2004 J. Anal. At. Spectrom. 19 1084.
[2] Liu C, Mao X L, Zeng X, Greif R, and Russo R E 2004 Anal. Chem. 76 379-383
[3] Poitrasson F, Mao X, Mao S S, Freydier R and Russo R E 2003 Anal. Chem. 75 6184
[4] Gonzalez J, Liu C, Mao X and Russo R E 2004 J. Anal. At. Spectrom. 19 1165 [3]
[5] Russo R E, Mao X, Gonzalez J and Mao S S 2002 J. Anal. At. Spectrom. 17 1072
[6] Koch J, Von Bohlen A, Hergenröder R, Niemax K 2004 J. Anal. At. Spectrom. 19 267
[7] Russo R E, Mao X, Liu H, Gonzales J, Mao S S 2002 Talanta 57 425-451
[8] Guillong M and Günther D 2002 J. Anal. At. Spectrom. 17 831
[9] H R Kuhn, M Guillong, Günther D 2004 Anal. Bioanal. Chem. 378 1069
[10] Telouk P, Rose-Koga E F, Albarede F 2003 Geostand. Newslett 27 5
[11] Margetic V, Niemax K and Hergenröder R 2003 Anal. Chem. 75 3435
[12] Margetic V, Bolshov M, Stockhaus A, Niemax K and Hergenröder R 2001 J. Anal. At. Spectrom. 16 616