THE EUROPEAN COMMUNITY RESEARCH CONCERNING LASER TECHNIQUES IN CONSERVATION: RESULTS AND PERSPECTIVES

R. Salimbeni[1], V. Zafiropulos[2], R. Radvan[3], V. Verges-Belmin[4], W. Kautek[5], A. Andreoni[6], G. Sliwinski[7], M. Castillejo[8], R. Ahmad[9]

COST Action G7

[1] Institute of Applied Physics "Nello Carrara", CNR, Florence, Italy
[2] Institute of Electronic Structure & Laser, FORTH, Crete, Greece
[3] National Institute of R & D for Optoelectronics, Bucarest, Romania
[4] Laboratoire de Reserche des Monuments Historiques, Paris, France
[5] Federal Institute of Materials Research & Testing, Berlin, Germany
[6] Università agli Studi dell'Insubria, Como, Italy
[7] Polish Academy of Science, IFFM, Gdansk, Poland
[8] Instituto de Quimica Fisica Rocasolano, CSIC, Madrid, Spain
[9] Centre for Applied Laser Spectroscopy, Cranfield Univ., Shrivenham, UK

Abstract

Laser techniques have demonstrated very promising applications for diagnostic and restoration purposes in art conservation. Nevertheless only in the last decade a growing interest in Europe has brought this innovative approach to be tested and validated on various important tasks: laser cleaning of stone, metals, paintings, paper etc; structural laser diagnostics of frescoes and art objects; compositional laser diagnostics of materials; environmental laser monitoring etc. Many programs funded by the European Commission (FP4, FP5, EUREKA, DG REGIO) have contributed to the development of laser instruments and techniques. Presently the COST Action G7 is pursuing the main task of monitoring the advancements achieved in the development of new instrumentation, accumulating validation of laser based techniques with case studies, extending the use of laser for conservation throughout Europe, preparing recommendations for best practices and safety guidelines.

Today laser techniques are being successfully employed in the conservation of a number of masterpieces in many European countries, featuring the advantage of preserving historical layers otherwise impossible, especially for stone and metals. Because of this, the general acceptance on laser methodologies by the conservation institutions appears continuously and convincingly growing. Technology transfer has been also pursued and many laser systems producers could make products out of these research projects. On the other hand an increasing number of professional restorers are being acquainted with these new instruments and methods. It remains clear that, because of its specific characteristics, the time scale for dissemination of such innovative methods in the conservation community requires a long investment period, along several frame programs. Under the light of these results, the future perspective of lasers in conservation will deal with still open issues and will propose new and more advanced technologies.

Introduction

The main problem affecting the cultural heritage present in our countries is its conservation against the many natural and anthropogenic sources of deterioration. Causes such as dust particles, humidity, light and bio-deteriogens affect museum collections. Even more aggressive chemical attack affects every piece of art exposed to polluted air in our cities and the loss of materials may become dramatic in statues, reliefs, figurative elements, all loosing slowly their artistic significance.
The specific features of laser radiation have been advantageously demonstrated in many different tasks in art conservation. In facts high power operation, leading to very precise ablation of materials, has allowed to employ laser cleaning techniques to remove deteriorated layers. The coherence properties of laser radiation have allowed holographic tri-dimensional representation and interferometric control, shearography, electronic speckle pattern interferometry and scanning laser Doppler vibrometry have been employed for determination of structural defects. The many wavelength options offered by the number of gas and solid state laser sources, and several spectroscopic techniques such as Raman spectroscopy, LIBS and LIDAR were used for determination of material composition.
As it appears lasers may give crucial contributions to many tasks of diagnostic, restoration and conservation monitoring of the artefact.
More than thirty years after the first proposal, laser based conservation techniques are experiencing in Europe along the last decade a renewed and finally mature interest, as underlined by the increasing number of case studies reported in the topical conferences LACONA[1,2,3], and in scientific journals of both conservation and laser technology fields. A fundamental contribution in this was given by several research initiatives within the 4th and the 5th Research Programmes of the European Commission. Besides research projects, innovation transfer projects and regional policy projects, a main networking function has been carried out by the COST G7 Action[4] “Artworks conservation with lasers” (33 Institutions in 19 COST Countries). The Action started in the year 2000 with the main priority to put in contact research centres, conservation institutions, technology producers and professional restorers, to provide a continuative exchange and confrontation of experience, to overcome with an insisted implementation the performance of the instruments, and finally to disseminate benefits and best practices of laser techniques through the organisation of workshops and conferences devoted to the European conservation community.
After three years of activity the COST Action G7 has achieved many strategic results. The aim of this work is to present in details their scientific value, the impact of laser techniques on the methodology presently used in most advanced restoration centres, the economic consistency of these practices at a professional level, and finally the importance of the artefacts, monuments and historical buildings, which have been beneficially treated with a laser technique.
To meet the objectives the organisation of the Action has put efforts in three main Working Groups: WG1 Laser Cleaning, WG2 Laser-based Diagnostics and WG3 Laser Monitoring of the Environment Effects on Deterioration. The description of their results follows in the text this sequence.

Laser cleaning

Laser cleaning can be a tool for restorers to remove deteriorated layers that cannot be removed by conventional methods. Most renowned features are:

- No chemical perfusion cleaning (cleaning without solvents).
- Selective removal of deteriorated layers or materials (differential optical absorption between substrates and deposits).
- Accurate control of amount of material removed (accurate spatial resolution & sub-micron depth accuracy).

Laser cleaning has been applied successfully to a large range of art objects materials: Stone, Bronze, Gilding, Paintings, Paper & Parchment, Terracotta, Wood, Plaster, Textiles.

The choice to use a certain laser for a specific conservation problem depends on which ablation mechanism yields the best and most efficient cleaning results. By carefully selecting the wavelength, energy density and pulse duration of the laser radiation the desired ablation mechanism can be realized. From a conservator's point of view, the choice of the laser is also based on the following arguments: the equipment must be available, affordable and easy to use.

By no means the application on stones is the most experienced and advanced. Q-switch Nd:YAG lasers have been employed on decorations of facades, in buildings and churches, on classical and renaissance statues. In all cases the laser technique could demonstrate its unique characteristic to preserve the original layers, due to the high control of the etching depth and some favourable discrimination effect. Neither the high precision micro-sandblasting or chemical pads may result in a removal of the encrustation with similar precision, and laser cleaning came out of any comparison as the most precise and preserving technique.

In France in the period 93-95 more than 20 monuments were experimentally treated especially in the portals of the cathedral of Amiens, Mantes-La-Jolie, Paris, Chartres, Saint Denis etc. In those cases they employed a Q-switch Nd:YAG laser with an articulated arm. The laser technique put in evidence the possibility to treat different problems by graduating the application of laser alone or in association with other techniques. In some cases yellowing of the stone was observed, also if some compensation was possible with suitable treatments. The EC project LAMA developed a Q-switch Nd:YAG laser system with an optical fiber delivery system to be very easily handled by the restorer. The EUREKA project RESTOR tried to scale-up the output average power of a Q-switch Nd:YAG laser in search of a competitive performance also in terms of productivity. In this case a rigid articulated arm was delivering the quite high power laser beam.

In England the most important activities have been carried out by the Conservation Centre in Liverpool, on a number of different cases and problems. Being the oldest industrialised country in Europe the materials have had also the longest period of time of exposition to deteriogenic aerosols, and had developed heavy conservation problems. By using Q-switch Nd:YAG laser they treated many different pieces and several classical sculptures.

Considering as a limitation the yellowing effect and unpractical on scaffoldings the rigid articulated arm, the first generation Q-switch Nd:YAG lasers produced contradictory results in various countries. After the laser was applied in a number of churches, the interest of conservators started to decay in France, while an extensive experience was being carried out at the St. Stephan cathedral in Vienna.

In Italy projects were organised at national level since 1995 with the Special Project Cultural Heritage of Italian CNR, and with a sequence of initiatives (1998-2003)of the Tuscany Region, within the framework of the EC Regional Policies General Directorate programs (Regional Network for High Technology, RITTS), the Regional Innovation Strategies project, RIS+, the PRAI project OPTOCANTIERI. They have involved an interdisciplinary group of research centres, conservation institutes, and companies. The results were a series of new Nd:YAG laser systems operating in the intermediate range 100 ns-20 μs, and devoted to provide the restorer with specific tools optimised for maximum control of the ablation, and for a versatile use on a number of different materials.

Figure 1: The Prophet Abacuc under restoration with laser.

The intermediate microsecond pulse duration laser, engineered by EL.EN. Spa put in evidence practical advantages, which substantially overcame some of the previously observed limitations, such as no yellowing effects on the cleaned material, an excellent selectivity of the cleaning and preservation of the patina, and practical use on the scaffoldings of the fiber cable with the handpiece for the laser beam delivery. While the productivity of this laser system was competitive with other techniques only on complex shapes and decorations.
With this approach the use of lasers in Italy has been continuously growing reaching today a considerable number of restoration interventions on facades of historical buildings (Palazzo Rucellai, Cathedral of S.Maria del Fiore in Florence, The Cathedral of Pisa) marble statues (the Prophet Abacuc by Donatello, the Santi Quattro Coronati by Nanni di Banco in Florence) and stone decorations (the Fonte Gaia by Jacopo della Quercia in Siena).
Another very recent approach to solve the yellowing effect has been proposed by FORTH-IESL in Crete, with the combination of two laser beams outcoming from the same Q-Switch Nd:YAG laser, at the fundamental wavelength in the IR and at the 3rd harmonic in the UV. The simultaneous irradiation of marble stone demonstrated a highly controlled cleaning without side effects on classic monuments in Athens.
The application of laser cleaning on metals has been employed in several laboratory studies and only on a few interventions. Recently very significant results have been reported. An example is the "Porta del Paradiso" by L.Ghiberti, the east door of the Baptistery of Florence, a gilded bronze masterpiece of the renaissance, composed by eight main panels and 48 small figured elements. Microscopic observations of the cleaned areas evidenced a complete removal of the encrustation and the high selectivity of the laser cleaning. Neither thermal and mechanical injuries to gilding nor cuprite blackening were observed on the cleaned surfaces.

Figure 2: Detail of the *Porta del Paradiso*

A first professional laser cleaning station for the removal of e.g. aged varnish and overpaintings from (painted) surfaces has been developed by

Art Innovation, in a project, following the pioneering work done by FORTH-IESL in Crete. The utilization of excimer lasers provided a method to remove layers from paintings untreatable using conventional methods. The laser beam can easily be manipulated, the cleaning process is controlled on-line to prevent excessive removal of material, and there is no mechanical contact with the artwork. The laser workstation developed by Art Innovation, employs a UV excimer laser and a Laser-Induced Breakdown Spectroscopy (LIBS) detection system for on-line process control. It is being applied for a broad range of conservation problems, in close collaboration with conservators.

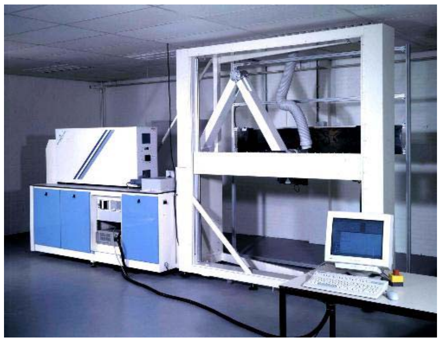

Figure 3: Laser workstation for cleaning of painting

The contact-less laser cleaning of biogenetic surfaces such as parchment, on the other hand, has been approached only in recent years. By now, laser beam delivery has been realized either via an optical fiber or an articulated optical arm to a hand-held output optics

Figure 4: Workstation for laser cleaning of paper. An example is reported.

common in facade laser cleaning, or it is immobile relying on the movement of a scanning mounting supporting the work piece. A prototype of a computerized laser cleaning system suitable for high-precision cleaning of flat large area substrates, e.g. paper and parchment objects, has been developed at the Federal Institute of Materials Research and Testing (BAM) in Berlin (BAM-System). It is based on a compact high pulse energy diode pumped Q-switched Nd:YAG laser operating at 1064 nm and 532 nm, and pulse duration of 8 ns. It can function under Laser Class I conditions, so that the operator does not require safety goggles. Objects can be scanned supported by a remote computer control system. The operator can follow the process on the computer screen through a camera system. The scanning can be controlled manually or programmed in the computer, defining the pulse energy, number of pulses, laser spot overlap and shape of the area to be treated. As an alternative, an optical fiber with an ergonomic hand piece can be used for manual cleaning of objects under Laser Class IV conditions requiring eye protection. The workstation features on-line visible, ultraviolet and fluorescence imaging for the identification and documentation of visible and chemical changes of the irradiated substrate areas. Examples of applications in paper and parchment conservation illustrate how complex pigment and ink structures can be preserved on paper and parchment by automated high-precision laser beam scanning.

Laser and Optical Systems in Analysis and Diagnostics

Over the last 20 years we have witnessed an increasing interest among art historians, archaeologists conservators and scientists, in exploring and applying laser-based methods for addressing problems in Cultural Heritage. This interest has clearly generated a very active and interdisciplinary community across Europe, involved in research on and actual use of advanced laser techniques in a wide variety of diagnostic and conservation problems.

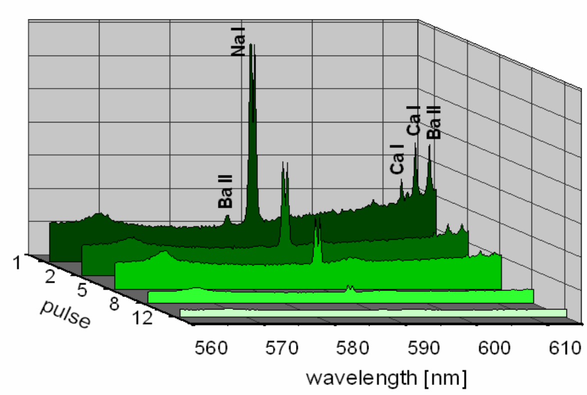

Figure 5: LIBS analysis applied for the laser cleaning process of the first Bible printed in Polish.

But what is special about lasers? Perhaps the answer lies to the fact that these powerful light sources can be used in many ways, exploiting different types of light-matter interactions, yielding effective, highly flexible tools, which can be used in analysis and structural diagnostics for restoration applications. The fundamental research is greatly devoted to the investigation of the potential of laser spectroscopic techniques (laser-induced fluorescence, LIF; laser-induced-breakdown spectroscopy, LIBS; Raman and IR spectroscopy) as tools for characterizing the materials (e.g. LIF for pigments, binding media, varnishes; LIBS for pigments, stratigraphic analysis, on-line monitoring etc). Other laser-based techniques (3-D scanning, holography, holographic interferometry, Doppler vibrometry) provide information about the structure defects; fluorescence imaging either spectrum or time-resolved or both, multispectral imaging (IR-VIS) and colorimetry are employed to detect underlying drawings and pigments composition in paintings.

The main objective of the G7/WG2 activity is to collect the knowledge on diagnostics and conservation methods in cultural heritage in an effort to catalyse an efficient interaction between the users (archaeologists, historians, curators) and providers (scientists) of this technology.

Emphasis is given on providing the user community with educational and training opportunities through meetings workshops and seminars.

The structuring of our approach is envisaged to take place in a 3D space consisting of three major axes:

- Q - question/problem the user faces (i.e. diagnostic, dating, provenance),
- M - material probed (organic, inorganic, pigment, metal, glass, encrustation to be cleaned),
- T - Technique used to provide answers (different spectroscopy/optical analysis tools).

Each analysis case lies somewhere in that QMT cube and has inevitably components/projections on all three axes. Picking a point in the cube and examine the art, the object/material type allows to examine and select the analytic tools one uses. Alternatively, moving along axes or within planes one can draw systematic information for specific laser techniques or the type of analytical approach one would use to analyse different types of materials etc.

The potential of G7 is based on the concentration of the network's unique expertise mostly along the T axis and the ability to develop across the TM and TQ planes and into the QMT space the aim being to fill in the QMT space in an efficient and organized way. The individual research projects cover a diverse variety of applications of laser based diagnostic techniques in cultural heritage.
Several projects focus on the use of analytical tools for diagnostic of the post-processing effects following applications of various conservation techniques (e.g. ablative cleaning) to historical objects. Reliable spectroscopic methods (UV-VIS-NIR, FTIR, DRIFT, colorimetry) and surface/morphology analysis instruments (SEM, AFM, XEDS, XRD) together with various irradiation/excitation sources are accessible at specialized European laboratories.

Laser Monitoring of Environment Effects of Deterioration
Prevention is always better than cure. To prevent the deterioration and degradation of artwork and artefacts from the antiquity , it is of course necessary to know how the environment affects such objects. The environment in which such objects are kept is diverse and its dynamic is ever changing. The effects are cumulative and complementary : The atmospheric pollutants affect the artwork in different ways and speed under different humidity and temperature conditions. Therefore, extensive research on those aspects is needed. Very little work has been so far reported on the global and long-term effects. However, it is now an established fact that some pollutants, particularly NOx, SO_2 and some VOC are main pollutant species, responsible for the degradation of artwork objects.

Table I.Pollutants of Concern – Sources & Effects

POLLUTANT	SOURCES	ADVERSE EFFECTS
Sulphur dioxide (SO_2)	Burning of fossil fuels, mainly coal (external)	➢ Tarnishes metals ➢ Degrades paints, dyes, photographic films, papers, parchments ➢ Embattles paper ➢ Weakens fabrics
Nitrogen dioxide (NO_2)	Automotive exhaust, combustion in cookers, boilers and industrial processes, decomposition of cellulose nitrates, photochemical reactions of other NO_x's	➢ Fades dyes. ➢ Weakens fabrics. ➢ Damages films
Ozone (O_3)	Photocopier, laser printer, electrostatic particle filters photochemical reactions.	➢ Cracks rubber. ➢ Fades dyes ➢ Degrades paper/parchment.
Hydrogen sulphide (H_2S)	Automotive exhaust (catalytic converter), bio-effluent, natural geo-chemical processes, vulcanised rubber, water logged organic materials.	➢ Tarnishes metals, specially silvers.
Carbonyl compounds, (formic acid, formaldehyde, acetic acid, carbonyl sulphide etc) (C = O)	Drying paints, wood and wood products, decomposition of cellulose, resins, thermoplastics etc.	➢ Corrodes metals particularly, lead, zinc and copper alloys. ➢ Damages calcareous and mineralogical specimens and other materials.
Particulate matters	Traffic, abrasion, pollen, combustion, insects, salts, carpets etc.	➢ Damages articles through deposition of acidic/alkaline species.

The recommended limits of these species, given by the artwork environment authorities of galleries and museums, are well below those for the normal outdoor environment acceptable for the human physiological protection. To protect the artwork object from the adverse effects of these species, the indoor parameters have to be controlled and consequently they need to be monitored.
The monitoring of these species at a few ppb (parts per billion) concentration is a difficult task. Such measurements can be carried out by grab sampling and retrospective laboratory analysis using sophisticated, costly and time consuming physical and chemical techniques. Therefore, such facilities are not widely available for most museums and gallery authorities. The conventional methods involve the use of gas tubes and collecting samples for a long period followed by laboratory analysis.
The survey that we have conducted as a task of the COST Action G7, on the users requirements and the present methodologies reveals some startling facts.

Very few end-users, museums and galleries etc, do use some sorts of optical and laser based techniques for environmental analysis.

The existing time averaged methods using different pre-concentration are still the preferred ones, only because there does not exist any cost effective monitoring systems for pollutants.

There exist a need for cost-effective, user-friendly optical system for real time monitoring of atmospheric pollution.

Optical and laser based techniques rely on various interactions processes and the responses from pollutant species under laser interrogations. These responses are in the form of fluorescence, Raman scattering, absorption, etc. The monitoring techniques based on atomic spectroscopy such as laser induced fluorescence, etc tend to be rather sophisticated and expensive. Monitoring systems based on absorption, using recently marketed tunable diode lasers or broad and thermal sources such as Xenon lamps, are being actively considered to be the fore runners for the implementation of cost effective and versatile environmental monitoring system for the near future. A programme is under consideration within the Working Group 3 of the COST G7 Action to conduct research utilising the innovations in laser electro-optical components and detectors as well as new developments in firmware and software for more effective data retrieval and manipulation.

Conclusions

The monitoring of the research efforts carried out in Europe in the development of laser techniques in conservation has conducted to the following conclusions:

- -the FP4 and FP5 have consistently financed R&D projects addressing the cleaning of stone as the most advanced application (LAMA-BRITE EURAM, RESTOR EU1644-EUREKA),
- -other projects have been financed, addressing the cleaning of paper and parchment (LACLEPA-EUREKA, PARELA-EESD),
- one project has been devoted to a system for cleaning of paintings (ENV 2C),
- a few projects were financed for laser diagnostics or holographic documentation (LASERACT-EESD, HISTOCLEAN-EESD, INTAS-IC).
- the DG Regional Policies has financed projects of the Tuscany Region (OPTOCANTIERI-PRAI).

Table 2. Laser based projects in conservation: main information

PROJECT	COORDINATION	FUNDING	PERIOD
LAMA	GTM BTP (France)	1.750.000,00 EUR	1994-96
RESTOR	BMI (France)	n.a.	1995-99
INTAS	UN.GENT (Belgium)	50.000,00 EUR	1995-96
LACLEPA	BAM (Germany	580.000,00 EUR	1996-00
PARELA	ART INNOV. (Nederland)	29.200,00 EUR.	2001-03
ENV2C	ART INNOV. (Nederland)	n.a.	1998-01
COST G7	IFAC-CNR (Italy)	300.000,00 EUR	2000-05
LASERACT	FORTH-IESL (Greece)	1.220.000,00 EUR	2003-06
HISTO-CLEAN	INGEN.FUER (Germany)	409.850,00 EUR	2003-05
OPTOCANTIERI	IFAC-CNR (Italy)	537.710,00 EUR	2003-04

Other projects financed under several EC frame programmes have determined an indirect funding of laser techniques in conservation of artworks in many countries.

As it happens for the sake of consistency in the exploitation phase of R&D projects, after the phase of the achievement of scientific results and the availability of demonstrators, a well funded strategy would need to find a continuity, with validation trials and technology transfer to end-users. It has to be appreciated that in the case of innovation in conservation the time scale for such a dissemination in the European conservation community cannot be measured in a few years, i.e. along a single project.

The experience gained along the COST G7 demonstrates that in this field the technology progress is acquired slowly and only through a direct involvement of conservation institutions (decision makers) and of restorers (professional practitioners).

Nevertheless this methodology progress happened for laser techniques in most of European countries, after the initial problems encountered in the nineties, and today the general acceptance of these physical methods is well acquainted in most of the conservation institutions. It is easy to forecast many further contributions outcoming from the continuous advancements in solid-state laser emitters and detectors through nano-technologies and micro-technologies.

It is expected that the EC will not loose the interest in the contribution that laser methodologies may give to the preservation an conservation of our common patrimony, as is suggested by the limited amount of investments of FP6 for these techniques. As a matter of fact not even a project has been approved under the first call of FP6, out of the many STREPs, Networks of excellence and Integrated Projects submitted by the COST G7 and G8.

This negative outcome is the result of approximate and superficial reviewing reports, which show a scientific gap between the average background of FP6 referees in physical methodologies in conservation, and the improvements achieved at the state of the art.

Also before the start of FP7 a change is needed, and the EC Directorate General Research should take some initiatives to avoid the contradictory outcome of a research field left without resources just when the demonstration of the importance asks for new contributions and proper dissemination and exploitation.

References

1. see Proceedings of Int. Conf. Lasers in the Conservation of Artworks, LACONA III, Journ. of Cultural Heritage S1, Elsevier Science, (2000).
2. see Proceedings of Int. Conf. Lasers in the Conservation of Artworks, LACONA IV, Journ. of Cultural Heritage S1, Elsevier Science, (2002)
3. see Proceedings of Int. Conf. Lasers in the Conservation of Artworks, LACONA V, Osnabrueck (2003).
4. see COST G7 Action web site http://alpha1.infim.ro/cost/