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Study and experimentation for a controlled laser cleaning of feathers

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ABSTRACT: This work focuses on the scientific experimentation and practical application of a laser cleaning methodology for the macaw (Ara ararauna) feathers of an ethnographic bow with arrows from the Museum of Anthropology and Ethnography of the University of Turin. The fragility of the object and its unique degradation characteristics suggested the use of a very selective physical method, such as laser cleaning. Prior to the intervention, a comprehensive systematic experimentation phase was conducted including commonly used diagnostic techniques along with a rarely employed analysis for cultural heritage characterization: X-ray Photoelectron Spectroscopy (XPS). The aim of the experimentation was to gain a deeper understanding of the physical-chemical effects of laser irradiation. Through a dedicated experimental setup, optimal operating parameters for laser treatment of macaw feathers were determined. XPS analysis enabled the examination of the treated material and the assessment of potential surface alterations, thus allowing to precisely define the damage threshold. Following the comparison of different Nd:YAG(1064 nm) lasers, the Long Q-Switched mode provided better results and it was selected for the overall intervention. This laser ensures effective removal of deposits, selectivity and respect of the fragile substrate.

1 INTRODUCTION

This contribution summarizes the work carried out within a Master thesis in Conservation and Restoration of Cultural Heritage at the Università degli Studi di Torino, in agreement with the Centro per la Conservazione ed il Restauro dei Beni Culturali “La Venaria Reale” (Mammoliti et al. 2020 unpubl.). The thesis work concerned the restoration of a Bororo bow with arrows owned from the Museum of Anthropology and Ethnography of the University of Turin. Here, we present and discuss part of the entire work, which involved the definition of the experimental protocol for the laser cleaning of ararauna macaw feathers (Figure 1).

Case studies in the scientific literature report critical comparisons between traditional feathers cleaning methods and more innovative approaches, such as that based on laser cleaning (see Ciofini et al. 2022 and references therein). In the specific case of the artefacts that are the subject of this study, the latter was considered particularly interesting. In order to ensure a rigorous control of the effects of the laser irradiation of the feathers, both at the level of possible visible alterations and, more in-depth, of possible chemical-physical modifications, a protocol was developed for the experimentation on prepared samples, which was preliminary to the definition of the overall laser treatment. The examination of the state of the art (Pandozy, et al., 2014, Ciofini et al. 2022) along with the skills of the working group on the application of laser treatments allowed for a thorough systematic investigation and the final application of the laser technique within the conservation intervention on the present artefacts.

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Figure 1. Bororo bow (top) and arrows (bottom) from the Museum of Anthropology and Ethnography at the University of Turin.

2 EXPERIMENTATION ON PREPARED SAMPLES

This work aimed at removing the deposits while safeguarding all the characteristics of the feathers, such as the following: 1) microscopic features producing optical effects, such as glossiness, iridescence, and other; 2) strong chemical and physical stability associated with by the keratin; 3) complex order of fragile structural elements such as barbs, barbules, hooks.

Preliminary tests were carried out on the same types of yellow and blue feather samples as those of the present ethnographic objects. In order to point out any possible chemical and physical changes induced by laser cleaning, a diagnostic protocol based on electron microscope (SEM) examinations, colorimetric analyses, and Reflectance Transformation Imaging (RTI) techniques was implemented and applied to all types of feathers decorating bow and arrows (Figure 1). Furthermore, laser-induced physicochemical changes were also studied on prepared samples of Ara ararauna using X-ray photoelectron spectroscopy (XPS), an analysis rarely used in diagnostics of cultural heritage.

The laboratory samples of Ara ararauna feathers were divided into the series 1a (samples 12a and 12b) and 2a (samples 13a, 13b, 14a, 14b), characterized by means of colorimetric and RTI analyses, aged in the UV chamber, and eventually soiled.

RTI images showed that the surface of the feathers was uniform and smooth: the barbs were perfectly aligned and there were no surface irregularities (Figure 2, left). Following artificial aging and adhesion of the dust, all investigations were repeated. In particular, colorimetric investigations were also conducted on the 14a and 14b samples at an intermediate stage, immediately after UV aging (before dust application) to have more comparison data. RTI analyses of the aged and soiled samples were conducted for comparison purposes after the laser treatment (Figure 4).

After the investigations and related documentation of the results, following the two aging stages, laser tests were carried out. The samples of series 1a (12a and 12b) were treated using QS Nd:YAG(1064 nm), while those of the series 2a (13a, 13b, 14a, and 14b) were treated using fibre coupled LQS Nd:YAG(1064nm) laser (Salimbeni et al. 2003).

The second harmonic of Nd:YAG laser (532 nm) was excluded due to the poor results reported in the bibliography on the present specific feather colors, which were confirmed through preliminary tests conducted on a sacrificial samples. The surface exhibited significant inhomogeneity spot marks due to the laser ablation, leading to a sort of abrasion already at relatively low fluences.

The results of the tests performed on the series 1a were in agreement with the those reported in reference case study (Ciofini et al. 2022): the laser QS did not prove to be suitable for the treatment, inducing damage at fluences higher than 0.20 J/cm^2, which was still insufficient for the effective removal of the soiling (lack of discrimination).

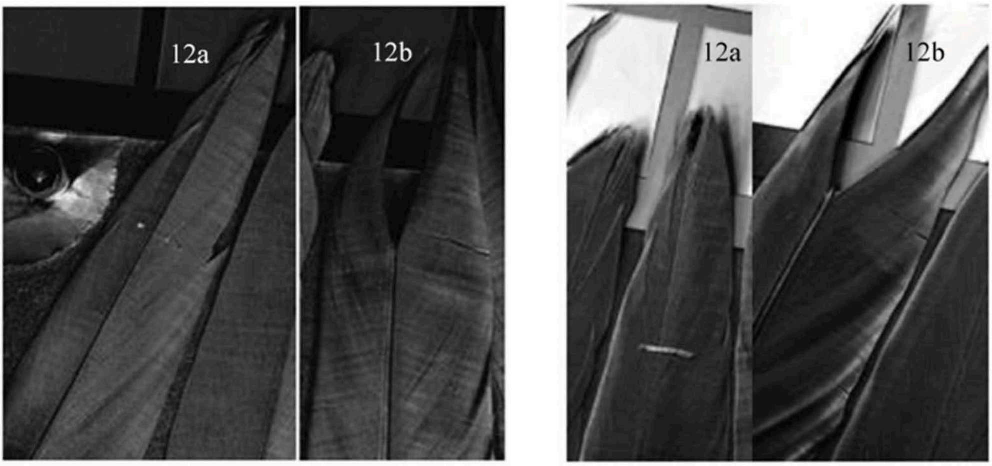


Figure 2. RTI image in Specular Enhancement (Diffuse color = 0; Specularity = 100; Highlight Size = 26): left) before aging (note the characteristic smooth and reflective surface of the intact feather), right) after artificial aging (surface matting and more irregular feather texture can be seen).

All tests with QS were carried out by keeping the pulse repetition frequency at 2 Hz to obtain more control and to be able to promptly verify the effect of the irradiation on the substrate. This allowed even a single irradiation to be carried out, and thus, to verify that surface damage occurs even with a single pulse.

Figure 3 show the samples in visible light (Figure 3a–b) and in RTI (Figure 3c) after laser treatment using the parameters listed in Table 1. Above the threshold fluence it was possible to observe a kind of surface abrasion produced by the inhomogeneity of the laser beam intensity distribution (This effect can be eliminated through the use of a homogenizer).

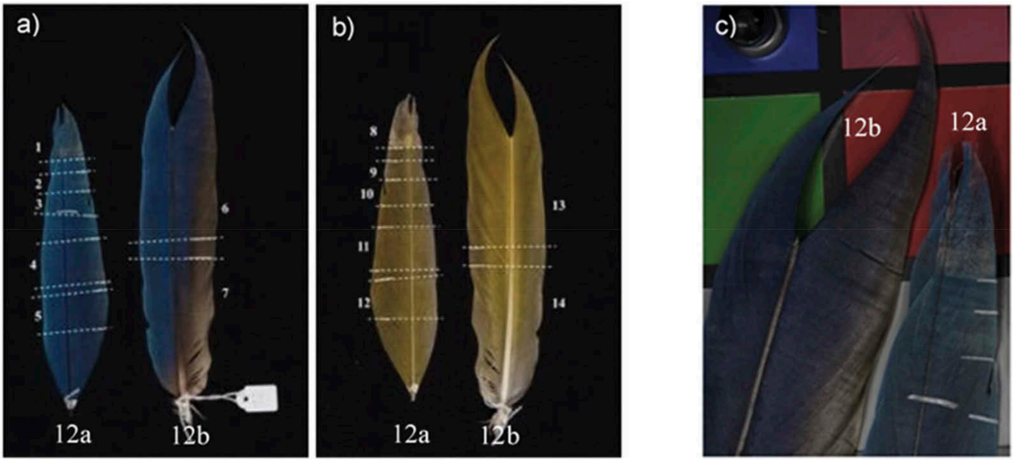


Figure 3. After laser treatment with QS: front (a) and back (b) of the samples 12a and 12b (treated zones marked by sequential number referred to in Table 2) and RTI image (c) in Specular Enhancement (Diffuse color = 59; Specularity = 70; Highlight Size = 75).

In the areas that macroscopically appeared to be intact after laser treatment, analyses were carried out in order to verify both the degree of damage and the effectiveness of cleaning reported in Table 1. In particular, the cleaning was monitored by colorimetric analysis, which made it possible to individuate the changes in colour from one stage to the next, thus starting from the analysis of the sample at level 0 (intact), going through level 1 (artificially aged specimen), and then analysing the laser-treated areas (level 2).

Table 1. Summary of tests performed with laser in QS mode on 12a and 12b specimens.

Sample	Area	Fluence (J/cm^2)		No. of pulses	Frequency (Hz)	Evaluation	
		Recto	Verso			Degree of damage (0-5)	Effectiveness (0-5)
12a	1	0.62	-	1	2	5	0
	2	0.48	-	2	2	5	0
	3	0.31	-	2	2	4	0
	4	0.44	-	2	2	5	0
	5	0.33	-	3	2	4	2
	8		0.40	1	2	4	0
	9		0.28	1	2	4	0
	10		0.27	1	2	4	0
	11		0.25	1	2	4	0
	12		0.24	1	2	3	1
12b	6	0.30		2	2	3	1
	7	0.25		3	2	2	1
	13		0.31	3	2	2	1
	14		0.20	3	2	2	1

Here, we report the most significant results of the colorimetric analysis, namely those including areas 4 and 5 of the blue side of the sample 12a and areas 12 and 14 of the yellow side of the same sample.

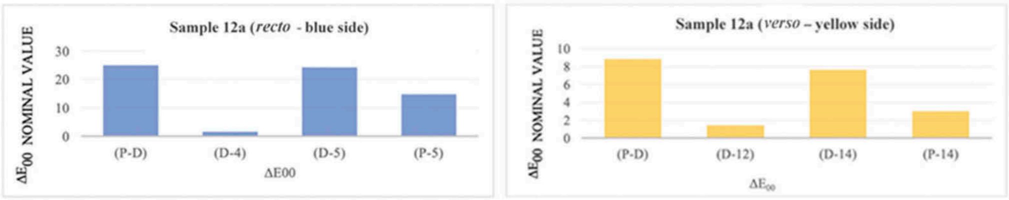


Figure 4. ΔE_{00} of the various treatment levels of the sample 12a (blue side and yellow side). P: before any treatment (level 0). D: after artificial ageing and soiling (level 1). 1; 2; 3 …: laser-treated areas (level 2, Table 3).

From the graph in Figure 4, relating to the blue side of the sample 12a, a strong colour change can be seen in the first ΔE_{00} (P-D): this is due to artificial aging and soiling. The ΔE_{00} (D-4), which allows comparison of laser-treated (level 2) and sample at level 1 (i.e. artificially aged), does not show a significant colour change, which means the cleaning was insufficient (the deposit was not removed). On the other hand, in ΔE_{00}(D-5), corresponding to the colour change between the sample at level 1 and area 5, a strong colour difference was measured, which can be attributed to two factors: surface damage and/or partial removal of dirt. The same hypothesis holds true for ΔE_{00}(P-5); in fact, in this analysis a rather large colour change can be seen, which can be attributed to both the dust still present over the surface and the laser-induced damage.

The same trend was observed in the analyses for the yellow side (Figure 4) of the sample 12a, although ΔE_{00} showed lower values than on the blue side. This could be attributable to the structure of the *verso* of the feather, which is less apt to retain particulate dirt and exhibits higher mechanical resistance. These two characteristics could make it less susceptible to colour change associated with deterioration and soiling.

The above described results suggest to rule out QS laser treatments because of their ineffectiveness and risk of damage at very low fluences, as also verified through SEM examinations (Figure 5).

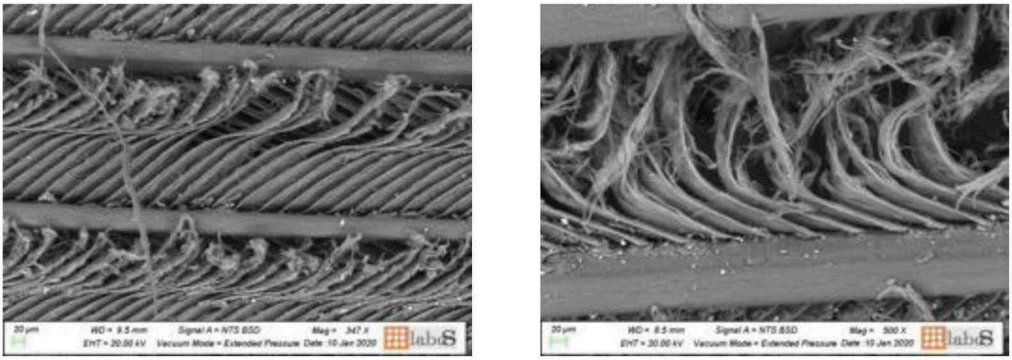


Figure 5. On the left: SEM image of a portion of Ara ararauna feather treated with laser QS at 0.25 J/cm^2 fluence. On the right: Example of unsuitable treatment in which a 0.48 J/cm^2 fluence QS laser was used. Note the severe damage created by the radiation on the barbules (©LaboS).

In particular, structural and textural damage were observed. The structure of the feather after the irradiation was devoid of its perfect periodicity, the barbs became defibrated and dehydrated, major deformations and breakings appeared in the originally smooth and intact areas (Figure 5).

Table 2. Summary of tests performed with laser in LQS mode on the samples 13a and 13b.

Sample	Area	Fluence (J/cm^2)		No. of pulses	Frequency (Hz)	Evaluation	
		recto	*verso*			Degree of damage (0-5)	Effectiveness (0-5)
13a	1	3.02		1	2	5	0
	2	1.03		1	2	5	0
	3	0.69		1	2	0	4
	4	0.10		3	4	0	0
	5	0.25		3	4	0	2
	8		0.69	1	4	0	3
	9		0.70	3	4	0	3
	10		0.75	3	4	0	5
13b	6	1.03		1	2	1	1
	7	0.69		3	6	0	5
	11		0.77	3	2	0	5
	12		0.77	3	6	0	5

This behaviour can be attributed to the short pulse duration of the QS laser (8 ns) and to the relatively high optical absorption of the blue feathers at 1064 nm (Ciofini et al. 2022).

It was interesting to note that in areas where visual or RTI observations showed little or no surface damage (e.g., area 5 of 12a), severe deterioration of the feather structure was produced at the micrometre scale, as it can be seen in Figure 5.

Given the inadequacy of laser QS, we proceeded with series 2a in which LQS laser was tested.

The samples 13a and 13b were irradiated (Figure 6) using the parameters listed Table 2 and characterized by means of colorimetric analysis, whose results are summarised in Figure 7 for the areas 7 (*recto* of 13a) and 10 (*verso* of 13b). These laser-treated areas were further investigated using XPS analysis in order to detect surface possible surface chemical effects.

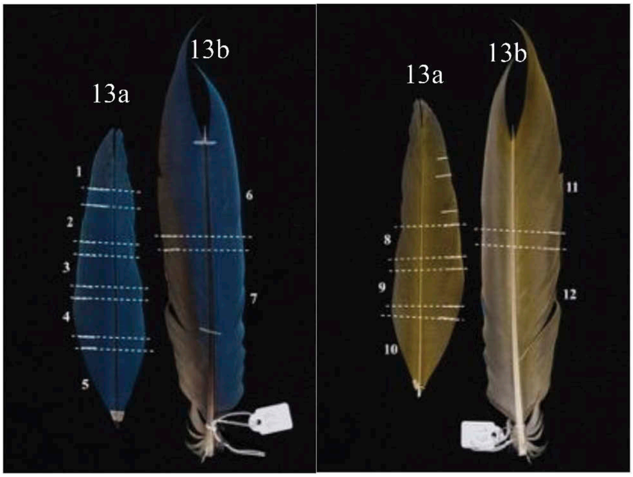


Figure 6. Recto and verso of the samples 13a and 13b after laser treatment with LQS laser. Treated zones marked with a sequential number referred to in Table 4.

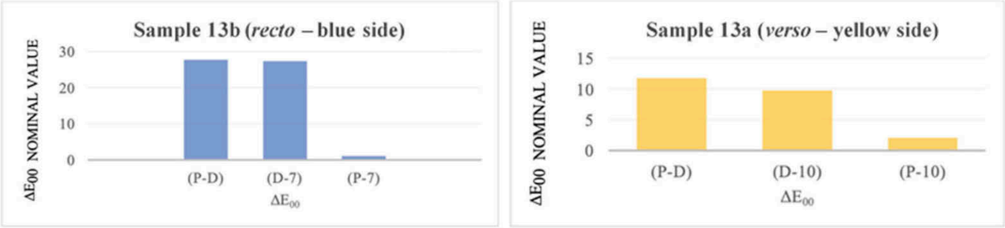


Figure 7. ΔE_{00} of the area 7 of sample 13b (blue side) after LQS laser irradiation at 0.69 J/cm^2 and of the area 10 of the sample 13a (yellow side) after LQS laser irradiation at 0.75 J/cm^2. P: before any treatment (level 0). D: after artificial ageing and soiling (level 1). 7, 10 = irradiated areas (Table 2).

Once the absence of colour change was established, based on the choices explained in the previous paragraph, feather specimens of the same sample taken before and after laser cleaning were analysed by SEM (Figure 8). The images showed that at the fluence of 0.69 J/cm^2, LQS (pulse repetition frequency 4-7 Hz) it was possible to effectively remove the deposits without any detectable injury to the feather barbules. Through SEM analysis of other samples, from areas treated at higher fluences, the damage threshold fluence was determined, which was 0.90-1.00 J/cm^2. The early damage that radiation induced at such energy density is displayed in Figure 9.

Following the microstructural observation of the samples through electron microscopy, we proceeded to assess possible undesired chemical-physical effects by analysing the areas representing the best cleaning results in terms of macroscopic and and microscopic observations (areas 3, 10, 11, 12).

2.1 *XPS analysis for chemical bonds diagnosis in Ara ararauna feathers*

The high sensitivity of XPS instrument made it necessary to subject the samples to be analysed prior to removal of dust, presenting a high risk of poor readability.

XPS measurements were carried out in two different points of each specimen listed in Table 3 in order to obtain information regarding the homogeneity of the chemical composition. Following the identification and quantification of the elements present in the analysed zone ("survey"), "high resolution" (HR-XPS) measurement was carried out only on the elements of interest for the study (S, N), which that allowed to trace the oxidation state of individual elements.

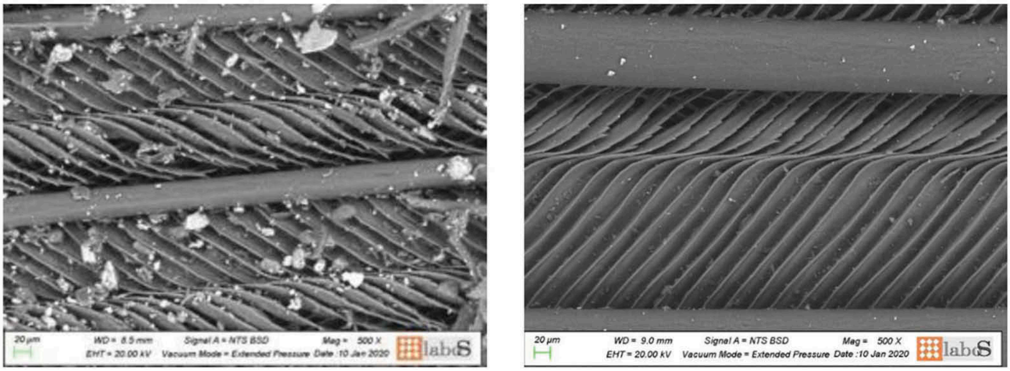


Figure 8. SEM details of 13b (blue side) before (left) and after (right) cleaning with LQS laser at 0.69 J/cm^2 (area 7) (Labos©).

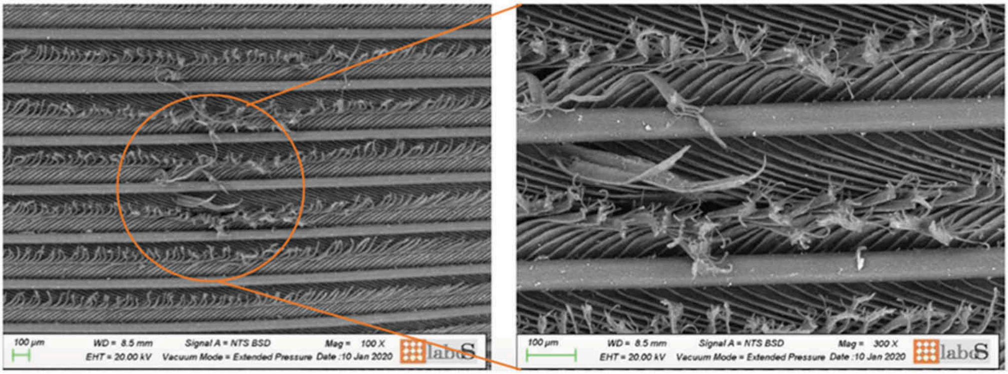
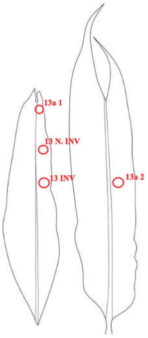


Figure 9. SEM images showing effect of a single laser pulse with a fluence of 1.03 J/cm^2. (Labos©).

Table 3. Specimens investigated using XPS analysis.

	SAMPLE	DESCRIPTION
	13 N.INV	Intact feather specimen, collected before any treatment
	13 INV	Feather specimen artificially aged with UV Solar Box soiled with particle dirt from the MAET cabinets (aged on the blue side)
	13a 1	LQS Nd:YAG(1064 nm) laser treated feather at 3.02 J/cm^2
	13a 2	LQS Nd:YAG(1064 nm) laser-treated feather at 0.69 J/cm^2

The survey analysis showed the presence of carbon (C), oxygen (O), nitrogen (N), and sulphur (S), with contamination of silicon (Si), attributable to the surface particulate deposit. In particular, the latter is present in the specimens 13 N.INV and 13 INV, the former contaminated naturally while the latter was artificially soiled. In the specimen 13a 1 treated with laser above the damage threshold, no contaminants were found due to the deep ablation that totally removed exogenous material. As for sample 13a 2, on the other hand, silicon residues were still noticeable. However, the cleaning result in the area from which the specimen 13a 2 was taken should not be considered unsatisfactory. In fact, the high sensitivity of the instrument (0.01 at.%) succeeds in detecting minute amounts of substances that are invisible to the naked eye.

Table 4. XPS “survey”: atomic concentration of the elements (at. %).

Specimen	Site of analysis	C1S	O1S	N1S	S2P	Other
13 N.INV	Zone 1	84.4	9.8	4.2	1.0	Si: 0.6
	Zone 2	80.5	12.3	4.7	1.0	Si: 1.5
	Average	**82.4**	**11.0**	**4.4**	**1.0**	**Si: 1.0**
13 INV	Zone 1	84.3	10.4	4.1	1.0	Si: 0.2
	Zone 2	82.4	11.9	4.6	0.7	Si: 0.4
	Average	**83.3**	**11.1**	**4.3**	**0.8**	**Si: 0.3**
13a 1	Zone 1	80.5	15.4	3.6	0.5	-
	Zone 2	74.8	17.7	5.9	1.6	-
	Average	**77.6**	**16.5**	**4.7**	**1.0**	**-**
13a 2	Zone 1	81.6	12.5	4.2	0.8	Si: 1.0
	Zone 2	83.3	12.4	3.5	0.7	-
	Average	**82.4**	**12.4**	**3.8**	**0.7**	**Si: 0.5**

In HR-XPS the S2p sulfur and N1s nitrogen signals provided information on possible laser-induced side effects. In particular, the S2p signal was rather uniform in not laser treated specimens (13 N. INV and 13 INV). In fact, the curves of the two distinct zones were similar each other (Figure 10), practically superimposable (the spectra were normalized for easier comparison).

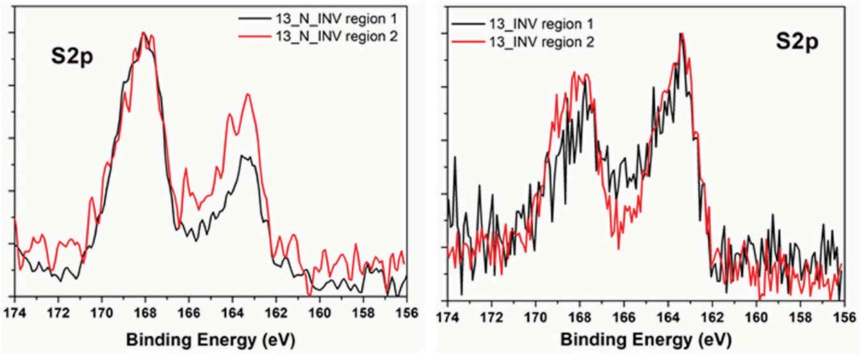


Figure 10. XPS spectrum of S2p for the specimen 13 N.INV (left) and 13 INV.

The XPS spectrum of S2p included two peaks corresponding to cysteine (163 eV) and oxidized cysteine (168 eV). The latter was more intense than the former in the naturally aged specimen (13 N. INV), while they got equivalent for the artificially aged specimen (13 INV), as well as for the laser treated specimen, 13a 2, at low fluence (LQS, 0.69 J/cm^2, 6 Hz). Conversely, both peaks got very noisy and their shape was barely recognisable at high fluence irradiation (specimen 13a 1, 3.02 J/cm^2) (Figure 11).

3 OPERATIVE PHASE

The preliminary experimentation to the select laser cleaning without carrying out risky tests directly on the artefact, having already determined the damage threshold (0.80 J/cm^2) and optimal fluence for the operation (LQS, 0,69 J/cm^2, 1-3 Hz).

A commercial LQS Nd:YAG laser was therefore used to clean the Ara feathers of the present bow and arrows by operating below the damage threshold. The cleaning was assisted by a soft-bristled brush and a chirurgical micro suction unit with the nozzle attached to the laser handpiece in order to suck up the removed material and prevent its redepositing.

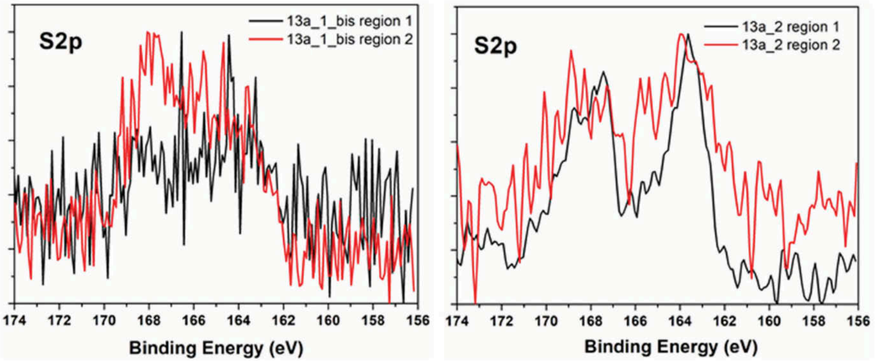


Figure 11. XPS spectrum for S2p in sample 13a 1 and in sample 13a 2.

After the validation test carried out on one of the ornithological elements most blackened by deposits, a small portion of the Ara ararauna feather on the bow was treated using LQS laser with a fluence between 0.65-0.69 J/cm^2. From the selected feather, two specimens were taken, one from laser treated and one from untreated area, respectively, in order to analyse them with XPS and verify the possible occurrence of chemical-physical alterations induced by laser irradiation.

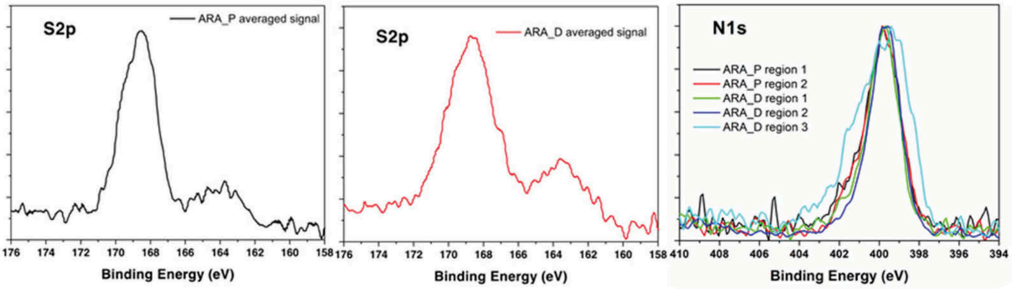


Figure 12. S2p signal of the non-irradiated specimen ARA_P (average from two measurement points), of the laser cleaned specimen, ARA_D, and N1s signal of all analysed specimens.

By comparing the S2p signal of the untreated sample, ARA_P, obtained as the average of the two measurement points, with that of the laser-treated sample, ARA_D, obtained as the average of the signals from the areas 1 and 3, no significant differences were pointed out (Figure 12). Thus, it demonstrates that the laser cleaning treatment did not induce any substantial changes in the oxidation state of S2p. By extending the comparison to the N1s signal (Figure 12), it was possible to further prove the absence of any changes of the cysteine, since this remains largely unchanged in all samples analysed. The laser treatment did not change the microstructure of the nitrogen component. Only a noisier and broader signal was noted in area 3 (Figure 12), due to the low intensity of the signal, but the position of the peak remained unchanged.

Following the assessment of the chemical-physical safety of the laser treatment, colorimetric analyses were carried out on all the cleaning tests, both on Ara ararauna feathers and on the feathers of the other bird species composing the artefact. This allowed to monitor in a non-invasive way the degree of cleaning, as compared to the results achieved in the experimental phase.

Cleaning was therefore conducted on all the coloured feathers, with the exception of the small red and yellow cover feathers attached to the shaft of the arch, which were particularly fragile and less dirty. These were treated with the sole purpose of dusting them with a soft bristle brush.

The laser cleaning operation yielded the most evident results on the yellow side of the Ara ararauna feathers, where the matting effect of soiling was well visible. Brush and micro-aspirator assists durin laser cleaning was very useful, as they facilitated the removal of the soiling concretion. (Figure 13)

A fundamental precaution was the positioning of absorbent paper behind the feather under laser treatment (Figure 13), so as to prevent dirt from passing onto the underlying feather, as all the ornithological elements are placed side by side and often bound together tightly, especially on the tassel.

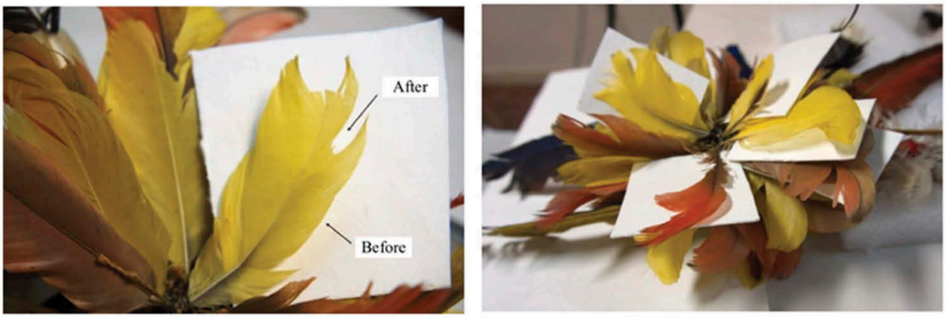


Figure 13. Left: a photographic detail of the ethnographic artefact during the laser cleaning showing the white paper used to protect the bow feathers durin. Right: a detail showing Ara ararauna feather during laser cleaning.

4 CONCLUSIONS

Based on the results of the experiments conducted on the feathers of different species and the outcomes obtained from the diagnostic protocol, it can be concluded that laser cleaning performed within a predetermined interval of fluence and frequency enables a satisfactory and controlled soiling removal that does not alter the microstructure and composition. In fact, it was observed in all the tests that the barbules of the feathers remained intact after treatment, and no changes in colour were detected.

More in detail, Ara ararauna feathers were found to be highly sensitive to QS Nd:YAG laser irradiation which can cause damage. At the same time, the same laser provided excellent results in cleaning feathers of other bird species.

LQS Nd:YAG laser (100 ns pulse duration) allows deposits to be effectively and safely removed from Ara ararauna feathers without any detectable alteration, when used at 0.50-0.70 J/cm^2 and maximum pulse repetition frequency of 6 Hz. Colorimetric values of the substrate did not change and XPS analysis allowed assessing the damage threshold and monitor the treatment at the molecular level. Here, XPS allowed to verify the absence of any modification to the S and N chemical bonds when operating in optimized irradiation conditions.

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