Abstract. Plasma plume emission spectroscopy signals induced in air by 0.8 mJ of a femtosecond-Single Pulse (fs-SP) laser beam were enhanced by using an orthogonal geometry ns-reheating Dual Pulse (DP) configuration. The plasma plume temperatures of several copper-based-alloy standards and calibration curves of their Sn and Pb contents were conveyed. The resulting data showed an independence from the matrix composition so that, even for significant wt % variation of Sn and Pb, good linear regression coefficients could be obtained (0.99 for Sn and 0.98 for Pb). The DP configuration, here reported, using a low energy (0.8 mJ) of the fs ablating laser beam, was considered for determining the Sn and Pb elemental contents of ancient copper-based-alloy artwork fragments coming from the “Canne della Battaglia” archaeological site of Minervino Murge (Apulia – South of Italy). The results showed that, even by employing this low energy of the fs laser, which did not cause any visible damage of the ancient samples, the DP configuration supplied large enhancements and very well resolved emission lines of spectra providing information about the Sn and Pb contents which could support archaeologists work.

1. Introduction
In the last years, a broad interest in investigating the advantages offered by ultra-short laser pulses, for spectrometric technique applications such as LIBS, has largely developed [1-9]. These laser sources have shown the benefit of preventing the ablated material from thermal ablation mechanisms and so ensuring a high preservation of the sample stoichiometry [10-13] and the possibility of using them for depth profiling and high spatial resolution analyses [8-9]. A peculiar characteristic of emitting plasma induced by ultra-short laser pulses is related to the absence of interactions between the laser beam and the formed expanding plasma. This effect provides background continuum and line intensity emissions lower than those induced by nanosecond (ns) laser pulses. The former can be considered as an advantage in order to obtain good analytical results even without gated detectors [2, 14], whereas the latter can be seen as a drawback for the technique sensitivity [15].
The use of double pulse LIBS, performed by either two ns laser pulses or a combination with ultra-short ones, has shown great advantages for LIBS applications [14, 16-21]. The emission signal enhancements showed by a double pulse LIBS scheme, where an ablating fs laser beam is followed by a ns one, can represent a valid development of this technique for reducing the sample damage without diminishing its sensitivity. With the aim of investigating the analytical capabilities of this double pulse configuration for analysis of ancient artworks, this experimental work was undertaken by using a very low energy ablating fs laser pulse (0.8 mJ). For highlighting the quantitative linear response of this set-up, the Pb and Sn calibration curves were drawn by the employment of several copper-based-alloy-certified standards. The obtained results were then applied for defining the Sn contents of ancient bronze artwork fragments coming from the “Canne della Battaglia” archaeological site of Minervino Murge (Apulia – South of Italy).

2. Experimental
The updated experimental apparatus reported elsewhere [22] has been employed. It consists of a 10 Hz ablating fs Twinkle Light Conversion Nd:Glass laser (λ = 527 nm, 250 fs) impinging at 45° on the target surface, a 150 mm focusing lens, a target holder where the samples were placed, and an optical system of two fused silica planoconvex lenses for delivering a 1:3 image of the plasma plume onto the fused silica optical fibre bundle (aperture diameter 0.6 mm) positioned collinearly to plasma expansion direction. The optical fibre was linked to a 500 mm focal length spectrograph (ARC 500i) equipped with a turret mounting a triple grating set 2400 g/mm, 1200 g/mm and 150 g/mm with spectral resolutions, at 500 nm, of 0.008 nm/pixel, 0.015 nm/pixel and 0.17 nm/pixel respectively, whose exit plane was connected to a fast ICCD detection system (PI Max II, 1024x1024 pixels and 2 ns temporal resolution). The reheating pulse was provided by a 10 Hz Handy Quanta-System Nd:YAG laser (λ = 532 nm, 7 ns), a 80 mm focusing lens coupled with a x,y micrometer translation stage (resolution 10 μm) and placed at 90° with respect to the target surface, and two SRS DG-535 pulse generators. The ablating fs laser energy was of 0.80 ± 0.03 mJ and its spot size diameter impinging on the target surface and relative fluence were of 0.3 mm and 1.1 J/cm², respectively. This operating energy was obtained by attenuating 3.2 ± 0.1 mJ of the fs laser pulse through a 75% neutral density filter. For the ns reheating pulse, the energy, spot size diameter and fluence were of 25 ± 1 mJ, 0.2 mm and 80 J/cm², respectively. The ns energy and its stability were always preserved for every fs/ns inter-pulse delay time by the employment of the two SRS DG-535 pulse generators. For varying the ns-reheating pulse distance (0 – 2 mm) from the target surface, the 80 mm focusing lens coupled with the x,y micrometer translation stage was moved. For the Dual Pulse (DP) configuration, the breakdown induced by the ns laser beam was arranged in such a manner that its centre crossed the longitudinal expansion direction of the first fs-pulse induced plasma.

Emission spectroscopy acquisitions were accomplished by the fast gated ICCD detector, which enabled delays with respect to either the fs pulse, for the fs-Single Pulse (fs-SP) configuration, or the ns one, for the DP configuration, between 0.01 - 2000 μs, and gate widths in the range of 0.1 - 50 μs. In order to increase the signal-to-noise ratio, all acquisitions were integrated over 50 accumulations by a PC running the Princeton WinSpec-32 software. The width of the entrance spectrograph slit was always 80 μm, whilst the grating employed was 2400 g/mm. In order to evaluate the single emission line intensities, Voigt line profile functions were employed for their fit. All the spectroscopic data corresponding to the investigated emission lines were obtained from the Kurucz atomic spectral line database [23]. The certified standard compositions reported in Table I refer to the eight (TechLab – Metz – France) commercial samples used.
3. Results and discussion

3.1. Inter-pulse delay enhancement

The DP emission plasma enhancement effects have been evaluated through the DP/fs-SP ratios of the Cu I (282.44 nm) emission line intensities obtained by considering the same fs laser pulse energy for both configurations. In order to avoid the strong continuous emission occurring during the fs-SP or DP initial processes, the spectra acquisitions were performed, respectively, after a delay time of 10 ns from the fs pulse or 50 ns from the ns one. As it was already shown elsewhere [22], the fs/ns inter-pulse delay time, as well as the distance of the ns-reheating laser beam from the target surface, takes effect at any distance between 0.5 - 2 mm if the inter-pulse delay time is varied in the range of 1 - 1000 μs. For a safe handling of the ancient artwork fragments here employed, the distance of 1.0 mm was considered. Figure 1 reveals the enhancements obtained at this distance for Cu I (282.44 nm), Pb I (283.30 nm) and Sn I (284.00 nm) lines by changing the inter-pulse delay time. It straightforwardly shows that for inter-pulse delays of 50-300 μs, the Cu, Sn and Pb emission maximum enhancements are in the range of 220 ± 20, 26 ± 3 and 14 ± 1 fold, respectively. For discriminating the most stable working inter-pulse delay time in the range of 50-300 μs, the pulse-to-pulse Sn/Cu and Pb/Cu signal ratios were considered. Our results showed that 200 μs was the most suitable one.

The excitation temperature temporal behaviours occurring in both fs-SP and DP configurations, reported elsewhere [22], showed that during the fs-SP induced plasma the excitation temperature reached a value of about 18000 K in the first hundreds of ns and then rapidly dropped down as $t^{-0.43}$ [6, 22, 24-25]. Then, after about 1.5 - 2.0 μs, the fs-SP temperature was characterised by a plateau at 8000 ± 300 K which could justify the low line emission intensities observed for this configuration at longer delay times. Conversely, the DP induced plasma line emission intensities lasting for roughly 50 μs could be caused by the slow temperature temporal decay proportional to $t^{-0.18}$ [22]. Therefore, the ns laser pulse can efficiently reheat the first plasma induced by the ablating fs laser beam so that high temperatures can be sustained for very long times, and emission intensities, fairly higher than fs-SP, can be provided. With the aim of evaluating if the DP configuration excitation temperature was affected by the standard material matrix, the non-resonant Cu I emission lines centred at 427.51, 465.11, 510.55, 570.02 and 578.21 nm [17] were used for performing Boltzmann plots relative to each different standard material here employed. The experimental data have shown that these temperatures are, anyway, all very close to each other within the range of 8500 ± 1000 K, hence the reheating mechanism may be assumed to be independent from the material matrix features. On the basis of these results, single calibration curves for the minor components belonging to different copper-based-alloy standard matrixes, such as the brasses and bronzes here used, could be drawn.

![Figure 1. DP/fs-SP intensity ratio enhancements of the Cu I (282.44 nm), Sn I (284.00 nm) and Pb I (283.30 nm) line emissions obtained at a distance of 1.0 mm of the ns-pulse and variable fs/ns inter-pulse delay times (detector gate = 50 μs), sample used: B21.](image-url)
Table 1. Certified sample compositions (wt %)

| Sample | Cu     | Sn     | Pb     | Zn     | Other elements |
|--------|--------|--------|--------|--------|----------------|
| B3     | 80.25  | 12.96  | 1.65   | 2.27   | 2.87           |
| B4     | 84.00  | 11.05  | 2.50   | 1.22   | 1.23           |
| B22-1  | 82.75  | 3.85   | 6.12   | 4.40   | 2.88           |
| B21    | 83.05  | 5.13   | 3.79   | 6.17   | 1.86           |
| LH-1   | 66.80  | 0.44   | 1.26   | 26.20  | 5.30           |
| L3     | 62.35  | 0.44   | 1.02   | 32.70  | 2.43           |
| LH-6-1 | 63.23  | 0.26   | 0.25   | 18.98  | 17.28          |
| UZS-60 | 78.98  | 0.40   | 0.57   | 15.30  | 4.75           |

3.2. Sn and Pb detection

As already reported, we aimed to verify the capability of the DP configuration for the detection of Pb and Sn in different brass and bronze materials covering a wide tin and lead wt % range (see table 1). With the purpose of drawing their relative calibration curves, a Cu I emission signal was considered as an internal standard. In particular, we took into account the ratios of Pb I at 283.30 nm and Sn I at 284.00 nm with Cu I centred at 282.44 nm. The experimental results suggested that, for neglecting the DP continuous emission, each spectral acquisition could start after a delay of 40 ns from the ns-reheating pulse and the gate width could be extended up to 50 µs. Figures 2a and 2b show the emission spectra induced, for the B21 sample, by the fs laser energy of 0.8 mJ and employing the DP and fs-SP configurations, respectively. It can be noticed that the DP provided an intensity increase between two order of magnitude for the Cu I , and one for the Sn I and Pb I emissions, and, on the contrary of the fs-SP configuration, the DP (figure 2a) provided a very low background noise fluctuation.

Figures 3a and 3b show the calibration curves obtained by the DP configuration for Sn and Pb respectively. The provided relative linear regression coefficients are of 0.99 and 0.98, and, on the contrary of the fs-SP [22], by increasing the contents of the species under investigation they do not show any saturation effect. At this stage three ancient bronze artwork fragments (figures 4a, 4b and 4c) coming from the “Canne della Battaglia” archaeological site of Minervino Murge (Apulia – South of Italy) were analysed. None of them showed any appreciable amount of Pb, whereas their Sn wt % contents were of 9.0, 8.2 and 3.2, respectively.
Figure 3. Calibration curves obtained, by the DP configuration (detector gate = 50 µs, time delay from the ns-pulse = 40 ns), for:

- a) Sn I (284.00 nm) / Cu I (282.44 nm) vs. Sn wt %;
- b) Pb I (283.30 nm) / Cu I (282.44 nm) vs. Pb wt %.

The results obtained are useful to the archaeologists for determining the kinds of objects, whose the fragments belong to, and so their historical period. Indeed, the fragments shown in figures 4a and 4b, as a consequence of their high percentage of Sn (9.0 and 8.2 wt %, respectively), can be attributed to warrior protections such as helmets or shields, whereas the figure 4c fragment could be related to burial vessels.

The technique here proposed can allow a fast analysis response without apparent damage of the sample and, hence, it can be suitably used as a first-stage diagnostic tool when the characterisation of a large number of ancient artwork objects is required.

Figure 4. Bronze artwork fragments and relative spectra whose amounts in wt % of Sn have been evaluated: a) 9.0 %; b) 8.2 %; c) 3.2 %.

4. Conclusions

The relevant enhancement of the emission signal intensities obtained by the DP configuration can be related to the slow excitation temperature temporal decay of its plasma (~ t^-0.18) due to longer time emissions of the species excited by electron impacts than those occurring during fs-SP (~ t^-0.43) [22]. The observed independence of the plasma temperature from the sample matrix composition lets us assume that this approach is not actually affected by changes in the matrix composition. The Sn and Pb calibration curves here obtained seem to support this hypothesis making this DP configuration suitable for analytical applications though the sample matrix composition does change. The very large emission intensity enhancements observed (1-2 order of magnitude) have permitted us to detect the species line emissions of each sample by using low fs laser energies. This opportunity has allowed us to establish the Sn amount of ancient artwork fragments without inducing any visible damage on their surface. The results show that,
even by employing a very low energy of the fs ablating laser beam, the DP configuration provides enhanced and very well resolved spectra which can be beneficial for archaeological work.

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5. References
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